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Fischer-Tropsch Refining

by

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Fischer-Tropsch Refining

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Synopsis

Energy carriers, such as coal, natural gas and biomass, can be converted by Fischer-Tropsch technology into synthetic crude (syncrude). Fischer-Tropsch derived syncrude can then be refined to transportation fuels, such as motor-gasoline, jet fuel and diesel fuel. These fuels meet the same specifications as crude oil derived transportation fuels.

Conventional refining technologies have to be adapted to deal with Fischer-Tropsch syncrudes, because they differ significantly from crude oil with respect to composition. Some of the key differences are the high concentration of oxygenates and olefins and absence of sulphur in Fischer-Tropsch syncrude. Imposing a crude oil refining methodology on syncrude can lead to unwieldy and expensive refineries. Yet, despite an abundance of literature of Fischer-Tropsch synthesis, there is little literature that deals with the refining of Fischer-Tropsch syncrude.

The present study investigated current refining practice for both crude oil and Fischer-Tropsch syncrude in order to identify fundamental differences in their refining focus and conversion behaviour. This was followed by a critical evaluation of the compatibility of syncrudes from high temperature Fischer-Tropsch (HTFT) and low temperature Fischer-Tropsch (LTFT) synthesis with the chemistry and catalysis of various conversion processes. The conversion processes that were evaluated include isomerisation, oligomerisation, etherification, alkylation, metathesis, hydrogenation, hydroisomerisation, hydrocracking, catalytic cracking, coking, thermal cracking, catalytic reforming and dehydration. The recommendations from the technology evaluation provided the foundation for the development of Fischer-Tropsch syncrude based refinery designs.

Refinery designs were developed to determine configurations that would maximise the production of on-specification motor-gasoline, jet fuel and diesel fuel respectively. It could be shown that less complex refinery designs were required to refine Fischer-Tropsch syncrude to motor-gasoline and jet fuel, than were required for crude oil refining. It was also shown that on a molecular level Fischer-Tropsch syncrude is unsuited for maximising the production of Euro-4 type diesel fuel.

The present study illustrates the advantage of considering fundamentals in developing refineries specifically for Fischer-Tropsch syncrude, rather than imposing crude oil design practises on Fischer-Tropsch syncrude refinery designs.

Keywords: Fischer-Tropsch, refining, syncrude, motor-gasoline, jet fuel, diesel fuel, refinery design, refining catalysis.

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CHAPTER I

Prologue

It is unlikely that transportation fuel will change from hydrocarbon based motor-gasoline and diesel in the foreseeable future. Most transportation fuel is refined from crude oil, which is considered to be a non-renewable (finite) resource and is likely to reach its global peak production in the near future. However, fuel supply is already under pressure, not due to limited oil production, but due to the refining infrastructure that is not capable of processing the increasing volume of heavy crude oils being produced. The declining number of refineries aggravates the situation and contributes to a sense of energy insecurity. Energy insecurity is partly responsible for the renewed interest in Fischer-Tropsch (FT) technology, since FT provides a way to convert coal and gas into synthetic crude oil. Yet, despite the increasing body of literature dealing with Fischer-Tropsch synthesis, little literature deals with the refining of Fischer-Tropsch products, which is equally important for the ultimate conversion of coal and gas into transportation fuel. Conventional refining technology has to be adapted to deal with syncrude feed peculiarities and imposing a crude refining methodology on a FT facility can lead to an unwieldy and expensive refinery configuration. There is consequently a need to study Fischer-Tropsch refining as a topic in its own right.

1. Introduction

1.1. Crude oil for transportation fuel

The dependence of modern day society on the use of transportation fuel has aptly been captured in the narrative of Paul Erdman's book "The Crash of '79".(1) Although it is a work of fiction, it explored the premise that the oil fields of the Middle East suddenly became inaccessible and the impact that such an eventuality would have on civilisation as we know it: "I liked the old days when we still had airplanes and television and …"

Transportation fuel and energy supply in general should not be seen as synonymous. There are many sources of energy apart from oil, like nuclear, coal, hydroelectric, natural gas and renewable sources (Figure 1).(2) However, crude oil plays an important role, and is

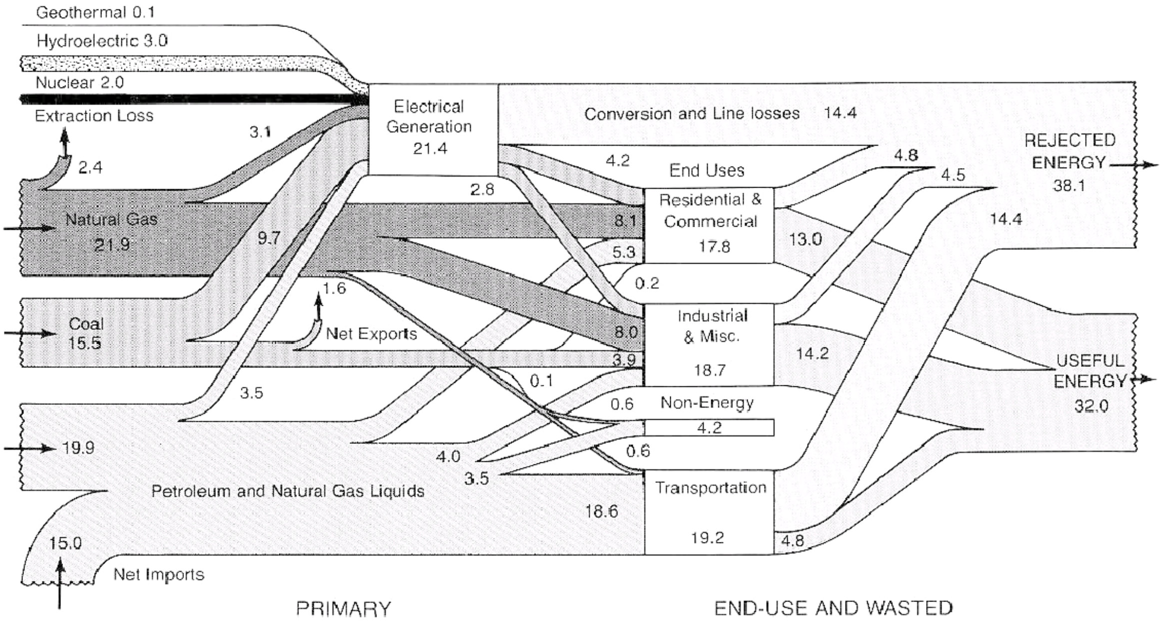

Figure 1. Primary energy inputs in the USA in 1976, shortly after USA peak oil production was reached in 1970. (This figure has been reproduced directly from Ref.(2) and is copyright protected).

definitely the main source of transportation fuel. Since crude oil is classified as a non-renewable[a] energy source, it should by definition have a finite lifetime. Under pressure of continuous demand, the exploitation of a non-renewable resource is expected to increase with time, passing through a maximum, followed by a natural decline. The model description of M. K. Hubbert,[b] who successfully predicted that USA oil production would reach its peak between 1967 and 1973, is probably the best-known description of this phenomenon. Hubbert used a logistic growth curve to describe cumulative production of a non-renewable energy source (Figure 2). Despite the success of his predictions for the USA, forecasts of world and regional oil and gas production using this model usually failed.(4) The point is nevertheless made that crude oil cannot indefinitely remain available to meet the growing demand for transportation fuel.

Global oil production does not seem to slow down and keeps on rising with the increase in demand (Table 1).(5) Despite rumours from time to time that the end of oil is near,(6) oil production seems to keep up with global demand. Yet, for a market that is not short on supply, there is definitely such a public perception, causing the oil price to react

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[a] The popular view of the origin of crude oil is that it is derived from plant and animal remains that were converted to oil and gas by the action of subterranean temperature and pressure. However, there is also an opposing view that ascribes oil formation to an inorganic origin, forming part of the planet's natural carbon cycle. If the latter viewpoint is correct, oil is a form of renewable energy. Ref.(3)

[b] Hubbert, M. K. *Energy resources, a report to the committee on natural resources of the NAS-NRC*; Publication 1000-D, NAS-NRC, 1962.

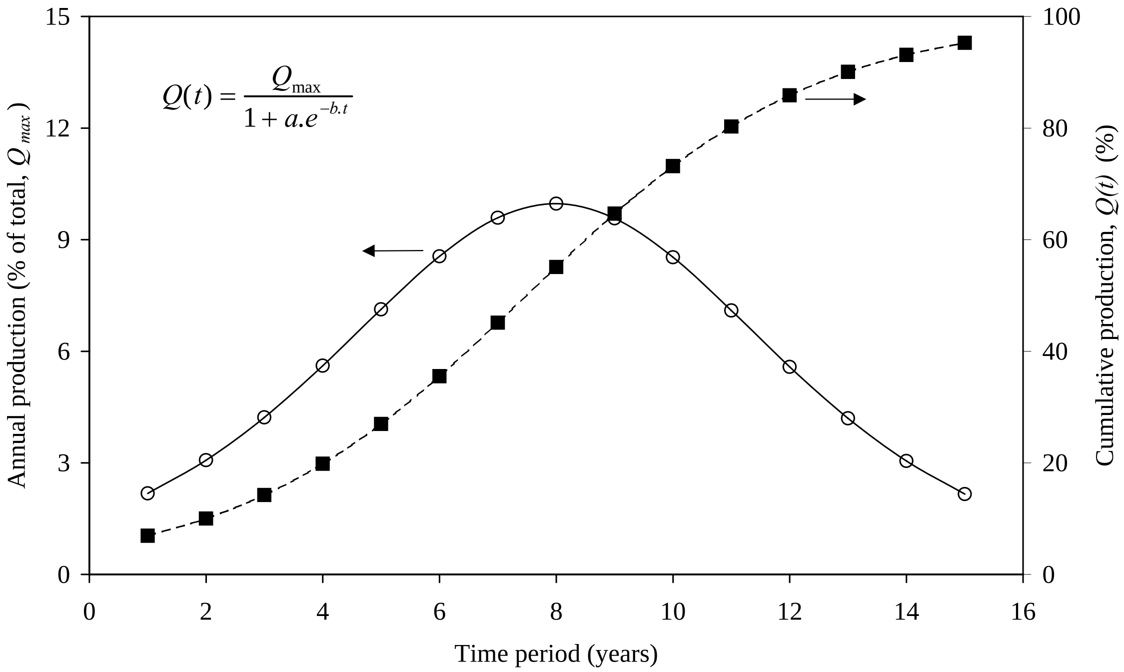

Figure 2. The Hubbert-model description of the production of a non-renewable resource, using arbitrary values for the model parameters a *and* b. *The annual production (○) of the total resource that is available, as well as the cumulative production (■) is shown.*

significantly to upturns and downturns in the economy or events that potentially threaten oil producing regions (Figure 3).(7) The fact that oil reserves are not growing at the same rate as oil production,(8) is not a perception, but a fact. To meet increasing oil demand, it has been estimated that 600 million barrels of oil reserves will be needed to generate 100 000 barrels per day (bpd) of new oil production capacity.(9) Between 1970 and 2000, the number of oil producing countries that passed their peak production rose from 0 to 22, about 50% of the total!(10) It is not clear when global oil production will peak, since any such predictions are subject to consumption predictability that is highly speculative at best, but it seems near.(11)

Table 1. Global oil production in thousands of barrels per day.

Source	1994	1996	1998	2000	2002	2004 ‡
OPEC-countries	25 109	26 040	27 850	27 110	25 190	28 710
Former USSR	7 220	7 070	7 290	7 920	9 370	11 180
United Kingdom	2 584	2 530	2 540	2 400	2 180	1 810
Unites States	8 455	8 340	8 010	7 750	7 670	7 255
Other	22 648	25 805	27 770	29 860	30 400	32 108
Total:	66 016	69 785	73 460	75 040	74 810	81 063

‡ Estimated from the average production figures.

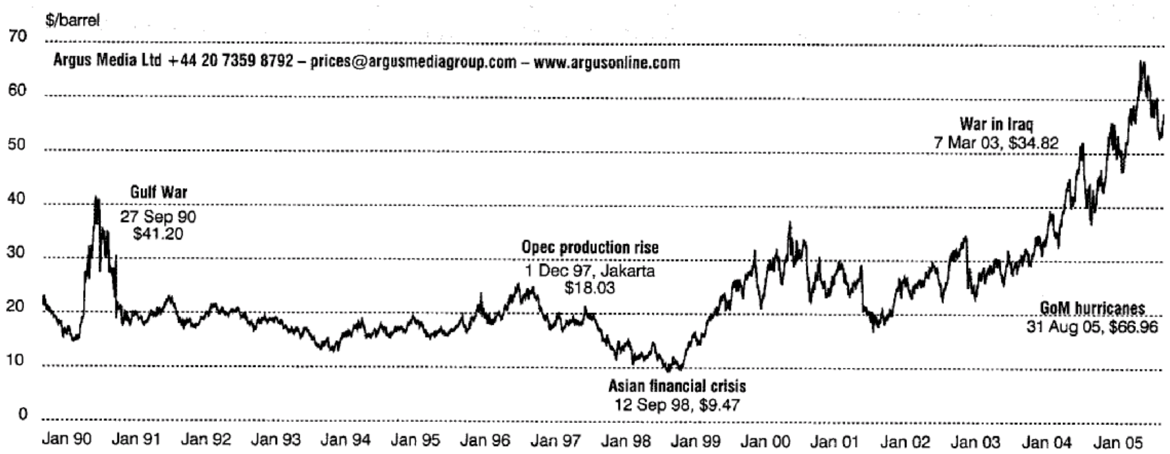

Figure 3. Brent crude oil price fluctuations during the period 1990-2005 (US$/barrel). (This figure has been reproduced directly from Ref.(7) and is copyright protected).

In the discussion thus far, the fact that crude oil is not a final product that can directly be used, has been tacitly been ignored. This has been made patently clear by Ali Al-Naimi,(12) Oil Minister of Saudi Arabia, at the 18th World Petroleum Congress held in Johannesburg in September 2006: “Deliverability, not availability, is oil’s problem!” To deliver transportation fuel to the market, which is the biggest user of oil, the oil must not only be transported to where it can be used, but it also needs to be refined. The bottleneck in delivery to the market is refining. Refineries, just like any other chemical plant, are designed for a specific crude diet (types of crude oil that can be processed).[c] It will later be shown that crude oils have widely varying properties and unless a refinery has been designed to deal with high viscosity, high sulphur or very heavy crudes, such crudes cannot be refined. Having crude oil available of an incompatible type is tantamount to not having crude oil available at all. This fact was clearly illustrated by the effect that hurricanes Katrina and Rita had on oil production and refining capacity in the Gulf of Mexico in 2005.(13) Despite countries like Saudi Arabia making more oil available, it was not the interruption of oil supply that caused problems in the USA markets, but the loss of refining capacity.(14)

The USA transportation fuel market is a good case in point. After the comparatively high oil prices of 1973, the oil companies in the USA made huge profits. This was seen by the politicians of the day (Carter regime) as a good source of revenue for the State and a windfall tax was imposed in 1980. Although this tax was later repealed, it did much damage,(15) but was politically quite successful at the time. It is therefore not surprising that this idea again came to pass in both the USA and South Africa in 2005/6. One of the less publicized effects of windfall tax in the USA, is that the incentive to reinvest money in

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[c] This dependency is related to equipment sizes and the control system.

refining infrastructure was removed - the last USA refinery was built in 1976.[d,(16)(17)] Despite follies like these, the refining business has not been all that profitable and globally very few new refineries were built. Concerns about future litigation associated with the environmental impact of especially the older refineries, caused a number of smaller refineries to close down and generally put a damper on the construction of new facilities. This does not imply that worldwide refining capacity became stagnant (Table 2),(18)(19)(20) but capacity is grown from a shrinking base mainly by expansions and improvements in refining technology. During the three year period 2003-2005, globally only two new refineries were build, a 30 000 bpd refinery in Pakistan(18) and a 32 500 bpd refinery in Papua New Guinea.(19)

Table 2. Global refining capacity for the period end-2002 to end-2005.

Description	2002	2003	2004	2005
Number of refineries	722	717	675	661
Refining capacity (thousands bpd)	81 900	82 100	82 400	85 100

In South Africa the position is not very different. Apart from a small oil refinery in Boksburg dating from the 1930's and that is no longer in operation, there are only four crude oil refineries in South Africa and all have been constructed before 1970:(21)

a) Enref, constructed in 1956 in Durban by Mobil with a capacity of 105 000 bpd.

b) Sapref, a joint venture between Shell and BP in 1963, also built in Durban with a capacity of 180 000 bpd.

c) Chevron (previously known as Calref), built by Caltex in 1966 in Cape Town, with a capacity of 100 000 bpd.

d) Natref, which was a joint venture between the National Iranian Oil Company (NIOC), Total and Sasol and was constructed in-land at Sasolburg in 1969, with a refining capacity of 85 000 bpd (nameplate capacity before expansion projects).

Another salient point that has been touched on is that crude oil is not a homogeneous commodity product. There are not only significant price differences between light sweet crudes and heavy sour crudes, but also differences in the refining units to upgrade heavier more sulphurous crude. Refineries capable of dealing with cheaper, but heavier crudes, typically include units like fluid catalytic crackers, cokers, visbreakers (thermal cracking)

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[d] The number of refineries in the USA has since declined from more than 300 to less than 150 in 2003 and by the end of 2005 the figure has been only 132. It should be noted that many of the refineries that were closed down, were small refineries and their closure were inconsequential in terms of refining capacity.

and/or deep hydroconversion, making the capital and operating cost of such refineries higher. Heavy-end upgrading is likely to drive refinery economics for the foreseeable future,(22) but whether this is driving capital investment, rather than crude selection, is less obvious.(23) Light sweet crude is still available in sufficient quantities for some refiners to opt for better quality crude, rather than investing in the infrastructure to upgrade heavy sour crudes. Oil availability is therefore more complex than just balancing supply and demand; a shortfall in transportation fuel can also be caused by a mismatch in crude type availability and refinery crude diet limitations.

The relationship between demand (increasing), proven reserves (decreasing)[e] and discovery of new reserves (not increasing to keep pace with demand) suggests that oil is not an infinite resource and that global oil production will reach a peak some time in the future. However, it is not oil production that is currently limiting, but supply of refined products. Although refining capacity is growing, it is growing from a shrinking base, which makes it more vulnerable. Furthermore, refinery design limits the crude oil types that can be refined and a mismatch between oil type and refinery type has the same effect as an oil production shortage. All these factors contribute to the precarious balance that has to be maintained to sustain economic growth and the price sensitivity that accompanies any event that threatens supply.(24) It is no wonder that energy security is a topical subject.

1.2. Energy insecurity

The value of good supply logistics has been realised by merchants and generals alike. In the present context, any country that is not self-sufficient in terms of oil production and refining capacity, is potentially at economic risk. Transportation fuel forms an integral part of how present day society is structured and access to transportation fuel is of strategic importance to all countries.[f]

The energy security with respect to transportation fuel can be addressed by fundamentally altering the energy carrier and its source. One such an approach is the notion of a hydrogen economy,(25) which it is claimed would wean people from oil-derived fuel. Another approach is to make use of electricity and battery operated vehicles. However, even with the dramatic rise in the oil price in 2004/5 (Figure 3), the increase in cost of oil-derived

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[e] Shell caused quite a furore when it substantially decreased its proven reserve figures based on a better understanding of the interpretation of geophysical data.

[f] The USA fought the Gulf War (Iraq) to maintain energy security (restore stability in the Middle East).

fuel is far too little to act as a change agent. The logistic infrastructure and vehicle ownership base is too large to change without significant incentive. Hydrocarbon based motor-gasoline and diesel are therefore likely to remain the main transportation fuel for the foreseeable future.(26)

This brings us back to the question of energy security. Although there is much press about the use of renewable energy sources,(27) presently there are only two energy sources that can realistically be considered as replacement for oil in the production of transportation fuel: gas and coal.(28) The decision whether to use gas or coal to provide energy security, depends by definition on its local availability. For example, in the USA coal reserves are estimated at 100-200 years(2) and although there are significant gas reserves in the USA, it is considerably less. In addition, gas price fluctuations of up to 5 times the base cost in winter,(7) makes it politically unattractive to consider gas a source of energy security. Interestingly enough, the same arguments in favour of coal as source of energy security that were published after the oil-crisis in 1973,(29) have surfaced again since 2004.(30)(31)(32) There is historic precedent for the use of coal as means of energy security in not only the USA, but also Germany and South Africa. This leaves the question of conversion – how do you convert gas or coal into transportation fuel?

1.3. Fischer-Tropsch technology

In times of uncertainty, when the energy security of a country is threatened, there is an incentive to develop and commercialise technologies that would make a country less vulnerable in terms of fuel supply. In the transportation fuels business the technology that had the most commercial success is Fischer-Tropsch synthesis.

At the end of the Second World War, Germany had eleven coal-to-liquids (CTL) plants based on Fischer-Tropsch technology in operation.[g] These plants were located at nine different sites.(34)(35) In addition to the Fischer-Tropsch plants, there were also seven direct coal liquefaction plants,[h] together producing 100 000 bpd of synthetic transportation fuels, over a third of Germany’s fuel requirements.(29) A further five Fischer-Tropsch plants that were based on German Fischer-Tropsch technology were constructed under license in France

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[g] Total German nameplate production of FT primary products was 675 ktpa (thousands of metric tons per annum). Ref.(33) The actual production figures were 556 ktpa. Ref.(34)

[h] In the present text “coal liquefaction” is used as term to describe only the CTL technology that converts coal by direct hydrogenation in the presence of a catalyst and solvent to liquid fuels. In some of the older literature the distinction between coal hydrogenation and conversion of coal via synthesis gas has not been made.

(one), Japan (three) and Manchuria (one) during the war-years.[i,(36)] At the end of the Second World War several of the FT plants were destroyed and operation of the remaining plants was forbidden. The restriction on FT operations were later lifted and operation was resumed at only Brabag, Bergkamen and Wanne-Eickel, but energy security was no longer an issue and the last German FT plant, Schering AG at Bergkamen, was closed in 1962 for economic reasons.(33)(35)

Coal liquefaction was investigated in the USA and Britain before the Second World War, while Fischer-Tropsch was actively investigated after the War with the return of the Field Intelligence Agency (FIAT). This led to the construction of a commercial FT plant by Cartage Hydrocol Co. at Brownsville, Texas,[j,(37)] which came into operation in the 1950's.(38) The Hydrocol plant was not based on coal, but on natural gas and it was the first gas-to-liquids (GTL) Fischer-Tropsch plant to be constructed. A second FT plant was planned by Standolind Oil and Gas Co. in Hugoton, Kansas,(39) but it was never built. The USA economic conditions in the 1950's made fuels production by neither Fischer-Tropsch, nor coal liquefaction financially viable. (In 1980 it has been estimated that a crude oil price in the region of US$ 25-30 per barrel is needed to make Fischer-Tropsch economical in the USA).(40) The U. S. Bureau of Mines was nevertheless tasked to investigate both CTL technologies as a strategic initiative and FT research was never stopped.

At about the same time, energy security became an issue in South Africa.[k] During the Apartheid-years energy security remained an issue and four commercial Fischer-Tropsch plants were eventually built.(41) Sasol One, Sasolburg, was the first South African FT plant, using both high temperature Fischer-Tropsch (HTFT) Kellogg and low temperature Fischer-Tropsch (LTFT) Arge reactors. It was designed as a CTL facility and produced its first FT products in 1955.[l,(42)(43)] Twenty five years later it was followed by another two CTL facilities that were constructed at Secunda, using only HTFT Synthol reactors.[m,(44)] Sasol Two started producing FT products on 1 March 1980 and Sasol Three started producing FT

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[i] The total capacity of FT plants outside Germany was 340 ktpa primary products. Ref.(35)

[j] The Hydrocol plant has been designed to produce 7000 bpd oil products.

[k] Strictly speaking the interest in South Africa to build a coal-to-liquids conversion facility was initially an economical one. Anglovaal was interested in the USA Hydrocol technology and expressed their interest to build such a facility in South Africa in November 1945, when they requested a license to produce synthetic fuels.

[l] The Sasol One plant had an original design capacity of about 6750 bpd, with five Arge fixed bed reactors each producing 550 bpd and two Kellogg circulating fluidised bed (CFB) reactors each producing 2000 bpd. The CFB reactors were later decommissioned and replaced by a LTFT slurry reactor (2500 bpd).

[m] The Secunda-plants were designed for 16 Synthol reactors, each with a design capacity of 7500 bpd, giving Sasol Two and Sasol Three a combined design capacity of 120 000 bpd. These reactors have been replaced at the turn of the century with Sasol Advanced Synthol (SAS) reactors with a higher capacity.

products on 10 May 1982.(45) The forth South African FT plant, Mossgas (now PetroSA),[n] in Mossel Bay has been designed as a gas-to-liquids (GTL) facility and also used HTFT Synthol reactors. It has been commissioned in 1992 and achieved full production in January 1993.(46)(47) All of these facilities were originally designed to produce transportation fuels, but in later years chemical co-production became increasingly important.

The only large scale FT facility that was constructed outside of South Africa in the latter part of the twentieth century, is the Shell Middle Distillate Synthesis (SMDS) plant in Bintulu, Sarawak, Malaysia.[o],(48) The plant started operation in May 1993 and after an explosion in the air separation unit damaged the plant in 1997, it was rebuilt and recommissioned in mid-2000.(49) This plant produces transportation fuels and chemicals.

The 21st century is still young and interest in Fischer-Tropsch technology has became significant. In 2007 Sasol commissioned its FT based Oryx GTL facility in Ras Laffan, Qatar(50) and the construction of another facility in Escravos, Nigeria is in progress. Most of the major oil companies have FT programmes, with more than a million barrels per day of FT based GTL capacity being considered,(49) which does not even take into account the studies

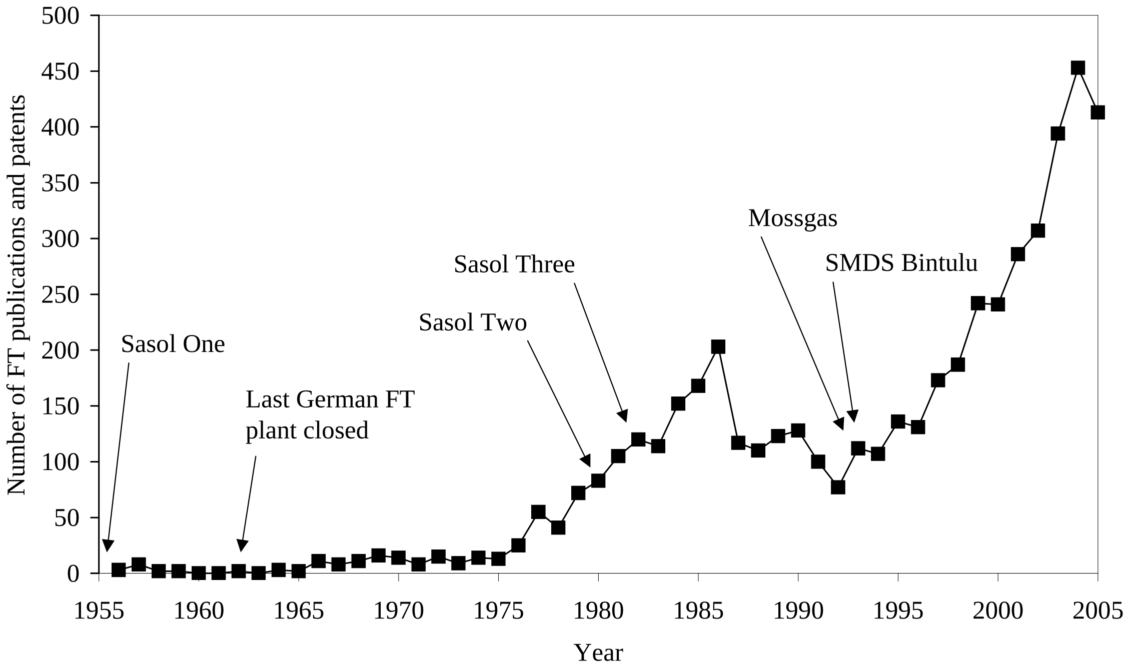

Figure 4. Number of publications in the past 50 years (1955-2005) having "Fischer" and "Tropsch" in the title, keywords or abstract, based on a Chemical Abstract Services SciFinder™ search of abstracted documents in English, German and French.

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[n] The Mossgas plant, operated by PetroSA, has been designed for 3 HTFT Synthol reactors with a total capacity of 22 500 bpd and 10 500 bpd associated condensate for an overall capacity of 33 000 bpd. Ref.(47)

[o] The design capacity of the SMDS plant at Bintulu is 12 000 bpd.

involving FT based CTL technology. For example, Sasol is presently considering another CTL facility under consideration in South Africa (Project Mafutha), as well as studies for CTL plants in China, India and the USA. This trend in CTL is not limited to Sasol.(51)

The interest in FT is indirectly mirrored by the increasing number of patents and publications that appeared (Figure 4),[p] after a long period of limited activity in the field. The data is not a measure of absolute interest, since the baseline is not constant and cognisance should be taken of the general upward trend in patenting and publishing, which is not restricted to the field of Fischer-Tropsch. What is conspicuous in its limited coverage though, is literature on the refining of Fischer-Tropsch products.

1.4. Refining of Fischer-Tropsch products

The output from a Fischer-Tropsch process is not a final product, but a synthetic crude, often called syncrude to emphasise the similarity with crude oil. Like crude oil, syncrude has to be refined to produce useful products. If one has a look at the basic flow diagrams of the commercial HTFT fuel refineries,(52) it seems that dealing with HTFT syncrude requires a number of processing steps over and above the normal separation steps involved in fuels refining. This is in stark contrast to the refinery flowscheme associated with an LTFT process, like the SMDS,(53)(54) which employs a hydrocracker and a hydrotreater as only refinery conversion units. A similar process scheme is used in the Oryx GTL plant in Qatar, but consists of only a single conversion unit, namely a hydrocracker.

The considerable difference in refinery complexity between commercial HTFT and LTFT facilities would explain the focus on LTFT technology and the virtual absence of interest in HTFT technology. However, a fact that is conveniently glossed over, is that the products from LTFT refining cannot directly be sold as transportation fuel. Despite the excellent performance of LTFT diesel,(55) it does not meet Euro-4 specifications, nor does it comply with any of the fuel categories in the World-wide Fuel Charter.(56) Furthermore, the naphtha, which is in the motor-gasoline boiling range, has to be sold as paraffins in the chemicals market, or as cracker feedstock,(57) due to its poor transportation fuel properties.

The refining of Fischer-Tropsch products to yield on specification fuels is seemingly quite complex and belies the assumption that is often made in Fischer-Tropsch literature, namely that Fischer-Tropsch syncrude can be refined in an analogous way to crude oil. This

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[p] The search was limited by language to English, German and French, but there is presently much activity in China in the field of Fischer-Tropsch, with an HTFT demonstration plant slated for commissioning (end-2006).

view is further strengthened by the fact that the commercial FT refineries have been built with conventional refining technology. The tacit assumption that is erroneously made is that conventional refining technology can be used without modification. In practice crude oil refining technologies must be adapted to deal with syncrude feed peculiarities. Furthermore, imposing crude oil refining methodology on a syncrude refinery comes at a high cost, as can be seen from the recent upgrade of the Sasol Synfules (Secunda) refineries. To comply with the 2006 South African fuel specifications, which is not yet on par with Euro-4 specifications, Sasol had to spend 13 000 000 000 SA Rand.[q],(58) This is more than the cost of a brand new crude oil refinery of similar capacity. This view has been challenged and it has been shown that a refinery design optimised for the refining of HTFT syncrude can be less complex, cheaper and more environmentally friendly than a crude oil refinery of similar capacity.(59)(60) This view was reinforced by the success of the syncrude specific contingency plans implemented at Sasol Synfuels,(61) which actually demonstrated that the 2006 South African fuel specifications[r] could met without much capital.

There is consequently a need to study FT syncrude refining, as opposed to crude oil refining, as a topic in its own right.

2. Justification

The introduction not only contextualised the present study, but also indicated a significant gap in published literature dealing with Fischer-Tropsch refining. Although this is surprising, considering the current interest in Fischer-Tropsch synthesis, it is also understandable. Very few researchers have access to unrefined Fischer-Tropsch products in sufficient quantities to do meaningful research on Fischer-Tropsch refining. This is important, because studies in refining should ideally have both academic and industrial significance.

2.1. Academic justification

The limited knowledge base available in open literature on Fischer-Tropsch refining leaves considerable room for the development and dissemination of new knowledge. The field is

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[q] To put this into perspective: In 2004 Sinopec announced their intention to build a new 205 500 bpd crude oil refinery, which would cost US$ 1.2 billion. At that time it was less than the cost to upgrade the existing HTFT refineries in Secunda. However, it should be noted that about 60% of the cost was for chemical (not fuel) units.

[r] The new fuel specifications were published by the South African Department of Mineral and Energy affairs (DME) in the Government Gazette Vol.492 no.28958 on 23 June 2006.

also academically challenging, since it deals with a topic that presupposes a broad understanding of Fischer-Tropsch products (composition and origin), refining technologies (especially chemistry and catalysis), transportation fuels (properties and legislation) and process synthesis. The topic therefore has enough scope for new knowledge to be contributed to the field and ample opportunity to explore specific aspects in sufficient depth to be academically meaningful.

2.2. Industrial justification

It has been postulated that the high cost associated with HTFT refining and the inability of LTFT based processes to yield on specification transportation fuel, are both related to an incomplete understanding of Fischer-Tropsch refining. This in itself is sufficient industrial justification for this study. Yet, a study such as this also holds the promise to make FT based processes more competitive in comparison to crude oil refining and natural gas liquefaction. This has far reaching consequences for the FT industry, since there is no guarantee that oil prices will remain comparatively high and associated gas prices will remain comparatively low. Should any of these premises change, FT could be forced back into its traditional role of an uncompetitive technology, useful only to those who seek energy security.[s] Nevertheless, despite the fact that Fischer-Tropsch has been discovered more than 80 years ago, it remained a relevant technology throughout this period and weathered the ebb and flow of interest.

3. Aim and Scope

The present study will be limited to Fischer-Tropsch refining where the main aim is the production of transportation fuel. Differences between syncrude and crude oil will be pointed out, as well as how these differences impact the refining methodology. The insights gained from such an analysis will be used to propose different refining approaches that can be followed in designing an FT refinery. To give structure to the work, the study has been divided into two sections. The first section deals with the background information necessary to investigate the refining of Fischer-Tropsch syncrude, while the second section deals with refining technology selection and refinery design.

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[s] For every trend, there may be a trend killer. In the case of Fischer-Tropsch the trend is being established by energy insecurity. The foremost trend killer is cost (as indicated), but fear of CO_2-related global warming is a political reality and cannot be discounted as a potential trend killer for Fischer-Tropsch.

3.1. Thesis part 1: Background

Any investigation dealing with refining to produce transportation fuels requires familiarity with general topics like fuel specifications, crude oil types and crude oil refinery design. In addition to these, an investigation dealing with Fischer-Tropsch refining also needs to incorporate an understanding of the composition of FT syncrude (as opposed to crude oil) and existing Fischer-Tropsch refineries. This will lay the foundation for the rest of the study.

3.2. Thesis part 2: Refining technology selection and refinery design

The main aim will be to arrive at FT specific refinery designs for fuels, specifically motor-gasoline (petrol), jet fuel and diesel fuel. The difference in composition between syncrude and crude oil is often at the root of incompatibilities when applying crude refining technology to syncrude streams. This necessitates an understanding of the chemistry and catalysis of the main refining technologies that can be considered for FT refinery design. Such a detailed analysis of the suitability of each technology for processing FT syncrude has not been done before, although the topic has been discussed in some recent literature.(52)(59)(60) The design of FT refineries for chemicals production will be noted, but not explored. There is some recent literature on this topic.(62)(63)(64)

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CHAPTER II

Fuel Specifications

The technical, environmental and political origins for motor-gasoline (petrol), diesel fuel and aviation turbine fuel (jet fuel) specifications are discussed. Some general trends were found and used to predict likely future specifications. Motor-gasoline specifications are moving towards unleaded, low sulphur ($\leq 10\ \mu g \cdot g^{-1}$), low benzene ($\leq 1\%$), high-octane fuel, with a likely reduction in olefin content to 10%. The oxygenate composition and content of motor-gasoline is mostly driven by politics and significant country specific differences are expected. Diesel specifications are focussed on meeting emission standards by reducing sulphur ($\leq 10\ \mu g \cdot g^{-1}$). Other directional changes are to increase cetane, lower polynuclear aromatics, decrease the T95 boiling point and narrowing the density and viscosity ranges. The mandatory inclusion of biodiesel as blending component is likely. Little change in jet fuel specifications are expected, although a reduction in naphthalene and sulphur content might be seen in future, as jet fuel evolves synergistically with the changes in motor-gasoline and diesel specifications.

1. Introduction

Fuel specifications have both technical and political origins. Most vehicle owners know little or nothing about fuel and assume that the stuff they put in their car or truck will allow the engine to start and to keep it running despite the variable demands imposed on the engine by different driving conditions. Moreover, they want it to be cheap and readily available. Vehicle manufacturers want their engines to live up to these expectations, so that they can sell more vehicles and keep their business thriving. The general population, irrespective of whether they own a vehicle or not, cares about the cost of transport. Traffic conditions may also bring other aspects of fuel performance and properties to people's attention, like air pollution, soil and water contamination and they might even be convinced by the popular press that CO_2 induced global warming is a reality. Then there are the refiners, who are not charity organisations as most people would want them to be, but are in the business of producing transportation fuel to make money. Transportation fuel is therefore constantly under scrutiny for both technical reasons, like engine performance and protection, as well as political reasons, like pollution control, environmental protection, cost and the opportunity to gain free publicity. Presently the main drivers for specification changes are environmental protection and health.(1)

The problem faced by refiners and vehicle manufacturers, who are at the technical end of the equation, is that they have to make the marriage between transportation fuel and engine performance work. This in itself is a source of many changes in the quality of transportation fuels.(2) These changes have to happen while obliging some political rulings that are based on political expediency,[a,](3) like the banning of methyl *tert*-butyl ether (MTBE),(4)(5)(6) the former sweetheart of politicians and public alike, or the inclusion of bio-derived feed materials such as ethanol,(7) which is not necessarily a good thing.(8) The technical merits of some political decisions can be questioned, but such political decisions are defining the reality within which refiners must operate. Nevertheless, fuel specifications protect the public, vehicle manufacturers and refiners, since it sets the ground rules of the transportation fuel business.

Irrespective of the political influences, there are some fuel properties that are necessary to meet the technical demands of engine performance and emission control too. These properties are embodied in the fuel specifications and have a rational basis that will be explored. Based on the fundamentals of fuel chemistry, combustion and engine design, predictions can be made about future fuel specifications. This is important, since any text dealing with refining has to look well beyond the present. Changes in fuel specifications create challenges for refiners, because modifying refinery infrastructure to comply with new fuel specifications not only takes time to plan and implement, but also comes at a cost, which can be quite substantial. Predictions are not reality and the political drivers are often even more important than technical drivers in determining the legislation that will ultimately govern fuel specifications.

Fuel specifications will be explored in such a way that the rationale behind it becomes clear. Only the three main transportation fuels produced by refineries will be dealt with in detail, namely motor-gasoline (petrol), diesel fuel and aviation turbine fuel (jet fuel). The

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[a] The inclusion and subsequent banning of MTBE is a classic example of political expediency. The oxygenate mandate in US motor-gasoline was originally intended to appease the corn-ethanol lobby. However, refiners and fuel distributors found that the high vapour pressure and de-mixing tendency of ethanol made it less desirable than MTBE. Furthermore, the use of MTBE rather than ethanol resulted in lower engine emissions, making it a sensible choice. Yet, failure to enforce the laws regulating underground storage facilities led to MTBE ending up in ground water as a result of leaking petrol storage tanks. The fact that benzene and other hydrocarbons also ended up in the soil, seemed to bother nobody, but MTBE has a low odour threshold and its presence in groundwater became a political issue. The result is that MTBE was banned, but that the leaking storage tanks are still contaminating the soil, albeit with no MTBE is ending up in the ground water.

fuel properties will be dealt with in general terms, but specific reference will be made to its impact on Fischer-Tropsch derived fuel where applicable.

2. Motor-gasoline (petrol)

Motor-gasoline, or petrol, refers to the transportation fuel used in spark-ignition engines. Its distillation range is dependent on the ambient temperature range of the locations where the fuel is to be used, but generally it is composed of material boiling in the C_5-C_{10} hydrocarbon range. Fuel characteristics that are necessary for the satisfactory performance and reliable operation of spark-ignition engines have been embodied in the ASTM D4814(9) specification for motor-gasoline. This specification makes specific reference to seven properties: volatility (vapour pressure, distillation and vapour-liquid ratio), gum content, oxidation stability, water tolerance, sulphur content, corrosion (copper and silver) and lead content.

It is immediately apparent that this list does not contain properties like octane number or restrictions on specific compound classes.[b] These parameters depend on variable factors like the compression ratio of the engine and environmental concerns related to exhaust emissions. This does not imply that such factors are unimportant, but it is important to distinguish between standard requirements for general fuel system and engine performance, specific requirements for high performance engines and requirements based on environmental concerns (emission standards).

Table 1. Auto/Oil Air Quality Improvement Research Programme (AQIRP) findings on the impact of motor-gasoline properties on emissions and air quality.

Fuel property	Exhaust emissions				Urban air quality	
	C_xH_y	CO	NO_x	Toxics	C_xH_y	Ozone
Decreasing vapour pressure	Lower	Lower	-	-	Lower	Lower
Decreasing T50 distillation	Lower	-	-	Lower	-	Lower
Decreasing T90 distillation	Lower	-	-	Lower	-	Lower
Decreasing sulphur content	Lower	Lower	Lower	Lower	-	Lower
Decreasing olefin content	-	-	Lower	-	-	Lower
Decreasing aromatic content	-	-	-	Lower	-	-
Adding oxygenates	-	Lower	-	-	-	-

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[b] The importance of the octane (anti-knock) properties of motor-gasoline is covered by appendix X1 of ASTM D4814-04b, although it does not form part of the main specification.

The Auto/Oil Air Quality Improvement Research Programme (AQIRP) initiated by General Motors in 1989 evaluated the effect of changing various fuel properties on emissions and air quality. The AQIRP findings are summarised in Table 1.(2)

2.1. International motor-gasoline specifications

Considering the political interest in fuel specifications, it is no wonder that each country has its own set of legislated fuel specifications. In countries like the USA, where there are national specifications, as well as state dependent variations, recent years have seen a proliferation of "boutique" motor-gasolines. These special requirements do not constitute international specifications.

Table 2. European motor-gasoline specifications, showing selected fuel properties.

Specification	Euro-2 (Jan 1994)	Euro-3 (Jan 2000)	Euro-4 (Jan 2005)
Research octane number, minimum	95	95	95
Motor octane number, minimum	85	85	85
Vapour pressure (kPa) †	35-70	45-60	≤ 60
Final boiling point (°C), maximum	215	210	210
Density ($kg{\cdot}m^{-3}$)	725-780	720-775	720-775
Olefins (vol %), maximum	‡	18	18
Aromatics (vol %), maximum	‡	42	35
Benzene (vol %), maximum	5	1	1
Oxygen (mass %), maximum	‡	2.7	2.7
Methanol (vol %), maximum	3	3	3
Ethanol (vol %), maximum	5	5	5
Iso-propanol (vol %), maximum	10	10	10
tert-Butanol (vol %), maximum	7	7	7
Iso-butanol (vol %), maximum	10	10	10
C_5+ ethers (vol %), maximum	15	15	15
Other ethers (vol %), maximum	10	10	10
Sulphur ($mg{\cdot}kg^{-1}$), maximum	500	150	50 / 10
Lead ($g{\cdot}l^{-1}$), maximum	0.013	0.005	0.005

‡ = Not limited by the fuel specification. † = Region specific

Table 3. Fuel categories defined by the World-wide fuel charter (WWFC).

Category	Description
1	Markets with no or minimal emission control requirements. Based primarily on fundamental vehicle/engine performance criteria.
2	Markets with stringent emission control or other demands, for example Euro-2 or US Tier 1 fuel.
3	Markets with advanced emission control or other demands needed by year 2000 technology, for example Euro-3 and Euro-4.
4	Markets with further advanced requirements for emission control to enable sophisticated after-treatment technologies to meet future needs, for example Euro-4 and US EPA Tier 2 fuel.

Table 4. World-wide Fuel Charter motor-gasoline volatility specifications, showing minimum (min.) and maximum (max.) values for selected fuel properties.

Category	Description	Minimum expected ambient temperature of the market				
		>15°C	5 to 15°C	-5 to 5°C	-15 to -5°C	< -15°C
All	Vapour pressure (kPa)	45-60	55-70	65-80	75-90	85-105
1	T10 (°C), max.	70	70	65	60	55
	T50 (°C)	77-110	77-110	77-110	77-110	77-110
	T90 (°C)	130-190	130-190	130-190	130-190	130-190
2-4	T10 (°C), max.	65	60	55	50	45
	T50 (°C)	77-100	77-100	77-100	77-100	77-100
	T90 (°C)	130-175	130-175	130-175	130-175	130-175
	DI (Equation 2), max.	570	565	560	555	550

Two guidelines that are widely used are the European fuel specifications and the specifications associated with four fuel categories defined in the World-wide fuel charter (WWFC).[c,(10)] The main difference between these two specifications is that the European specifications (Table 2) have been legislated, while the WWFC defined a generic set of guideline specifications to help refiners, motor manufactures and legislators form a consensus opinion on likely future fuel specifications. The WWFC fuel categories (Table 3) mirror the market demands required by different countries and it is made clear that categories 2-4 are modifications of the basic technical fuel requirements based on differences in emission

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[c] The World-wide fuel charter is a product of the joint efforts of the European Automobile Manufacturers Association (ACEA), Alliance of Automobile Manufacturers (Alliance), Engine Manufacturers Association (EMA) and the Japan Automobile Manufacturers Association (JAMA).

control standards. The generic motor-gasoline specifications for the different WWFC categories are listed in Tables 4 and 5.

Table 5. World-wide Fuel Charter motor-gasoline specifications, showing minimum and maximum values of selected fuel properties.

Specification	Category 1	Category 2	Category 3	Category 4
Research octane number, min.	91 / 95 / 98	91 / 95 / 98	91 / 95 / 98	91 / 95 / 98
Motor octane number, min.	82 / 85 / 88	82½ / 85 / 88	82½ / 85 / 88	82½ / 85 / 88
Vapour pressure (kPa)	Table 4	Table 4	Table 4	Table 4
Final boiling point (°C), max.	215	195	195	195
Density (kg·m^{-3})	715-780	715-770	715-770	715-770
Olefins (vol %), max.	‡	20	10	10
Aromatics (vol %), max.	50	40	35	35
Benzene (vol %), max.	5	2.5	1	1
Oxygen (mass %), max.	2.7	2.7	2.7	2.7
Methanol (vol %), max.	0	0	0	0
Ethanol (vol %), max.	10	10	10	10
C_3+ alcohols (vol %), max.	0.1	0.1	0.1	0.1
C_5+ ethers (vol %), max.	‡	‡	‡	‡
Other ethers (vol %), max.	‡	‡	‡	‡
Unwashed gums (mg/100 ml), max.	70	70	30	30
Washed gums (mg/100 ml), max.	5	5	5	5
Oxidation stability (h), min.	6	8	8	8
Sulphur (mg·kg^{-1}), max.	1000	200	30	5-10
Lead (g·l^{-1}), max.	0.4	†	†	†
Manganese (mg·kg^{-1})	†	†	†	†

‡ = Not limited by the fuel specification.
† = No intentional addition.

It should realised that the wish-list of motor manufacturers, as embodied by the WWFC, and the legislated European specifications, exceed the specifications necessary for vehicle performance, engine protection and emission control. These specifications are the result of political debate and specific agendas being driven.[d] The evolution of the European

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[d] Specific agendas may include popular perceptions exploited for political goals, or economic reasons, like shifting more cost of emission control to fuel producers, rather than vehicle manufacturers.

specifications is a case in point. This is discussed in detail in Appendix A, showing how political expediency, rather than technical grounds, governed specification changes.

2.2. Motor-gasoline properties

2.2.1. Octane number

The octane number is a measure of a fuel's ability to resist auto-ignition. Auto-ignition can take place during the compression cycle before spark-ignition, causing a metallic rapping noise, called engine-knock. Historically, in older model engines, lower octane fuels provided the same anti-knock performance at high altitude as higher octane fuels at low altitude. Newer engines are equipped with knock-sensors that can compensate for changes in temperature and pressure. Such engines can use the same octane fuel at all altitudes,(11) although this strategy does not always render the engine altitude-blind.

There are two octane measures commonly used, namely *research octane number* (RON) and *motor octane number* (MON). The RON value is typically higher than the MON value, but the difference in a commercial fuel should not exceed 10 units. RON correlates best with mild conditions of driving and is evaluated according to the ASTM D2699(12) test method (previously D237). MON correlates best with severe conditions of engine operation and is evaluated according to the ASTM D2700(13) test method (previously D236). An arbitrary scale is used, where *n*-heptane by definition has an octane number of 0, and 2,2,4-trimethylpentane by definition has an octane number of 100.

In South Africa the octane rating of the fuel displayed on service station pumps refer to the RON. In countries like the USA the octane value indicated on service station pumps is the *road octane number* or *anti-knock index* (Equation 1).[e]

$$\text{Anti-knock index} = \tfrac{1}{2}\cdot(\text{RON} + \text{MON}) \qquad \ldots (1)$$

The octane value of a fuel can be directly related to the molecular composition of the fuel (Table 6).(14)(15) The compound classes with the highest octane values are aromatics and oxygenates. In general olefins also have good octane values, except for linear olefins and especially linear α-olefins, which have low octane values. The octane values of the paraffins

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[e] This has a significant impact on refinery design, since it easier to meet a road octane number specification.

are very dependent on the skeletal structure of the paraffins, with the octane value generally increasing with increasing degree of branching and decreasing carbon number. Various attempts have been made to correlate the octane number to molecular properties(16) and compound classes.(17) These correlations may on average yield good predictions, but significant variation of octane numbers within a specific group may result in considerable error if the refining process is predisposed to a specific skeletal structure.

Table 6. Octane value of various C_7 compounds.

Class	Compound	RON	MON	Equation 1
Linear paraffin	*n*-Heptane	0.0	0.0	0.0
Branched paraffin	3-Methylhexane	52.0	55.8	53.9
	2,3-Dimethylpentane	91.1	88.5	89.8
	2,2,3-Trimethylbutane	112.2	101.3	106.8
Linear olefin	1-Heptene	54.5	50.7	52.6
	trans-2-Heptene	73.4	68.6	71.0
Branched olefin	3-Methyl-1-hexene	82.2	71.5	76.9
	trans-3-Methyl-2-hexene	91.5	79.6	85.6
	2,3-Dimethyl-1-pentene	99.3	84.2	91.8
	2,3,3-Trimethyl-1-butene	105.3	90.5	97.9
Cyclo-paraffins	Methylcyclohexane	74.8	71.1	73.0
	Ethylcyclopentane	67.2	61.2	64.2
Cyclo-olefins	1-Methylcyclohexene	89.2	72.0	80.6
	1-Ethylcyclopentene	90.8	71.4	81.1
Aromatics	Toluene	120.0	103.5	111.8
Oxygenate	C_7 ethers	104.0	98.0	101.0

The octane number specification is important for vehicle performance and engine protection. Although fuel specifications only require a minimum octane number for the total fuel, it is important that the fuel should have good octane over the whole distillation range. This is especially important for older vehicles with carburettor engines, since differential distillation may occur in the carburettor, causing the engine to see more of the lighter boiling fraction during warm-up. If the fuel has a poor octane number in light boiling range, the engine may still experience knocking, despite the fact that the fuel meets the overall octane number requirement. From a refinery perspective it is therefore unacceptable to have a fuel that includes a lot of low octane *n*-pentane and *n*-hexane in the light end, with the octane deficit being made up purely by aromatics in the heavy end.(18)

2.2.2. Volatility

Volatility is characterised mainly by the vapour pressure of the fuel and its distillation characteristics. The vapour pressure determines the hot handling properties of the fuel and should be determined by the average ambient conditions (see Table 4). If the vapour pressure is too high, vapour lock can occur, resulting in rough engine operation or engine stalling. The evaporative emissions during filling will also be high, which is an environmental, safety and health concern. Fuel specifications typically refer to the *Reid vapour pressure* (RVP) of a fuel, which is the vapour pressure at 37.8°C (100°F) as measured by the ASTM D323(19) test method.

The *distillation characteristic* of fuel is measured by the ASTM D86(20) method and can be expressed either as T-points or E-points.[f] The need for a T10, T50 and T90 characteristic is related to various aspects of engine performance. If the T10 is too high, the fuel exhibits poor cold starting behaviour and when it is too low, problems with vapour lock, hot starting and evaporative losses can be encountered. If the T50 is too high, the fuel will have poor short-trip economy, exhibit rough acceleration and have poor warm-up performance, while injector icing can occur if the T50 is too low (fuel too volatile and flashes over injector port). If the T90 is too high, combustion deposits may form in the engine and if it is too low, it will result in poor long-trip fuel economy.

The distillation characteristic has a direct influence on the driveability/distillation index (DI), but it is also influenced by the oxygenate content of the fuel (Equation 2). A high DI generally leads to poor performance and increased exhaust emissions.(10)

$$\text{DI} = 1.5(\text{T10}) + 3.0(\text{T50}) + 1.0(\text{T90}) + 11.0(\%\text{O}) \qquad \ldots (2)$$

Strictly speaking adherence to the RVP and distillation characteristic specifications is not enough to prevent vapour lock and the WWPC calls for the vapour/liquid ratio at various

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[f] The T-point terminology refers to the temperature at which a certain amount of material has been distilled. For example, the T10 refers to the distillation temperature at which 10% (volume) of the material has been distilled overheads. The E-point terminology refers to the percentage of fuel that has been distilled at a specific temperature and is essentially the opposite of the T-point terminology. For example, E100 refers to the volume of fuel that is distilled overheads at 100°C. A high T10 will therefore imply a low E70.

temperatures too. Applicability of this measure to vehicles with pressurised fuel systems is questionable.

2.2.3. Density

Although *density* is included in motor-gasoline specifications, it is not an important property for engine operation or protection. It has an influence on the energy value of the fuel and therefore on vehicle performance, but its real importance is in refinery economics. Fuel is sold on a volumetric basis and marketing a fuel with the lowest possible density is advantageous to the refiner (least mass sold for the highest income).

2.2.4. Oxygenate content

Two events in the USA had a worldwide impact on the composition of motor-gasoline, namely the 1985 decision to allow oxygenates to be added to motor-gasoline and the regulations passed in 1990 as the Clean Air Act Amendments, which included the need for reformulated gasoline. By 1 January 1995 the addition of oxygenates to motor-gasoline was mandatory in the USA.(15) This was in part due to the findings of AQIRP (see Table 1), although these emission benefits have been eroded by the inherently lower emissions obtained with modern electronic feedback controlled engines.(10) The octane benefit of oxygenates is indisputable though, but it should be noted that the inclusion of oxygenates influences the DI adversely (see Equation 2).

Although the intent of the USA legislation was to promote ethanol use, ethanol has only been used extensively in Brazil and South Africa.[g] The de-mixing tendency of alcohols makes strict control of distribution systems imperative. According to the WWFC *ethers* are preferred over *ethanol*.[h] However, with legislation that came into effect on 1 January 2004, a number of states in the USA banned MTBE and forced USA refiners to focus on heavier ethers or to switch to ethanol. Despite this change, the inclusion of ethanol may be limited by various other factors. Future growth of ethanol usage beyond the equivalent replacement volume of MTBE seems to be capped by the distribution network and availability of flexible-

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[g] The use of ethanol in motor-gasoline in South Africa is due to the large quantities of ethanol co-produced during Fischer-Tropsch synthesis, which were consequently available to the South African fuel market.

[h] The California Air Resources Board (CARB) conducted emission tests comparing fuels with 10% ethanol and 11% MTBE. It was found that ethanol decreased toxic emissions by 2% and CO by 10%, but that it increased

fuel vehicles (FFV) that are able to use fuel blends with more than 10% ethanol.(21) Note that MTBE use has not been banned in Europe. The requirements for adding 1-10% ethanol to motor-gasoline are described in the ASTM D4806(22) standard. Nevertheless, it will be interesting to see how this will affect public perception in the USA, since the banning of MTBE was a result of poor storage tank care, something that is crucial to keep ethanol containing fuels from de-mixing and ethanol ending up in the ground water. Refiners may therefore opt to include the ethanol as ETBE, which has similar properties to MTBE, but that has not (yet) been banned.

The use of *methanol* is restricted in motor-gasoline, since it can lead to corrosion of metallic components in fuel systems and cause the degradation of plastics and elastomers. The reason for the difference in opinion between European specifications and WWFC recommendations about the inclusion of *heavier alcohols* is not clear. This has an impact on Fischer-Tropsch refineries, since alcohols are one of the main oxygenate compound classes produced during FT synthesis.

2.2.5. Olefin content

Olefins are reactive molecules that can lead to gum formation and engine deposits, but this is mostly caused by dienes and not by mono-olefins. Evaporative emissions of olefins, due to their reactive nature, contribute to ozone formation. This is probably the primary reason for legislation to reduce the *olefin content* in fuels.[i] The olefin content is a critical fuel specification for Fischer-Tropsch refineries, since the gasoline-range material produced by FT synthesis is olefinic in nature (typically 40-70% depending on the FT catalyst used).(23)

2.2.6. Aromatics content

Aromatic molecules are good octane components with a high energy density. The AQIRP study showed that aromatics only influenced the toxic content of emissions, most of which could be related to the benzene content. Benzene is a known human carcinogen and limiting the benzene content of fuel reduces not only the toxic emissions, but also benzene emissions

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NO_x by 14%, hydrocarbon emissions by 10% and ozone forming potential by 9%. Ethanol also has a higher heat of vaporisation than MTBE, resulting in some driveability degradation.

[i] It is mainly the short chain olefins that cause these problems, since there are very volatile and reactive.

due to evaporative losses at filling stations.[j] Motor-gasoline specifications therefore limit the *total aromatic content* (that includes benzene), as well as the *benzene content* specifically.

Heavier aromatics have been shown to result in engine deposits, particularly combustion chamber deposits, which increase exhaust emissions. The heavy aromatic content is indirectly controlled by specifying the final boiling point (FBP) of motor-gasoline.

2.2.7. Sulphur content

Sulphur is present in fuel because it is a natural component of crude oil and no positive effects of having sulphur in motor-gasoline have been noted. Sulphur increases exhaust emissions, increases ozone formation potential, adversely affects exhaust gas oxygen sensors and inhibits catalytic activity of exhaust gas catalytic converters. Consequently there is general consensus that *sulphur* should be eliminated from fuel. This conclusion is supported by numerous studies showing significant improvements in exhaust emissions when the sulphur content of the fuel is decreased (Table 7).(10)

Table 7. Studies showing the effect of sulphur reduction in motor-gasoline on reducing exhaust emissions.

Study	Sulphur (ppm)		Emission reduction, high→low S (%)		
	high	low	C_xH_y	CO	NO_x
AAMA/AIAM	600	30	32	55	48
AQIRP	450	50	18	19	9
CRC	630	30	32	46	61
EPEFE (extra-urban test)	382	18	43	52	20
EPEFE (urban test)	382	18	9	9	10
JARI	197	21	55	51	77

AAMA = American Automobile Manufacturers Association (Chrysler, Ford & GM - dissolved end-1998)
AIAM = Association of International Automobile Manufacturers
AQIRP = Air Quality Improvement Research Programme (part of USA Auto Oil programme, 1989-1992)
CRC = Coordinating Research Council (USA)
EPEFE = European Programme on Emissions, Fuels and Engine technology (part of European Auto Oil I programme, 1993-1995)
JARI = Japan Automobile Research Institute

When sulphur is present in fuel, even at the very low concentrations prescribed for WWFC category 3 fuels, there are significant technological hurdles to overcome to meet the

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[j] Benzene has a very high vapour pressure. Although it has a freezing point of 5.6°C, it has a RVP of 22.5 kPa.

long-life requirements for Low Emission Vehicle (LEV)/Euro-3 and Ultra-Low Emission Vehicle (ULEV)/Euro-4 standards. The long-life requirements translate into efficiencies of 98% or better that must be maintained for exhaust gas catalytic converters over a service period of 160 000 km.(10) Considering that sulphur is a known catalyst poison for exhaust gas catalytic converters, it points towards the need for zero sulphur fuel in the future in order to maintain such high catalyst efficiencies.

Fischer-Tropsch derived fuels have an inherent advantage in this respect, since sulphur is removed as pre-treatment step(24) before FT synthesis.

2.2.8. Metal content

Lead was introduced into motor-gasoline in the 1920's as a cheap and easy way to boost the octane number to allow the development of engines with a higher compression ratio. The Ethyl corporation was established jointly by General Motors and Esso to produce the octane enhancer tetra-ethyl lead (TEL). TEL was used to boost the octane number of motor-gasoline by 5-7 units in the 1960's when it was realised that it also had insalubrious side-effects.(2) The phasing out of lead was an expensive exercise for refiners, since it required additional upgrading capacity to make good for the octane shortfall.

There were also concerns from motor manufacturers that valve seat recession (VSR)[k] would cause problems when lead was phased out. In practice this has not been seen in countries where lead was phased out, since most engines manufactured since the late 1980's are not susceptible to VSR and VSR is only a problem when older engines are operated for long periods at high load or high speed conditions. Some additives have been employed to provide lead replacement motor-gasoline for older vehicles. These additives are based on phosphorous, alkali metals[l] or manganese.

Unleaded gasoline is necessary to support vehicle emission control technologies, due to the poisoning effect that lead has on the exhaust gas catalytic converters. Furthermore, lead has been found to pose a health hazard and consequently the *lead content* of gasoline is restricted. Low-lead gasoline (0.05 g Pb/l) is still supported in leaded gasoline markets, but it is only a question of time before only unleaded gasoline will be sold world-wide.

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[k] Valve seat recession (VSR) takes place due to the action of the hot exhaust gases leaving the cylinder head under conditions of continuous high load or high speed operation. The hot gases "erode" the valve seat on the cylinder head. Proper cooling and mixed-mode driving limits the chance of VSR taking place in the absence of lead, which binds to the valve seat and protects it from VSR.

Some alternatives that have been used to provide protection against VSR and boost octane, is the addition of other metal containing compounds like *methylcyclopentadienyl manganese tricarbonyl* (MMT)[m] and *ferrocene*. MMT is being used in various countries, amongst other, Canada and South Africa. Extensive studies have been done on MMT, showing little negative effects, apart from increased hydrocarbon emissions and some positive effects have even be noted.(10)(25) However, the overall health and technical issues surrounding the use of MMT remain unclear.[n]

2.2.9. Oxidation stability and gum formation

In the presence of air, hydrocarbons can be oxidised to form various oxygenates, like hydroperoxides, alcohols and carbonyls as primary products and esters and carboxylic acids as secondary oxidation products.(26)(27)(28) The oxidation reactions take place by a radical mechanism and there is typically an induction period during which radical initiation takes place. This period can be shortened by the presence of some metal ions.(29)(30) It is important to note that the metal promotion of the oxidation reaction is not due to the action of the metal surface of the storage vessel.(31) The *oxidation stability* of motor-gasoline is therefore often expressed in terms of the induction period as determined by the ASTM D525(32) method.

The oxidation products are usually soluble in the motor-gasoline, but on evaporation heavier oxidation products may remain as a sticky residue (gum). During fuel testing a distinction is made between potential and existing gums. The *potential gum* relates to the oxidation stability and is determined by the ATSM D873(33) method. Anti-oxidants[o] and metal deactivators[p] can be added to prevent oxidation and prolong storage stability. The *existing gum* content of motor-gasoline leaving a refinery is generally very low and it is determined by the ASTM D381(35) method.

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[l] Side-effects are found when using alkali metal based additives, like inlet-valve sticking and the formation of corrosive alkali metal fluxes causing exhaust valve burning and hot corrosion of turbo chargers.

[m] MMT can only be used in relatively low concentrations (0.018 g Mn/l) and causes fuel instability and lack of octane response at higher concentrations.

[n] Both MMT and ferrocene are metal containing additives and therefore has ash-forming potential.

[o] Anti-oxidants are free-radical chain terminating agents. There are two main types, alkylphenols and aromatic diamines. An excellent review of the function and chemical mechanism by which different oxidation inhibitors work has been given by Ingold. Ref.(34)

[p] Metal deactivators are typically chelating agents that prevent metals that are active for autoxidation catalysis to be trapped, for example N,N'-disalicylidene-1,2-propane diamine.

3. Diesel

Diesel refers to the fuel used in compression ignition engines and is generally material boiling in the C_{11}-C_{22} hydrocarbon range. The requirements for diesel fuel are often diametrically opposed to that of motor-gasoline. In motor-gasoline it was important to suppress auto-ignition of the fuel, to allow spark-ignition to be correctly timed for good engine performance. In diesel fuel it is important that the fuel auto-ignites, since it is used in compression-ignition engines.

Unlike the ASTM D4814(9) standard for motor-gasoline, the ASTM D975(36) standard for diesel is more country specific and addresses the properties of different grades of diesel fuel in the USA. It is nevertheless a useful specification, since it addresses many of the specifications important in diesel fuel. A notable exception is diesel density.[q] This has important implications for Fischer-Tropsch derived diesel fuels, since such fuels have good emission characteristics,(37)(38)(39) but invariably have a low density (less than 820 $kg{\cdot}m^{-3}$). Fuel economy is of paramount importance in the road-transportation industry and irrespective of legislated specifications, fuel users may opt for fuels giving them better economy, which are fuels with a higher volumetric energy density.

In recent years significant changes have occurred in the design of diesel engines and it is doubtful whether the standard test engines used to assess emission performance of fuels are still valid.[r],(40) The high-pressure common rail injection system requires the diesel fuel to be kept at higher temperatures during engine operation, while injection nozzles are getting smaller and smaller.[s] These changes place more emphasis on certain fuel properties, like stability, than is evident from the fuel specifications. Although the fuel specifications governing diesel fuel are not less demanding than that governing motor-gasoline, compression ignition engines are in general more fuel tolerant and will operate on lower quality fuels. The importance of the additive packages used in final fuel formulation, rather than just the base fuel properties, should also be noted, since it is these additives that are crucial for engine protection.(41)

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[q] Although ASTM D975 excludes density, in practice there are density specifications for pipeline transport.

[r] Conflicting results are seen between light duty and heavy duty diesel engines with respect to the effect of different fuel properties. There are also natural trade-offs that cannot be neglected, for example, at higher combustion temperatures particulate formation is reduced, but thermodynamically NO_x formation is favoured.

[s] Conditions for gum formation is therefore enhanced, while the tolerance of the injector nozzles for such deposits are diminished.

3.1. International diesel specifications

It has previously been noted that European fuel specifications (Table 8) are legislated specifications, while the World-wide fuel charter fuel specifications (Table 9) are guidelines associated with the fuel categories listed in Table 3.

Table 8. European diesel specifications, showing selected minimum and maximum values.

Specification	Euro-2 (Jan 1994)	Euro-3 (Jan 2000)	Euro-4 (Jan 2005)
Cetane number, minimum	49	51	51
Density at 15°C (kg·m^{-3})	820-860	820-845	820-845
Viscosity at 40°C (cSt)	2.0-4.5	2.0-4.5	2.0-4.5
Flash point (°C), minimum	55	55	55
Lubricity at 60°C (µm), maximum	460	460	460
T95 distillation point (°C), maximum	370	360	360
Total aromatics (mass%), maximum	‡	‡	‡
Polycyclic aromatics (mass%), maximum	11	11	11
Sulphur (mg·kg^{-1}), maximum	2000 / 500	350	50 / 10
Water (mg·kg^{-1}), maximum	200	200	200

‡ = Not limited by the fuel specification.

The European specifications mainly focus on lowering the sulphur content of diesel, with a moderate increase in cetane being required. These are realistic goals and have already been achieved by the refineries in Europe, despite the effect of politics on the legislated specifications (see Appendix A).

The WWFC has set more ambitious goals, especially with respect to the aromatic content, T95 boiling point and cetane requirements. There will be a high refining cost associated with achieving such specifications, mostly due to additional hydrogen demand. The reasoning behind the more stringent WWFC guidelines is mostly based on emission reduction and environmental impact and may well indicate future direction in terms of legislated specifications. This should also be understood in terms of the origin of the WWFC guidelines, which is mainly an automotive and engine manufacturing point of view. Any emission reduction that can be achieved by using a more refined fuel shifts the cost of meeting vehicle emission targets from the vehicle and engine manufacturer to the refiner, irrespective of what is the most cost effective solution for the end user. It is speculated that some of these changes, hinting at a more paraffinic (kerosene-type) diesel fuel, might be paving the way for new engine technologies, such as homogeneous charge compression ignition (HCCI) engines.[t] However, considering the impact of oxidation stability and gum formation on the new high-pressure common rail injection engines, it is somewhat surprising that this aspect received comparatively little additional attention in WWFC specifications.

Table 9. World-wide Fuel Charter diesel specifications, showing selected minimum and maximum values.

Specification	Category 1	Category 2	Category 3	Category 4
Cetane number, min.	48	53	55	55
Cetane index, min.	45	50	52	52
Density at 15°C (kg·m^{-3})	820-860	820-850	820-840	820-840
Viscosity at 40°C (cSt)	2.0-4.5	2.0-4.0	2.0-4.0	2.0-4.0
Flash point (°C), min.	55	55	55	55
Lubricity at 60°C (µm), max.	400	400	400	400
T95 distillation point (°C), max.	370	355	340	340
Total aromatics (mass %), max.	‡	25	15	15
Polycyclic aromatics (mass %), max.	‡	5	2	2
Sulphur (mg·kg^{-1}), max.	5000	300	30	5-10
Water (mg·kg^{-1}), max.	500	200	200	200

‡ = Not limited by the fuel specification.

The cold flow properties of diesel fuels are also important, but are not limited to a specific value by the diesel fuel specifications. The cold flow property specification is determined by the locale specific climate. The maximum temperature for the cold filter plugging point (CFPP), cloud point or low temperature flow test is typically set relative to the lowest expected minimum ambient temperature.

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[t] The future fuel for HCCI engines, is still a point of speculation. Although diesel fuels are being considered, Ref.(42), diesel fuel has the drawback that it is not volatile enough to readily allow complete evaporation to create the "homogeneous charge". Kerosene range material is more likely to become a successful fuel for HCCI applications than diesel fuel. It is even easier to rapidly and completely evaporate naphtha range material and it seems that a lot of work is being done with motor-gasoline. There are HCCI engine studies involving high-octane motor-gasoline, which includes mixtures with methanol, dimethylether and LPG as fuels, Ref.(43)(44)(45), as well as investigations with low octane *n*-heptane based as model fuels, Ref.(46).

3.2. Diesel properties

3.2.1. Cetane number

The cetane number is a measure of the compression ignition delay behaviour of a fuel. The *cetane index* is the “natural” cetane number of the base fuel without addition of cetane improvers,(41) while the cetane number reflects the effect of any such additions, since it is a property of the final diesel fuel sold to the market.[u] The *cetane number* (CN) is measured on a test engine in accordance with ASTM D613.(48) A derived cetane number can also be obtained from the more recently developed Ignition Quality Tester (IQT™),(49) which measures the time from the start of fuel injection into a combustion chamber to the start of combustion.

A low cetane number signifies a long compression ignition delay, while a high cetane number signifies a short compression delay. This is the opposite of motor-gasoline octane number (section 2.2.1) that is a measure of auto-ignition suppression and these two properties are interrelated.[v](50) The cetane number is defined on an arbitrary scale where *n*-hexadecane (*n*-cetane) has a value of 100 and α-methylnaphthalene has a value of 0. Since 1962, α-methylnaphthalene has been replaced by heptamethylnonane as a primary reference fuel, where heptamethylnonane has a cetane value of 15 (as measured relative to the original definition of cetane number).

Various strategies for the estimation of the cetane number have been proposed based on physical properties,[w] nuclear magnetic resonance (NMR) spectrometry and chromatography.(51)(52)(53)(54)(55)(56)(57) These general trends have also been used to suggest CN improvement strategies on refining level, as opposed to the use of cetane improvers, noting that CN improves when moving from aromatics to cyclo-paraffins to paraffins (Table 10).(58)

The test work done by the European Programme on Emissions, Fuels and Engine technology (EPEFE) showed that an increase in cetane number would decrease engine crank time (cold startability is improved), combustion noise, hydrocarbon emissions, CO formation and NO_x emissions.(10) Increasing the CN of diesel fuel is therefore beneficial. However, it

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[u] It can be argued from a combustion perspective that the discrimination between cetane index and cetane number is arbitrary and not relevant. However, with modern common rail injection engines, where the fuel loop is operated at temperatures of up to 160°C, cetane improvers can be prematurely decomposed. Ref.(47)

[v] This implies that material with good diesel cetane properties, is tantamount to poor motor-gasoline.

[w] The most commonly used correlation for CN prediction is the ASTM D4737 equation that correlates density and distillation range to CN. This is an empirical correlation, but has been found to work well for describing various fuels and fuel blends in the petroleum industry.

seems that this is not a limitless benefit, since premature combustion before proper fuel-air mixing takes place can deteriorate engine performance and increase vehicle emissions.

Table 10. Cetane numbers of various hydrocarbon compounds.

Class	Compound	Cetane number
Linear paraffin	*n*-Decane	77
	n-Dodecane	87
	n-Tetradecane	95
	n-Hexadecane	100
	n-Octadecane	106
Branched paraffin	2,2,4,4,6,8,8-Heptamethylnonane	15
	7,8-Dimethyltetradecane	40
	5-Butyldodecane	45
Linear olefin	1-Decene	56
	1-Dodecene	71
	1-Tetradecene	80
	1-Hexadecene	86
	1-Octadecene	90
Branched olefin	5-Butyl-4-dodecene	45
Cyclo-paraffins	*n*-Butyldecalin	31
	n-Octyldecalin	31
	3-cyclohexylhexane	36
	trans-Decalin	46
Aromatics	2,6-Dimethylnaphthalene	-13
	1-*n*-Butylnaphthalene	6
	Tetralin	13
	n-Butyltetralin	16
	n-Hexylbenzene	26
	n-Octylbenzene	32

FT derived products are rich in *n*-paraffins, which have high cetane numbers (Table 10) and meeting the cetane specification does not present a problem to the FT refiner.(59) The low aromatic content of FT derived diesel should simplify cetane prediction from analytical methods based on NMR. Yet, in practice it seems that there is not agreement on which method performs the best with Fischer-Tropsch products, with the O'Connor, et al.(54) and the SAE861521(51) methods being alternatively recommended.[x]

3.2.2. Flash point

The *flash point* (FP) of diesel is mainly controlled from a safety point of view, since it gives an indication of the tendency of the fuel to form a flammable mixture with air. It is extensively used to assess the fire risk associated with storage of potentially flammable products. One often-used test is the closed cup Pensky-Martens ASTM D93 test method.(60)

3.2.3. Density and viscosity

The injection of diesel fuel into a compression-ignition engine is controlled either by a solenoid valve, or volumetrically by positive displacement. The performance of these injection systems, as well as the injection timing of mechanically controlled injection equipment, is determined by the density and viscosity of the fuel. If diesel *density* and *viscosity* are not within the narrow range for which the engine has been calibrated, engine performance will suffer and exhaust emissions could increase.(10) This is the main reason for the narrowing of the density and viscosity ranges in international fuel specifications (Tables 8 and 9). Both of these specifications present a problem to the FT refiner, since FT derived products inherently have a lower density and viscosity than crude oil derived products due to the more aliphatic nature of the FT material.

Decreasing the density of diesel reduces particulate emissions and under some operating conditions, NO_x emissions too. This in part explains the good particulate emission reduction seen with FT diesels.(38)(39) Furthermore, it has previously been noted that particulate emissions and NO_x formation are interrelated due to their dependence on the combustion temperature in the engine. However, the EPEFE study also showed that as the diesel fuel density decreases, the energy density decreases, with the result that engine power is reduced and volumetric fuel consumption is increased.[y]

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[x] Both methods were in use at the Fischer-Tropsch Refinery Catalysis (FTRC) group of Sasol. The O'Connor, et al. method was recommended by R. de Haan (FTRC report 363/01, June 2001), while the SAE861521 method was found to be more accurate by A. M. Liwanga (memorandum FTRC 0444, 22 July 2003).

[y] If diesel with a density of 840 $kg\cdot m^{-3}$ is used as benchmark, EPEFE found that engine power increased by 2-3% on increasing the density to 860 $kg\cdot m^{-3}$ and decreased by the same amount on decreasing the density to 820 $kg\cdot m^{-3}$. This is a linear relationship, implying a >5% reduction in engine power with FT diesel (<800 $kg\cdot m^{-3}$).

3.2.4. Aromatic content

According to the fuel specifications a molecule is considered an aromatic if it contains at least one benzene ring in its structure. There are consequently a wide variety of molecules, with very different fuel properties, that can be classified as aromatics. This is why the fuel specifications differentiate between total aromatics and polynuclear aromatics (aromatics with three or more benzene rings).

The *total aromatic content* determines the flame temperature during combustion, with a higher aromatic content leading to higher NO_x emissions. The density of diesel fuel is also related to the total aromatic content and some relationship between particulate emissions and aromatic content can be expected. The *polyaromatic content* that is often seen as the main contributor to particulate and polyaromatic hydrocarbon (PAH) emissions. This value is regulated by European fuel specifications, while both the total and polynuclear aromatic content is specified in the WWFC guidelines.[z] Neither specification presents problems for FT derived diesel, because it is low in aromatics.

Nevertheless, the role of the polyaromatic hydrocarbon content of diesel fuel has not conclusively been linked to either particulate or PAH emissions. Particulate emissions are also influenced by engine technology, operating conditions, exhaust after-treatment and lubricant quality. Furthermore, it has been demonstrated that PAH emissions are due to pyrosynthesis reactions during the combustion process and not the PAH content of the fuel.(61) In another study by ExxonMobil and Toyota using a modern high-speed direct-injection engine, it was found that particulate matter showed a statistically significant correlation with aromatics, naphthenes, cetane number and density.(62) This challenges the notion that aromatics is the only precursor for particulate matter emissions.

3.2.5. Sulphur content

The *sulphur content* of diesel fuel is the fuel specification that has changed most in recent years, decreasing from more than 0.1% down to 0.001%. This is in part due to concerns about SO_x emissions and especially SO_2 emissions. The harmful effect of SO_2 on vegetation

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[z] Diesel density and total aromatic content cannot be seen as two totally separate specifications. The lowering of the diesel density specification implies a reduction in total aromatics. By regulating both total aromatics and density, the WWFC might be over specifying the fuel.

has been extensively studied(63) and extends well beyond the publicised concept of "acid rain", which caused sulphur emissions to become a politically charged issue.

The sulphur in diesel fuel has a negative influence on engine performance and exhaust emissions. It contributes significantly to the formation of fine particulate matter through the formation of sulphates in the exhaust stream and atmosphere. It can also lead to corrosion and wear of engine systems and it reduces the efficiency of the exhaust emission after-treatment systems.(10) Unfortunately deep hydrodesulphurisation (HDS) of distillates to meet the low sulphur specifications also results in a significant loss of diesel lubricity.(64)

The reduction in sulphur specifications does not affect the production or refining of FT diesel fuel, since it is already sulphur free. It nevertheless affects the marketing strategy of FT derived diesel, since the advantage of having a low sulphur content is no longer a differentiating feature in the market.

3.2.6. Lubricity

Diesel fuel pumps that do not have an external lubricating system, relies on the lubricity of the fuel to reduce wear. Diesel *lubricity* is usually determined by ASTM D6079,(65) which makes use of the high-frequency reciprocating rig (HFRR) method.[aa] Although other test methods[bb] can also be used, this test has been shown to have a good correlation with actual diesel fuel pump wear.(10) Inadequate lubricity can result in excessive pump wear and even pump failure. This is indeed what happened to passenger cars in the Swedish market, shortly after the introduction of ultra-low sulphur diesel (10 $\mu g \cdot g^{-1}$) in 1992. Cars using the Bosch rotary pump reported failures within 3000-10000 km and other manufacturers reported reduced pump performance at short service life.(66) It turned out that the natural lubricating properties of the diesel were destroyed during the sulphur removal process.

The loss of lubricity during the production of low sulphur diesel from crude oil, as well as the inherently poor lubricity properties of sulphur-free FT derived diesel,(37) seemed to indicate that lubricity is linked to sulphur containing species. This was shown not to be the case, with the heteroatom derived lubricity enhancing properties in diesel following the trend $O > N >> S$.(67)

[aa] This method measures the wear on a test sample at constant temperature (25 or 60°C) and under constant load while vibrating at 50 Hz over a period of 75 minutes. The wear is measured in units of length, with a longer wear length indicating worse lubricity.

[bb] For example ASTM D6078, the Scuffing Load Ball-On-Cylinder Lubricity Evaluator (SLBOCLE).

The issue of diesel lubricity is of especial interest to FT refiners, not only due to the poor lubricity properties of hydrotreated FT diesel, but also because oxygenates are lubricity enhancing and FT products are naturally rich in oxygenates. FT diesel can therefore in theory be optimised for lubricity if the origin of lubricity is understood.

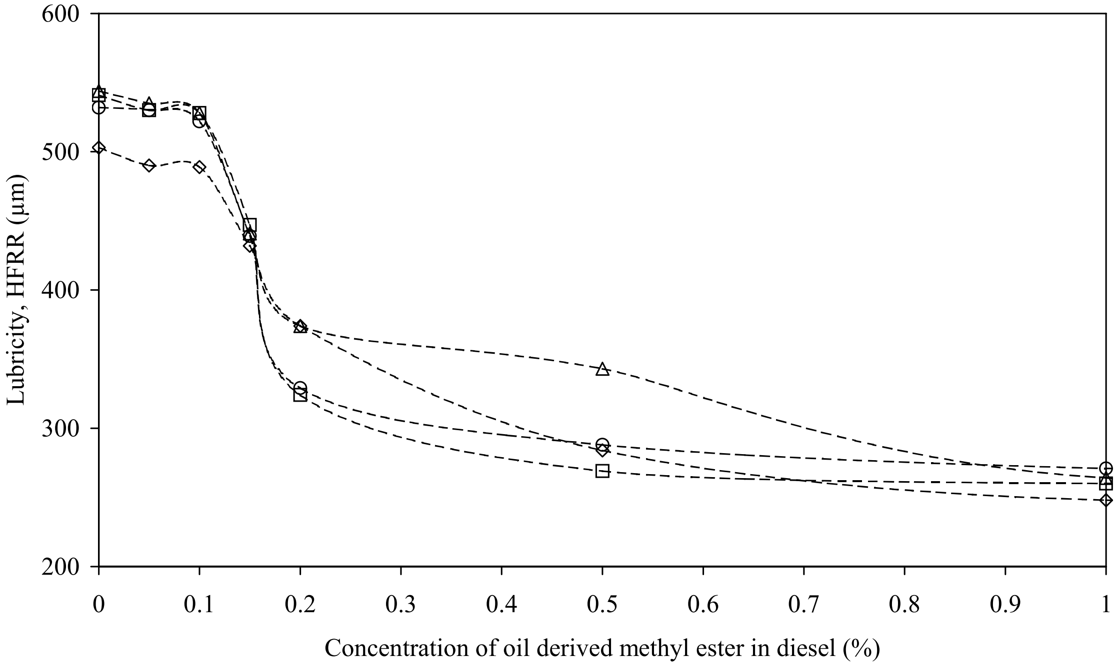

Figure 1. Non-linear lubricity response of low sulphur diesels to the addition of methyl esters of fatty acids from sunflower oil (□), olive oil (◊), corn oil (○) and used frying oil (Δ).

Boundary layer lubricity is imparted by surface-active species(64) and the reported non-linear response of diesel lubricity to lubricity improvers (Figure 1)(68) is to be expected, since a critical surface concentration is necessary to impart lubricity. The lubricity enhancing properties of various oxygenates have been investigated,(66)(68)(69)(70)(71)(72) because species with polar and non-polar regions are expected to show some surface-active behaviour. Not all oxygenates are equally effective as lubricity providers and it has been shown that the lubricity of biodiesel, which is rich in methyl esters, can itself be improved by mild oxidation.(73) When oxygenates of the same chain length were added to diesel fuel, the lubricity was improved in relation to the polarity of the oxygenate used: ethers < ketones < methyl esters < 1-alcohols < aldehydes < carboxylic acids.(67) The four main types of lubricity additives are long chain mono-carboxylic acids, dimer acids (two carboxylic acid groups), amides of long chain mono-carboxylic acids and long chain alkyl esters, typically fatty acid methyl esters (FAME) derived from the esterification of plant oils with methanol. The most widely used lubricity additive is long chain mono-carboxylic acids.(74)

It should be noted that boundary layer lubricity improvement is not the only requirement, hydrodynamic lubricity that is related to viscosity, is also important.(75)

3.2.7. Cold flow properties

Although the specifications for cold flow properties are region specific, it is a vitally important fuel specification. At low temperatures the highest cetane components, the *n*-paraffins, tend to crystallise out of solution as a paraffin wax. Should this happen, the properties of the diesel will change and it is likely that the fuel system will be blocked by the waxy deposits, rendering engine operation difficult or impossible.

The cold flow properties of a diesel are therefore defined by wax-related tests, namely *cloud point* (CP), *cold filter plugging point* (CFPP) and the *low temperature flow test*. The CP is the temperature at which the heaviest paraffins start to precipitate and it is determined by the ASTM D2500(76) method. The CFPP is determined by the EN116 method and is the lowest temperature at which the fuel can still pass through a filter. The CFPP will in general be lower than the CP,[cc] since it will be possible for small wax crystals to pass through the filter and the CFPP can be lowered by addition of cold flow additives. These additives, or middle distillate flow improvers (MDFI) change the crystallisation behaviour, causing it to form needles, rather than slabs. This slows crystal growth and makes it easier for the crystallised particles to move through the fuel filter and when they get stuck, to still allow liquid to pass through.(74)

The low temperature flow test, as defined by the ASTM D4539(77) method, has been developed as a more stringent way of determining cold operation of diesel and is considered a more reliable indicator than CFPP.(10)

4. Aviation turbine fuel (jet fuel)

The requirements for a good aviation turbine fuel are fundamentally different from that of either good motor-gasoline, or good diesel. The energy content and combustion quality of the fuel are key performance properties. The fuel is directly and continuously combusted

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[cc] It is recommended that when the CFPP is used as fuel specification, that it should never be more than 10°C lower than the CP.

with compressed air in a combustion chamber and the hot gases are used to drive a turbine. Poor combustion will not only lead to energy loss and high hydrocarbon emissions, but particulate matter generated by poor combustion can damage the turbine.

The first fuel to be used for turbine engines was illuminating kerosene, which was produced for wick lamps. It was initially thought that turbine engines are relatively insensitive to fuel properties and kerosene (typically in the 160-260°C boiling range, which is C_{10}-C_{15} hydrocarbons) was chosen due to its availability.[dd] After the Second World War, a wider cut that included some lighter material was used, but it was abandoned for general use due to greater evaporative losses at high altitude and the safety risks involved in dealing with such a volatile fuel. Presently the wider cut fuel (Jet B) is only used in Arctic regions due to its good cold flow properties. Apart from the USA that still uses Jet A, as defined by ASTM D1655,(78) the rest of the world has standardised on Jet A-1 as aviation turbine fuel. The main difference between Jet A and Jet A-1 is the lower freezing point of Jet A-1 that makes it more suitable for long international flights.

Aviation turbine fuel (jet fuel) is not the same as aviation gasoline (Avgas). Aviation gasoline is a high energy content, high octane, low freezing motor-gasoline range fuel used in aircraft piston engines.[ee] Specifications for aviation gasoline are given in ASTM D910.(79)

4.1. International specifications

The nature of air travel requires that there must be a single international standard for all commercial aircraft using aviation turbine fuel (Table 11).(80) There are other specifications for domestic air travel, like the TS-1 jet fuel specification used in Russia and parts of Eastern Europe, which is described in the Russian GOST 10227 specification. Aviation turbine fuel for use by military aircraft also has its own specifications, for example the JP-5 for US Naval aircraft and JP-8 for the US Air Force aircraft.[ff]

Additives are also strictly regulated. In Jet A-1 antioxidants are required in any fuel composition that has been hydroprocessed. The approved antioxidants for aviation fuel are hindered phenols,(81)(82)(83) with a maximum allowable concentration of 24 $mg \cdot l^{-1}$.(80) The

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[dd] Turbine engines were pioneered during the Second World War, when motor-gasoline was scarce, since it was not only used for ground transportation, but also the high-performance spark-ignition engines used on propeller aircraft.

[ee] The use of aviation gasoline during the Second World War was extensive (about 115 000 m^3 per day for the Allied forces). Present global consumption is only 10 000 m^3 per day, while jet fuel consumption is more than 800 000 m^3 per day (1998 data).

[ff] The main difference between JP-5 and JP-8 ("Jet A-1") is the flash point, which is 60°C for JP-5.

addition of a metal deactivator is allowed. The only approved metal deactivator is N,N'-disalicylidene-1,2-propane diamine (Figure 2).(80)

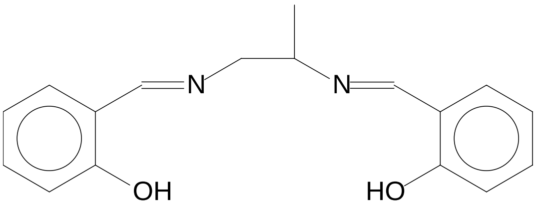

Figure 2. N,N'-disalicylidene-1,2-propane diamine.

Table 11. International specifications for civilian aviation turbine fuels, showing minimum and maximum values for selected fuel properties.

Specification	Jet A	Jet A-1	Jet B
Net heat of combustion ($MJ\cdot kg^{-1}$), min.	42.8	42.8	42.8
Aromatic content (vol %), max. ¶	25	25	25
Naphthalene content (vol %), max.	3	3	3
Sulphur content (mass %), max.	0.3	0.3	0.3
Mercaptan content (mass %), max.	0.003	0.003	0.003
Acidity (mg KOH/g), max.	0.1	0.1	‡
Smoke point (mm), min. †	25	25	25
Flash point (°C), min.	38	38	‡
Density @ 15°C ($kg\cdot m^{-3}$)	775-840	775-840	751-802
Viscosity @ -20°C (cSt)	8	8	‡
Freezing point (°C), max.	-40	-47	-50
Vapour pressure (kPa), max.	‡	‡	21
Distillation (°C): §			
T10, max.	205	205	‡
T20, max.	‡	‡	145
T50, max.	‡	‡	190
T90, max.	‡	‡	245
Final boiling point, max.	300	300	‡

‡ = Not limited by the fuel specification.
¶ = For jet fuel containing synthetic components the aromatics content must be in the range 8-22 vol %.
† = Can be lowered to 18 mm if used in conjunction with naphthalene content.
§ = Specifications for fully synthetic jet fuel is likely to contain a requirement for a minimum distillation versus temperature slope to ensure gradual evaporation and reduce single-component addition to such fuels.

4.2. Aviation turbine fuel properties

4.2.1. Heat of combustion

The heat of combustion is the amount of energy released when the fuel is completely oxidised to produce carbon dioxide and water vapour, also referred to as the net energy content of the fuel.[gg] The reference method for the *net heat of combustion* is the ASTM D4809(84) method, which is based on oxidation in a bomb calorimeter. Estimation methods can also be used, as described in ASTM D3338 and ASTM D4529. It will be noted that the aviation turbine fuel specification (Table 11) places a limit on the minimum gravimetric energy content, which is different to the volumetric energy content. A fuel with a low density, which is generally rich in paraffins, will have a high gravimetric energy content and will easily meet the energy specification. Conversely, a fuel with a high density, which is generally rich in aromatics, will have a high volumetric energy content, but low gravimetric energy content. Typical values for some aviation fuels are given in Table 12.

Table 12. Typical values for different aviation fuel types.

Aviation fuel type	Density	Net energy content	
	($kg{\cdot}m^{-3}$)	($MJ{\cdot}kg^{-1}$)	($MJ{\cdot}l^{-1}$)
Aviation gasoline	715	43.71	31.25
Jet B (wide-cut) aviation turbine fuel	762	43.54	33.18
Jet A-1 aviation turbine fuel	810	43.28	35.06
JP-10 missile fuel	-	-	39.43

In practice there is a trade-off between using a fuel with a high gravimetric energy content as opposed to a fuel with a high volumetric energy content. Aircraft have only limited fuel tank space, which is a volumetric constraint. Carrying fuel with a high volumetric energy content (high density) will give it better range and military aircraft will invariably select a fuel with high volumetric energy content to achieve the best flight range. Selecting a fuel for commercial aircraft is less obvious. Although fuel tank capacity is also limited, commercial aircraft take on only enough fuel to reach their destination plus some

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[gg] The net energy content should be differentiated from the gross energy content, which includes the heat of vaporisation of water. Although water is a liquid at standard conditions, the water will be in the gas phase after combustion in a jet engine and its heat of vaporisation will not be available.

additional fuel to give it an adequate safety margin. Selecting a fuel with a high gravimetric energy content (low density) is more efficient, because the energy weighs less, and in practice fuel tank capacity is not constraining. However, fuel is sold volumetrically, which implies that you have to pay more for the same energy, which complicates the decision. In most cases a fuel with high volumetric energy density (high density) is preferred, but airliners seldom have the luxury to pick the energy content of their fuel.

4.2.2. Density and viscosity

The fuel viscosity and to a lesser extent the fuel density influence the spray pattern and droplet size of the fuel when it is injected under high pressure into the combustion chamber of a turbine engine. The fuel system is designed to produce a fine spray that can easily evaporate when it is mixed with the hot air from the compression section. If the *viscosity* is too high it changes the droplet size distribution to produce larger droplets.(85) This can affect performance, but more importantly, it poses a safety risk, because it makes it difficult to re-light an engine in flight after a flameout[hh] has occurred.

With increasing fuel viscosity the pressure drop in the fuel lines also increases, as well as the pump duty required to maintain a constant fuel flow. If the viscosity is too high, the fuel system will not be able to supply the engine with the required amount of fuel. The maximum viscosity is therefore regulated.

Viscosity also affects the hydrodynamic lubricity of the fuel and on the lower end of the scale a fuel with a too low viscosity may cause excessive wear on pump parts and flow control units. Although there is not a minimum limit for viscosity, the distillation range effectively sets the lower viscosity limit. Viscosity is not the only factor controlling lubricity and boundary layer lubricity (section 3.2.6) that is imparted by surface-active compounds should also be considered.

From the previous section it is clear that *density* is not really an independent variable. The specifications allow a wide density range and in practice density is not controlled, but a result of the limitations placed on the fuel composition and especially the aromatic content.

[hh] Continuous combustion of the fuel air mixture in the combustion chamber of the engine requires a stable flame, which in turn requires that the fuel and air flow rates are matched to the flame propagation rate. Under turbulent flow conditions the hydrocarbon flame propagation rate is 10-30 $m \cdot s^{-1}$. The flame will only be stable if the flame propagation velocity is higher than the velocity of the primary air inlet into the combustion chamber. Under conditions where the air velocity exceeds the flame propagation velocity, flameout occurs.

4.2.3. Aromatic content and smoke point

In a jet engine, small carbonaceous particles can be formed as combustion commences. As these particles travel through the combustion chamber, they continue to burn and should be completely consumed before leaving the combustion chamber. The formation of such carbonaceous particles in the combustion chamber is detrimental in two ways. Firstly, the particles become incandescent at the high temperature and pressure conditions of the combustion chamber, which can cause hot spots on the chamber wall due to the high additional heat transfer rate. This may cause cracks and lead to premature engine failure. The particles can also block the holes in the combustion chamber wall that supply air to the combustion section, thereby disrupting the flow pattern. Secondly, if these particles are not consumed in the combustion chamber, they impinge on the turbine blades and stators, causing erosion of the turbine section.(80) These particles are also responsible for the visible smoke that some engines emit. It is consequently clear that fuel components that have a tendency to form such carbonaceous particles during the early stages of combustion should be avoided.

Aromatic compounds and especially naphthalenic compounds are more prone to the formation of such particles than aliphatic hydrocarbons. Both the total *aromatic content* and the total *naphthalenic content* of jet fuel are therefore regulated by the aviation turbine fuel specifications. The *smoke point* is a measure of the tendency of a fuel to form particles (black smoke) during combustion and the method for its determination is described by ASTM D1322.(86) It is a simple test whereby the fuel is burned in a wick-fed lamp, where the smoke point is the maximum flame height that can be achieved without smoke being formed.

4.2.4. Sulphur content

The limitation on the *sulphur content* is mostly to reduce SO_x emissions, but it has the added advantage of reducing microbial growth.[ii] In terms of fuel quality, the limitation placed on the *mercaptan content* is more crucial. Marcaptans (thiols) and organic acids can cause corrosion of some engine and fuel system components and are therefore limited by jet fuel specifications.

[ii] The control of biological growth during fuel storage is discussed in ASTM D6469. The key aspect to limiting biological activity is limiting free water, but reducing elemental nutrients like sulphur also helps.

4.2.5. Freezing point

The freezing point is defined as the highest temperature at which all of the compounds in the fuel are still in the liquid phase. The primary reference method for *freezing point* determination of aviation fuel is ASTM D2386,(87) but there are other methods too.[jj] Since the fuel is a mixture of many compounds, the fuel mixture does not become a solid at the freezing point temperature. As the temperature is lowered below the freezing point of the fuel, compounds will start crystallising out of solution to create a slush of fuel and solid hydrocarbons. This affects the ability of the fuel to be moved from the fuel tanks to the engine and jet fuel remains pumpable only to between 4 and 15°C below its freezing point.(80)

4.2.6. Volatility

The volatility as specified by the ASTM D86(20) distillation range, is used as an indirect measure to control properties like the minimum viscosity and combustion quality. However, for jet fuels containing synthetic components, a minimum slope for the volume recovered versus distillation temperature curve is likely to be specified.(88) This will ensure gradual evaporation of the fuel and avoid the formation of fuel-rich and air-poor pockets in the turbine engine due to flash evaporation associated with narrow boiling synthetic compounds. The addition of large volumes of single-compound synthetic additives will not be possible.

4.2.7. Thermal stability

The thermal stability of jet fuel is important, since the fuel serves as a heat exchange medium in the engine and airframe to cool engine oil, hydraulic fluid and air conditioning equipment. This is not the same as storage stability, which relates to the autoxidation propensity of the fuel. The *thermal stability* is measured by ASTM D3241(89) and is a measure of the tendency to form particulates, gums and deposits when the fuel comes into contact with hot surfaces. This is a key fuel property, especially in high performance aircraft such as used by the military.

[jj] ASTM D4305, ASTM D5901 and ASTM D5972 are all acceptable methods for determining the freezing point of aviation fuel.

5. Trends for future fuel specifications

5.1. Future motor-gasoline

The complete phase-out of lead and other metal containing additives has already taken place in many countries.[kk] Too meet the octane shortfall refiners had to invest in octane generating capacity and it resulted in many refineries having "surplus" octane generating capacity. The public perception that octane is a good all-round measure of motor-gasoline performance was exploited by marketers and the surplus octane generating capacity was used to produce fuels with higher than legislated octane numbers. This trend of *high-octane unleaded motor-gasoline*, typically RON 98 and MON 88, is seen to become the norm in countries where the fuel market is deregulated and pump-price is determined by supply and demand. In future this trend will also force other countries to follow suit, since engine manufacturers are sure to exploit the benefits of high octane fuels to produce engines with higher compression ratios.

The marked reduction in sulphur content is likely to continue in future. Many refineries opted for installing sulphur removal capacity that allows them to produce fuels with 10 $\mu g \cdot g^{-1}$ or less sulphur. Since sulphur has no benefit at all in motor-gasoline and the capital investment required for sulphur reduction has already been made by many refineries, it is just a question of time before such low levels of sulphur are legislated worldwide.

Although the maximum allowable aromatic content decreased in successive motor-gasoline specifications, there is a high cost associated with the hydrogen needed to decrease the aromatic content further. In addition to this, a decrease in high octane aromatics implies that a higher paraffin quality is required, which can hardly be justified considering the limited impact it has on emissions. However, it is expected that the trend in *benzene reduction* will continue and that in future benzene will be required to be less than 1% in motor-gasoline. Benzene is a known carcinogen and the technology exists to keep refinery benzene levels low, in many instances lower than the legislated requirements. The Environmental Protection Agency (EPA) claims that 70% of the benzene emissions in the United States are due to transportation fuels and in the USA from 2011 onwards the benzene content in motor-gasoline will be limited to 0.62% by volume.(90) Other countries are sure to follow.

[kk] Aviation gasoline, which initially escaped the lead-ban, is likely to become low lead or lead-free too. Some lead-free grades are already available, but considering that grades 100 and 100LL Avgas has a minimum MON requirement of 99.5, phasing out lead is more difficult, because it requires a very good base stock.

There is no real trend in the addition of oxygenates, with Europe still using ethers (including MTBE), while there is a strong political lobby in the USA to ban ethers and include ethanol. It is *unclear what the future holds for oxygenates*.

In crude oil refineries olefins are mainly produced by fluid catalytic cracking (FCC) and inclusion of olefins in motor-gasoline is limited. The problem is that crude oil refiners also include short chain olefins in the motor-gasoline, which contributes to storage instability and increases some exhaust emissions, notably ozone forming potential. This is an easy specification to change, because the refinery impact is usually small, unlike in FT refineries where this has a serious impact. Nevertheless, it is likely that future specification will include an *olefin content reduction* to about 10%.

All of these likely changes point in one direction, namely better quality paraffins for motor-gasoline (Appendix B). The only compound class that is not limited by fuel specifications is the paraffins and the refining focus for motor-gasoline will in future be directed towards producing high octane paraffins.

5.2. Future diesel

Many of the diesel specification changes have been incremental, nudging the *cetane up* possibly to 55, *narrowing the density and viscosity ranges* and *lowering the T95* boiling point to 340°C. These changes are significant, but not disruptive and are likely to be adopted as refineries move in that direction in any case. No specifications dictating the distillation curve of diesel fuels are anticipated and it is expected that the initial and final boiling points of diesel fuel will continue to be regulated indirectly by the flash point and T95 boiling point specifications.

The most dramatic change has been the reduction in sulphur content. As is the case for motor-gasoline, refining capacity has been installed to *reduce sulphur* in diesel fuel to levels of 10 $\mu g \cdot g^{-1}$ or less. In future such low levels of sulphur will be legislated.

The level of polynuclear aromatics are already limited by diesel specifications and the trend is to reduce heavy aromatics in diesel also by other specifications, like lowering the T95 boiling point. In future much *lower polynuclear aromatics* is likely to be legislated and even a *limitation on total aromatics* is probable. A limitation of total aromatics may make it uneconomical to refine heavy aromatic crude to distillate range products, which will have an influence on especially European diesel production in future. It is therefore uncertain that total aromatics will be targeted, since it could result in over specification of diesel.

There is a definite trend, fuelled by environmental and political reasoning, to include renewable material in diesel. Much work has been done on esterification of plant materials and spent cooking oil to be included as blending component in diesel. It is predicted that a *minimum biodiesel content* may in future be legislated, typically 5% or more.

Future diesel specifications point to an increased refining focus on hydrogen generating and carbon rejection technologies to upgrade heavy-ends. Refiners will also have to take note of renewable fuels. The emphasis on fuels with a high H:C ratio is not new and the benefits of such typical Fischer-Tropsch diesel fuels have been advocated for quite some time,(91) but it is unlikely that niche fuel specifications and engine tuning to exploit such characteristics will become significant in the short to medium term.

5.3. Future aviation turbine fuel

The nature of aircraft and jet engines and the air transport industry in general is such that changes in aviation turbine fuel specifications are difficult to make. There is a significant safety aspect involved and fuels must be qualified on different engine types before it can be accepted as safe for use. It is therefore doubtful whether significant changes in the specification of Jet A-1 will be seen. If any, it is likely that a *lower naphthalene content* will be targeted.

The reduction in the sulphur content of motor-gasoline and diesel may result in a lower sulphur content for all fuel types, including jet fuel. Since sulphur is not needed and poor lubricity is already addressed by the specifications, the specifications may in future change to reflect the *lower sulphur content* in jet fuel that is already being seen.

It would be wrong to imply that kerosene is a by-product, but the refinery and fuel specification changes that affect motor-gasoline and diesel have a natural spill over effect on jet fuel. With the increasing need for high octane paraffins (highly branched paraffins) for motor-gasoline and distillate cetane being nudged upwards, the unwanted low octane C_7-C_{10} paraffins in motor-gasoline and unwanted low cetane C_{11}-C_{15} components in diesel may end up in jet fuel to balance the overall refinery needs. This seems to be a good fit, since there are few paraffinic compounds in the C_7-C_{10} range that do not meet the freezing point specification,[ll] while the unwanted lower aromatics in diesel can provide some density. If the

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[ll] The freezing point of the C_7-C_{10} linear paraffins are: *n*-heptane (-91°C), *n*-octane (-57°C), *n*-nonane (-53°C) and *n*-decane (-30°C).

diesel components are limited to less than 215°C boiling range material (C_{11}-C_{12}), no naphthalene will be included either.

One interesting development in the USA is the formulation of a "Battle Use Fuel of the Future" (BUFF). This is a multipurpose kerosene type fuel, very similar to Jet A-1 in properties, which is required by the USA Department of Defence (DoD) for use in aircraft, tanks and other miliraty vehicles to simplify fuel supply logistics. There is significant interest in Fischer-Tropsch products as feed material for BUFF due to the potential energy security that can be provided.(92)(93) At present the specifications are being fixed as part of a joint BUFF development programme.[mm] Should the BUFF development prove to be successful, it is possible that the qualifying tests done on military aircraft might give enough credence to also qualify it for commercial aircraft. This in turn could provide the impetus to align the Jet A-1 specifications with BUFF specifications.

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[mm] Same specifications as Jet A-1, but with lower minimum density (751 kg·m^{-3}) and higher flash point (60°C).

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APPENDIX A

Origin of the European Euro-3 and Euro-4 fuel specifications

The aim with the fuel specification changes after the Euro-2 specification was to meet European air quality requirements as set out by the European Union. A recommendation was made based on technical grounds by a joint Auto-Oil study committee, that looked at the most cost effective ways to reduce emissions by changing fuel specifications and modifying engine and after-treatment characteristics of vehicles. The study concluded that only minor changes were needed in terms of fuel specifications and that the most cost-effective way of meeting the emission standards was to modify vehicles to include some additional emission control equipment. The Auto-Oil proposal was submitted to the European legislature and was debated in both the European Council and European Parliament (Table A1).[nn]

Table A1. Evolution of the Euro-3 and Euro-4 fuel specifications by political debate.

Maximum values	Auto-Oil	EU Parliament		EU Council		EU Parliament		Conciliation	
for specifications	18 Jun 1996	10 Apr 1997		20 Jun 1997		11 Feb 1998		29 Jun 1998	
	Euro-3	Euro-3	Euro-4	Euro-3	Euro-4	Euro-3	Euro-4	Euro-3	Euro-4
Motor-gasoline									
Sulphur (μg·g^{-1})	200	50	30	150	50	100	30	150	50
Aromatics (vol %)	45	35	30	42	35	35	30	42	35
Benzene (vol %)	2	1	1	1	1	1	1	1	1
Olefins (vol %)	18	10	10	18	18	14	14	18	18
Diesel fuel									
Cetane, minimum	51	52	58	51	51	51	58	51	51
Density (kg·m^{-3})	845	837	825	845	845	845	825	845	845
PAH (%) ‡	11	6	1	11	11	11	1	11	11
Sulphur (μg·g^{-1})	350	100	50	350	50	200	50	350	50

‡ PAH = Polynulear aromatic hydrocarbons, that is aromatics with 2 or more aromatic rings.

The timing was inopportune, since it was at this time that the European Parliament got increased executive powers and some political friction between the European Council and

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[nn] Hutcheson, R. Gasoline and diesel fuel technology: Oxford Princeton programme 8793, 2006.

European Parliament was bound to occur. The proposed legislation from the Parliament and Council were not aligned and a process of conciliation had to be invoked to reach the final agreement between the European Council and Parliament. The outcome was not only two specifications to be implemented at different dates (instead of a single new specification), but also fuel specifications that by far exceeded the requirements necessary to meet the European air quality targets! The cost to the European Union in terms of refinery modifications and increased fuel price had been the unnecessary expedient of political debate and the need to compromise on political level.

APPENDIX B

Theoretical limitations and implications of petrol specifications

Background

The need for fuel specifications is clear, since it is a form of fuel quality control and performance guarantee. However, fuel specifications are not as constant as the name implies. Because it influences so many people's lives (voters), it is more often than not a political issue, rather than anything else. Different pressure groups influence political thinking and this essentially drives the legislation governing fuel specifications: Consumers, who become increasingly environmentally conscious; Urbanites, demanding a limit on vehicle emissions due to uncomfortable pollution levels in cities; Motor manufacturers, who keep on improving engine design for better fuel economy and performance; Industry, wanting to maximise profits and minimise expenses; and Farming lobbyists who see fuel as a large commodity market for their products.

In the past there had been a lot of leeway in terms of fuel specifications, but we are quickly approaching a level of regulation that will make refining prohibitively expensive. This is clearly illustrated by the following quote from ExxonMobil in their 2000 USA Election campaign briefing: "Energy is a fundamental part of the global economy … The election on 7 November is important because government policies, laws, and regulations affect all aspects of energy development … Overregulation is one reason that no new refineries have been built in this country in more than 25 years."

This begs the question, how stringent can specifications be and how much leeway do refiners have?

Methodology

A theoretical approach to fuel formulation was taken to try and answer this important question. It is known that vapour pressure and octane numbers do not scale linearly with respect to the volumetric blending ratio, but to simplify the calculations, this type of blending model was selected. This may introduce some numerical deviation from the real numbers, but would not seriously detract from the trends or conclusions to be drawn.

Synthetic fuel blends containing only olefins, aromatics and oxygenates were postulated. These would just meet the fuels specifications with respect to those components, if the remainder were made up of paraffins. The quality of the paraffin blending stock that would be required to meet the RON, MON and vapour pressure requirements was then calculated. The aromatics, olefins and oxygenates were selected in such a way that it would constitute a realistic but ideal blending stock (Table B1). This would give an indication of the minimum requirements for the paraffin blending stock. In practice, the quality of the aromatics would generally be lower and a better quality paraffin blending stock would be needed to meet fuel specifications.

Table B1. Fuel components used for ideal synthetic blending stock.

Component	RON	MON	RVP (kPa)	Quantity used
Olefinic Poly petrol	95	81	70	Maximum allowable
Benzene	100	115	22	Maximum allowable
Toluene	119	103.5	7.1	Remainder for max. aromatics
TAME	115	100	25	Maximum allowable
Ethanol	120	99	154	Remainder for max. oxygen

Results

The minimum quality paraffin blending stock was calculated for the European and World-wide Fuel Charter specifications (Table B2).

Discussion

From the data in Table B2 it is evident that the move from Euro-3 to Euro-4 cut out a lot of the fat in the fuel specifications. Although the change in maximum aromatics content from 42% to 35% seemed moderate, the effect on the paraffin quality required to meet the new specification is 20–30 octane units. Still, it was a realistic change and in practice, even with lower quality aromatics, it is quite feasible to achieve.

The WWFC category 1 motor-gasoline is strictly speaking a “historic” fuel and illustrates how much leeway had been present in refineries. The WWFC category 2 fuel compares well with Euro-3 specifications and it requires a similar paraffin quality. However, when moving to WWFC category 3 and 4 fuels, it is clear that the reduction in olefin specification to 10% (Euro-4 is 18%), has a significant impact on the quality of paraffins required to meet fuel specifications. This difference is very real to a Fischer-Tropsch refiner, who has access to large volumes of olefins, but crude oil refineries probably have to include 80-85 octane paraffins in any case. Euro-4 and WWFC category 3 & 4 fuels are therefore quite similar in paraffin requirements for crude refiners.

It should nevertheless be clear that any change from Euro-4 in the direction of less legislated high-octane components (olefins, aromatics and oxygenates) has a significant impact on the quality of paraffins required for to meet fuel specifications. This emphasises the need to focus on paraffin upgrading technologies to meet future motor-gasoline specifications.

Table B2. Paraffin quality needed for various motor-gasoline specification scenarios.

Description	Euro-3	Euro-4	WWFC1	WWFC2	WWFC3 & 4	
Specification						
Octane, RON	95	95	95	95	95	98
Octane, MON	85	85	85	85	85	88
Reid vapour pressure (kPa)	60	60	60	60	60	60
Olefins (vol %)	18	18	30 †	20	10	10
Aromatics (vol %)	42	35	50	40	35	35
Oxygen (mass %)	2.7	2.7	2.7	2.7	2.7	2.7
Blending stock						
Olefinic Poly petrol (vol %)	18	18	30	20	10	10
Benzene (vol %)	1	1	1	1	1	1
Toluene (vol %)	41	34	49	39	34	34
TAME (vol %)	15	15	15	15	15	15
Ethanol (vol %)	1	1	1	1	1	1
Paraffin blend requirement						
RON, minimum value	32	59	-36	33	83	93
MON, minimum value	35	59	-23	37	80	89
RVP (kPa), maximum value	125	127	96	121	145	145

† = Not regulated, used current Sasol internal olefin specification for South Africa.

CHAPTER III

Crude Oil

Crude oil is rich in hydrocarbons, mainly paraffins (alkanes), naphthenes (cyclo-alkanes) and aromatics, with no or very little olefins (alkenes) present. Compounds of the same skeletal structure, but containing heteroatoms like sulphur, nitrogen, oxygen and metals like nickel and vanadium, are also present. Sulphur (≤ 5%) and nitrogen (≤ 0.5%) are the heteroatoms that affect refining the most. In addition to these, corrosion problems may result from oxygenates in the form of carboxylic acids (≤ 3 mg KOH/g) and salts in the form of $MgCl_2$ *and* $CaCl_2$ *(≤ 350* $\mu g\cdot g^{-1}$*). The importance of crude density and distillation characteristics on refining has also been highlighted.*

1. Introduction

Crude oil is a collective term used to describe a hydrocarbon rich mixture of compounds that is usually found as a subterranean deposit that accumulated over millions of years. The physical and chemical characteristics of crude oil vary widely from one production field to another and even within the same field. Colloquially terms like “light”, “heavy”, “naphthenic”, “paraffinic”, “sweet” and “sour” are used to characterise crude oil in terms of its boiling range, composition and sulphur content.[a] These are important properties, because they have a big impact on the refinery, but it belies the true complexity and diversity of crude oil. The crude oil composition determines its price and although specific oil types, like Brent crude, are used as an international measure of oil price, more difficult to refine oils command a much lower price. The selection and scheduling of crude oil feed to a refinery is a highly specialised field in its own right,(1) and it directly affects the production economics.

It is important to discuss crude oil properties, because refining technology has been developed in response to the differences between crude oil properties and final product specifications. Furthermore, Fischer-Tropsch derived syncrude is different from crude oil in many respects and it is important to understand these differences, because they relate to the

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[a] The terms “sweet” and “sour” originated as measure of corrosiveness. Crudes with more than 6 $\mu g\cdot g^{-1}$ dissolved H_2S were considered “sour”, because it led to observable storage tank corrosion. These terms are no longer applicable and it is strictly speaking incorrect to directly relate “sweet” and “sour” to sulphur content.

ability of refining technologies to deal with Fischer-Tropsch products. Crude oil will be discussed in terms of its composition and characterisation in sufficient detail to enable these objectives to be met.

2. Crude oil composition

The compounds and compound classes present in the lighter fraction of crude, which is typically the fraction that can be recovered by atmospheric distillation, can be identified by chromatographic and spectroscopic techniques. The heavier fraction is more difficult to characterise, because it contains molecular structures with molecular masses that can exceed 10 000 $g \cdot mol^{-1}$. The heavy fraction is classified based on solubility (Figure 1),(2) with *maltenes* being soluble in *n*-heptane and *asphaltenes* being soluble in benzene.[b] The usefulness of this method of classification is doubtful, since it is unlikely that the chemical nature of the molecules is adequately captured. The point has aptly been made by Gray(3) that these heavier fractions are better described as heteroatom species with limited hydrocarbon character, which tend to associate (almost like Velcro™) making separation by solubility and precipitation untenable. The popular notion of heavy crude oil molecules being polycondensed aromatic hydrocarbons (almost like graphite) does not explain the properties and conversion propensity of heavy crude.

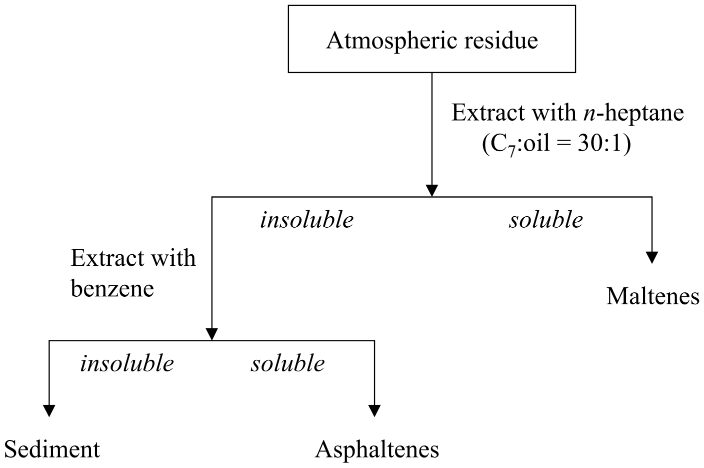

Figure 1. Classification procedure for heavy crude oil fractions (> 360°C boiling fraction).

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[b] The asphaltene content is determined by precipitating the asphaltenes from the benzene solution with a light paraffin. Industrially propane or butane is used, but practice varies and in the USA *n*-pentane is used. This can lead to differences in the reported asphaltene content and composition of a crude oil. If a light paraffin is used, some heavier paraffins may co-precipitate with the asphaltene fraction, reducing its reported aromatic content.

The asphaltene content of crude oil varies from 0.1% to more than 20% depending on the production field. Asphaltenes contain high concentrations of heteroatoms, like sulphur and nitrogen, as well as metals, like nickel and vanadium. Due to the heavy nature of the asphaltenes, their characterisation is mostly done by techniques used in polymer analysis, like size exclusion chromatography. In refineries equipped with a deasphalting unit, the asphaltenes are recovered as asphalt and not upgraded to transportation fuel.

Crude oil can be classified by chemical composition, density, viscosity and distillation characteristics to name a few.(4) The classification system based on composition refers to only the hydrocarbon nature of oil, namely paraffinic, naphthenic or mixed(5) depending on the compound class that is dominant.[c] The other classification systems find utility in giving an indication of the straight run content of the various distillation ranges, which are important in determining the product slate that can be expected. This might have been useful in the past, but it is doubtful whether these classification systems have adequate value for present refineries, where the true composition of the crude is more important in determining the refining pathways. The point is aptly made by Speight:(4) "Clearly the use of one physical parameter, be it API gravity or any other physical property for that matter, is inadequate to the task of classifying conventional petroleum, heavy oil, and tar sand bitumen."

2.1. Hydrocarbons

The main hydrocarbon compound classes present are paraffins (alkanes), naphthenes (cycloalkanes) and aromatics, with very little or no olefins (alkenes) present.[d] The presence of dienes and alkynes are extremely unlikely.(4) The *paraffins* found in crude oil tend to have a high linear hydrocarbon content. This has implications for the fuel quality of straight run products. Light straight run (LSR) naphtha has a low octane number and can generally not be included in motor-gasoline without further refining. Conversely, straight run middle distillates, especially from paraffinic crudes, only needs to be desulphurised (sweetened) to yield good jet fuel or high cetane diesel.

The *naphthenes* most frequently encountered in crude oil have 5- or 6-membered rings and multiple rings may be present. In some cases systems with 4- and 5-membered

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[c] This is ironic, since the point has already been made that crude oil is rich in heteroatom containing compounds.

[d] The presence of olefins in crude oil is a point of dispute. It has been claimed by some that olefins are indeed present, but since such claims generally refer to distilled fractions, cracking cannot be ruled out. There is one exception, however, namely Pennsylvanian crudes, where spectroscopic and chemical methods indicated the presence of olefins (up to 3%). Ref.(4)

rings are found, which serve as biochemical markers.[e] The naphtha range naphthenes make good reforming feedstock, while middle distillate range naphthenes make good jet fuel.

Mono-, di- and polynuclear *aromatics* are found in high concentrations in most crude oils. In the motor-gasoline range, these molecules contribute significantly to the octane number of straight run products and the gravimetric energy density of jet fuel. However, the higher homologues are not desirable.

2.2. Sulphur containing compounds

Sulphur is the heteroatom most commonly found in crude oil and the total sulphur is usually in the range 0.1% to 5% depending on the crude[f,(6)] and seldom falls outside the range 0.05-6.0%.(4) It is also the least desirable heteroatom from a transportation fuel perspective. The distribution of sulphur compounds is not equal over the distillation range and the sulphur content generally increases with boiling point (Table 1).(7)

Table 1. Distribution of sulphur compounds over the distillation range of a 1.2% sulphur containing crude oil.

Distillation	Sulphur	Sulphur compound distribution (%)			
range (°C)	content (%)	Thiols	Sulphides	Thiophenes	Other †
70-180	0.02	50	50	trace	-
160-240	0.2	25	25	35	15
230-350	0.9	15	15	35	35
350-550	1.8	5	5	30	60
>550	2.9	trace	trace	10	90

† = Benzothiophenes and heavy sulphides.

The sulphur can be present in an inorganic form[g] as elemental sulphur, carbonyl sulphide (COS) or hydrogen sulphide (H_2S), or it can be present in an organic form. The organic classes most often encountered are sulphides, thiols (mercaptans) and thiophenes.

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[e] Hydrocarbons with 4-membered rings give an indication of the crude oil origin, since such compounds are remnants of the structure of the living matter from which it has been derived.

[f] The sulphur content of the crude is related to its origin. For example, on a water-free basis plants contain 0.1-0.4%, molluscs about 0.4% and marine algae percentage levels. There are oil sources with a very high sulphur content, like 14% sulphur crude from Rozel Point in Utah, USA, where it is not clear whether the sulphur only comes from organic material.

[g] Free sulphur is not often present in crude oil, but it can be present as a suspension or it can be dissolved in the oil. H_2S is found in the reservoir gas, but the amount dissolved in the oil is typically less than 50 $\mu g \cdot g^{-1}$.

Thiols have the general formula R-SH and are sulphur equivalents of alcohols. Due to the presence of the S-H functional group the thiols are acidic in behaviour (much more than alcohols).(8) They are also extremely malodorous. The thiols are mainly present in the lighter boiling fractions, but their concentration in crude oil is generally quite low.

Sulphides can either be mono-sulphides of the general formula R-S-R′, or disulphides of the general formula R-S-S-R′. Both acyclic and cyclic sulphides are present, including sulphides that are attached to aromatic rings, like thiaindane (Figure 2).

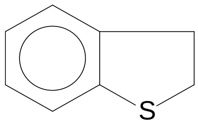

Figure 2. Molecular structure of thiaindane.

Thiophenes are aromatic compounds containing sulphur as part of the ring structure and may take the form of thiophene, benzothiophene, dibenzothiophene and even heavier thiophene derivatives (Figure 3). Most of the sulphur in crude oil occurs in this form. The thiophenes and especially the sterically hindered dibenzothiophenes present a significant challenge to deep hydrodesulphurisation (HDS)(9) to reduce the sulphur content to less than 10 μg·g^{-1} for transportation fuel. This led to some other avenues being explored in order to deal with these difficult to HDS compounds.(10)(11)(12)

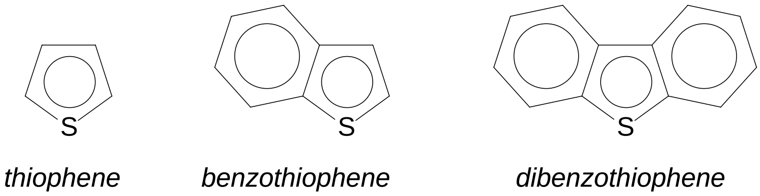

Figure 3. Molecular structures of thiophene derivatives.

2.3. Oxygen containing compounds

The oxygen containing compounds in crude oil is probable the least discussed of all the heteroatom compounds. This is understandable, because oxygenates are generally present in lower concentrations (0.05-1.5%)(4) than sulphur compounds and apart from carboxylic acids that are present in some crudes, the other oxygenates have little impact on transportation fuel quality or the refining processes. Most of the oxygenates are converted to hydrocarbons during hydrotreating, but information on hydrodeoxygenation (HDO) specifically is quite limited.(13) The main oxygenate classes present in crude oil are furanes, phenols, esters and carboxylic acids.[h]

Furans are the oxygen equivalent of thiophenes and contains oxygen as part of an aromatic ring structure (as Figure 3, but with O instead of S).

Phenols are aromatic compounds of the general formula Ph-OH. Although phenol itself is responsible for transportation fuel elastomer incompatibility, the alkyl derivatives of phenol are used as oxidation inhibitors(14)(15)(16) in fuel and quite useful at the concentrations normally present in crude oil.

Esters have the general formula $R(CO)OR'$ and are considered quite benign in transportation fuel.[i] Both aliphatic and aromatic esters can be found in crude.

Carboxylic acids can cause corrosion problems when processing crude at high temperature.[j] The acids are not evenly distributed over the whole boiling range, but have a peak concentration in the 400-450°C range.(6) In lighter cuts some linear aliphatic acids can be found, but the acids are mostly naphthenic acids (5- and 6-menbered ring cycloalkane carboxylic acid derivatives) and can include a variety of polycyclic naphthenic acids (Figure 4).(17) The acid number of crudes typically varies from 0 to 3 mg KOH/g.

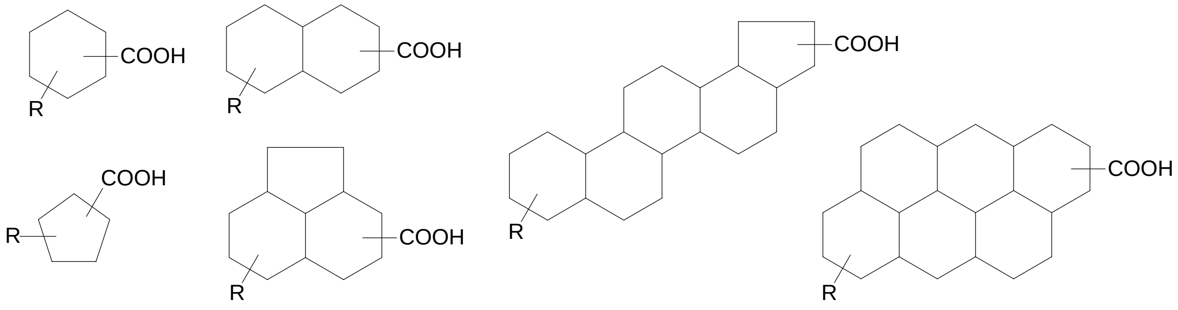

Figure 4. Some of the naphthenic acids identified in Bohai crude oil.

Although naphthenic acids appear to be the most prevalent type of carboxylic acid, some crude oil deposits are rich in aliphatic carboxylic acids (>0.1%), such as the crude oil from the Kutei Basin in Indonesia.(18)

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[h] Amides are also present, which contains the -(C=O)-N< function group. The amides will be discussed with the nitrogen compounds.

[i] The methyl esters of fatty acids in various plant derived oils form the main constituent of biodiesel.

[j] Although crude oil generally does not contain some of the very aggressive short chain aliphatic acids, the heavy naphthenic acids that are present in the crude become quite aggressive at temperatures of 350-400°C, which are often encountered during desalting and lubricating oil production. At such temperatures carbon steel is readily corroded and special alloys are required to deal with acidic crudes.

Crude can also contain *water*, which can be seen as a form of inorganic oxygen. The water is found partly as dissolved water and partly as emulsions.[k] The water content can range from traces to about 2% depending on the crude.

2.4. Nitrogen containing compounds

Nitrogen containing compounds are mostly found in crude oil fractions boiling above 250°C. The nitrogen content depends on the crude origin, but is generally less than 0.5%, although it may be as high as 2%.(4) Basic, neutral and acidic nitrogen compounds are present, with the main nitrogen containing compound classes being amines, amides, pyrroles and pyridines.[l],(2) The basic nitrogen containing compounds reduce the acidity of refining catalysts and are especially undesirable. Nitrogen compounds may also contribute to gum formation in products such as domestic fuel oil.(4)

Amines are basic nitrogen compounds and are found as primary ($R\text{-}NH_2$), secondary (R-NH-R′) and tertiary (R-NR′R″) amines.

Amides are acidic nitrogen compounds containing the –(C=O)-N functional group and are found as both aliphatic and aromatic compounds.

Pyrroles are aromatic compounds containing nitrogen as part of a 5-membered ring structure and may be present as pyrrole, indole, carbazole and even heavier derivatives of pyrrole (Figure 5). These are all neutral compounds, despite the presence of the N-H functionality.[m]

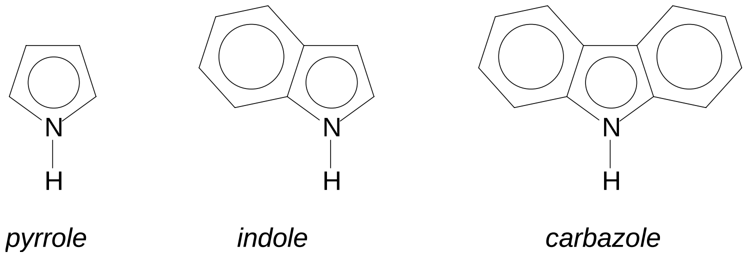

Figure 5. Molecular structures of pyrrole derivatives.

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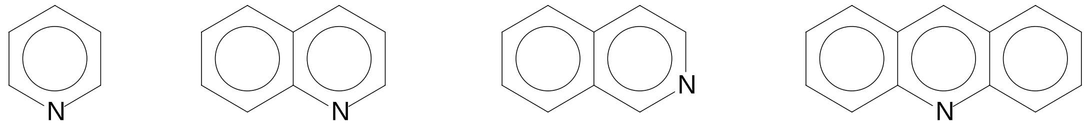
[k] Such emulsions may be caused by the soaps of the carboxylic acids present in the crude oil, which are known to be surface-active compounds.

[l] Crude oil also contains nitrogen compounds of the porphyrine family, which chelates some metal ions and will be discussed with the metal containing compounds.

[m] This is the result of the lone-pair electrons on nitrogen being delocalised in the aromatic π-cloud and they are consequently not available for sharing with acids. In most of the resonance structures of pyrrole, the nitrogen carries a positive charge.

Pyridine and its derivatives like quinoline, isoquinoline and acridine (Figure 6) are basic nitrogen compounds, with the nitrogen forming part of a 6-membered aromatic ring. These compounds and their heavier derivatives occur throughout the distillation range.



pyridine *quinoline* *isoquinoline* *acridine*

Figure 6. Molecular structures of pyridine derivatives.

2.5. Metal containing compounds

The main metal impurities in crude oil are *nickel*, *vanadium* and to a lesser extent *iron* too.(7) These metals are generally found in the heaviest fractions and end up as deposits in the residue processing units of a refinery. Some of the metals are trapped in molecules of the porphyrine family (Figure 7), which act as efficient chelating agents for ions like Ni^{2+} and VO^{+}.(2) The metal content is very crude dependent and may vary from less than 1 $\mu g \cdot g^{-1}$ to more than 1000 $\mu g \cdot g^{-1}$. However, it should be noted that not all Ni and V are contained in porphyrine structures.(19)

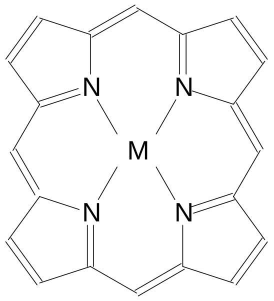


Figure 7. Porphyrine structure for chelating metal ions (M) like nickel and vanadium.

Metals are also introduced in the form of salts of *sodium*, *magnesium* and *calcium*, usually as the chlorides (NaCl, $MgCl_2$ and $CaCl_2$), but calcium can also be present as the sulphate or carbonate ($CaSO_4$ and $CaCO_3$).(6) The salt levels vary, with most crudes having a salt level of between 25-350 $\mu g \cdot g^{-1}$ of NaCl equivalent. The major portion of salt is found in the residues, causing problems in the refinery, like fouling of burners and deterioration of product quality. Furthermore, magnesium and calcium chlorides start to hydrolyse at 120°C (Equation 1), a reaction that proceeds quite readily at higher temperatures and that can lead to severe corrosion in the presence of water.

$MgCl_2 + 2\ H_2O \rightarrow Mg(OH)_2 + 2\ HCl$ … (1)

There are other metal impurities too, which can be present at low concentrations, like mercury and arsenic. Impurities like Si, Cu, Pb and P may also be introduced during refining and recycling of petroleum wastes.(7) Organometallic soaps of Zn, Ti. Ca and Mg may also be present as surface-active compounds in the oil-water interface.(4)

3. Crude oil physical properties

3.1. Density

The density of crude oil is reservoir dependent and generally falls between 800 and 1000 $kg\cdot m^{-3}$. It gives an indirect indication of the crude composition, giving rise to the classification of crude based on density (Table 2),(6) which affects its price. In the oil industry the density is often expressed in degrees API and the conversion to SI units is given by Equation 2, where density (ρ) is in units of $kg\cdot m^{-3}$:

$$°API = 141.5 / (0.001\cdot\rho) - 131.5 \qquad \text{… (2)}$$

Table 2. Crude oil classification based on density at 15°C.

Classification	Density range ($kg\cdot m^{-3}$)
Light crudes	< 825
Medium crudes	825-875
Heavy crudes	875-1000
Extra-heavy crudes	> 1000

3.2. Pour point

The pour point of crude oil is important from a processing point of view. It essentially defines the temperature that is required to pump the crude.[n] Since crude oil is a complex mixture of compounds, it does not congeal at a specific temperature, but different compounds crystallise out of solution at different temperatures. The thermal history of crude also plays a role in determining the pour point and must be known. Heating a crude to 45-65°C re-dissolves some of the paraffinic seed crystals, thereby lowering the pour point, while heating it to 100°C would again raise the pour point due to loss of light material by evaporation.

In practice pour point is determined after preheating to 45-48°C, as defined by the ASTM D97(20) method. Crude oil pour points usually range between –60 and +30°C.(6)

3.3. Viscosity

The viscosity of crude mainly influences pumping cost, because it determines the pressure drop in pipelines and refinery units. The viscosity-temperature relationship depends on the crude composition, with paraffinic crudes showing a rapid increase in viscosity with a decrease in temperature, while naphthenic crude have a more gradual response. The viscosity of crude oils varies over a wide range, having values of less than 10 to more than 5000 cSt.[o]

3.4. Vapour pressure

The vapour pressure of crude oil as it is produced can be as high as 2 MPa. Storage and transportation of crude with such a high vapour pressure is uneconomical. To reduce the vapour pressure, the crude oil goes through a number of pressure reduction stages, which are basically flash drums in series. The pressure is reduced from the wellhead pressure to less than 0.1 MPa. The associated gas[p] obtained during the pressure reduction is separated from the crude, leaving the crude oil with a vapour pressure of less than 0.1 MPa.

3.5. Distillation

Of all the physical properties, the distillation curve probably has the biggest impact on refining, since it determines the distribution of straight run[q] products. The actual distillation

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[n] This is an oversimplification, since "pumpability" is affected by pumping itself, which increases fluidity by inhibiting crystallisation processes.

[o] Viscosity measurements refer to the kinematic viscosity at 20°C in centistokes ($mm^2 \cdot s^{-1}$), as measured by the ASTM D445 method.

[p] The production of associated gas is unavoidable and recovery is not always economical, despite it sometimes being a significant fraction of the product. For example, the reservoirs in the Middle East have a high associated gas production, typically in the order of 0.14 kg gas per kg of crude. That is why it makes economic sense to construct liquefied natural gas (LNG) and gas-to-liquids (GTL) plants there.

[q] A straight run product is a product obtained by distillation only.

fractions (cuts) that will be produced on the refinery are determined by the refinery design, as well as the specifications of the fuel types to be produced. Typical cuts are given in Table 3.(6)

Table 3. Typical distillation cuts produced in a refinery.

Description	Hydrocarbon range	Distillation range (°C)
Gas	C_3-C_4	< 20
Light gasoline	C_5-C_6	20-80
Heavy gasoline	C_7-C_{10}	80-180
Kerosene	C_{10}-C_{14}	160-260
Gas oil	C_{15}-C_{22}	260-360
Residue	C_{22}+	> 360

Table 4. Distillation characteristics of Arabian Light crude oil, as example to show its relationship to refining requirements.

Property	Gas	Light gasoline	Heavy gasoline	Kerosene	Gas oil	Residue
Distillation range (°C)	< 20	20-80	80-180	180-250	250-370	> 370
Fraction (vol %)	1.7	6.3	17	11.7	21.9	41.4
(mass %)	1.1	4.9	14.8	11	21.9	46.3
Characterisation						
Density @ 15°C ($kg \cdot m^{-3}$)	-	659	747	798	854	956
Sulphur content (mass %)	-	0.024	0.036	0.16	1.4	3.2
Aromatic content (mass %)	-	1.5	14.3	20.7	-	-
RON	-	60.6	23.5	-	-	-
Pour point (°C)	-	-	-	-48	-6	10

Knowing the volume fractions going to the various distillation columns and refinery units if a specific crude is to be processed, enables proper scheduling of the crude.[r] It also allows an economic analysis of intended crude purchases, by matching the crude oil

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[r] Every refinery unit has a production capacity range, the upper limit set by the maximum operating capacity of the design and the lower limit set by the turndown ratio of the design. The crude oil composition of the feed to the refinery must be such that all refinery units can be operated within their design limitations. The economics of refinery operation is determined by selecting the crude slate in such a way that all units can be operated as close as possible to their maximum capacity given the final product market constraints.

characteristics to the market requirements for final products. The cost of processing the crude oil into transportation fuels has to be factored into these calculations. The straight run product yield gives an indication of the amount of work that has to be done by the conversion units in the refinery to produce marketable products (Table 4).(6) This topic will be explored in much more detail when dealing with crude refinery design in the next chapter.

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CHAPTER IV

Crude Oil Refineries

The history of crude oil refining is used to illustrate how refinery design is influenced by raw material cost and availability, as well as product specifications and market demand. Four generations of refinery design are described: Distillation only (1st generation), topping-reforming (2nd generation), topping-reforming-cracking with vacuum distillation and optionally visbreaking (3rd generation), and topping-reforming-cracking-visbreaking-alkylation-isomerisation with vacuum distillation (4th generation). The change drivers, namely raw materials, profitability and market demands, are resulting in certain trends that will determine how future crude oil refineries will look. These trends are: Intensification of residue upgrading, making more hydrogen available, increasing refinery complexity, addition of renewable fuels and the possibility to produce synthetic fuels. As consequence, future crude oil refineries will process more olefin intermediates and be more hydrogen rich.

1. Introduction

The purpose of a refinery is to transform a raw material into a more valuable end product that meets market demands. This is a general definition and holds true for all refineries.[a] Since the production of crude oil started in the 1850's, the market for crude oil derived products changed dramatically. As a natural consequence, crude oil refineries had to change in design and complexity to keep up with the changes in the market. As crude became available from more and more sources, refinery design not only had to cope with changes in products, but also with changes in feed.

In the middle of the nineteenth century a market was created for kerosene (lamp oil), when it was realised that it could be used in wick lamps, because it burns with a bright smokeless flame without leaving a residue.[b,(1)] The first crude oil refineries consisted of a

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[a] The combination of processes to transform metal bearing ores into metals is also rightly called a refinery.

[b] It is wrong to imply that kerosene was initially made from crude oil, it was not, it was made from coal. In 1850 a process for making "coal oil" was patented in Scotland. This process was developed to augment the dwindling supplies of whale oil. The ability to produce kerosene from oil was demonstrated at Dartmouth college in 1854 and became significant with the increase in oil production in 1859, when Edwin L. Drake started drilling for oil. By 1862 kerosene from oil had completely displaced kerosene from coal.

pot-still[c] to boil the crude oil so that the middle-boiling fraction (kerosene) could be collected and sold as lamp oil. Soon afterwards the internal combustion engine was invented,[d] which burned gasoline instead of methane (coal gas). This created a market for the light-boiling fraction of the distillation-only refinery too. These two products, gasoline and lamp oil (kerosene), were in high demand from 1890 onwards, especially with the boom in the automobile industry after the introduction of the Ford model T in 1908.[e,(2)] As a matter of fact, world consumption of oil doubled every decade since 1880 until the Oil Crisis in 1973 (Figure 1).(3)

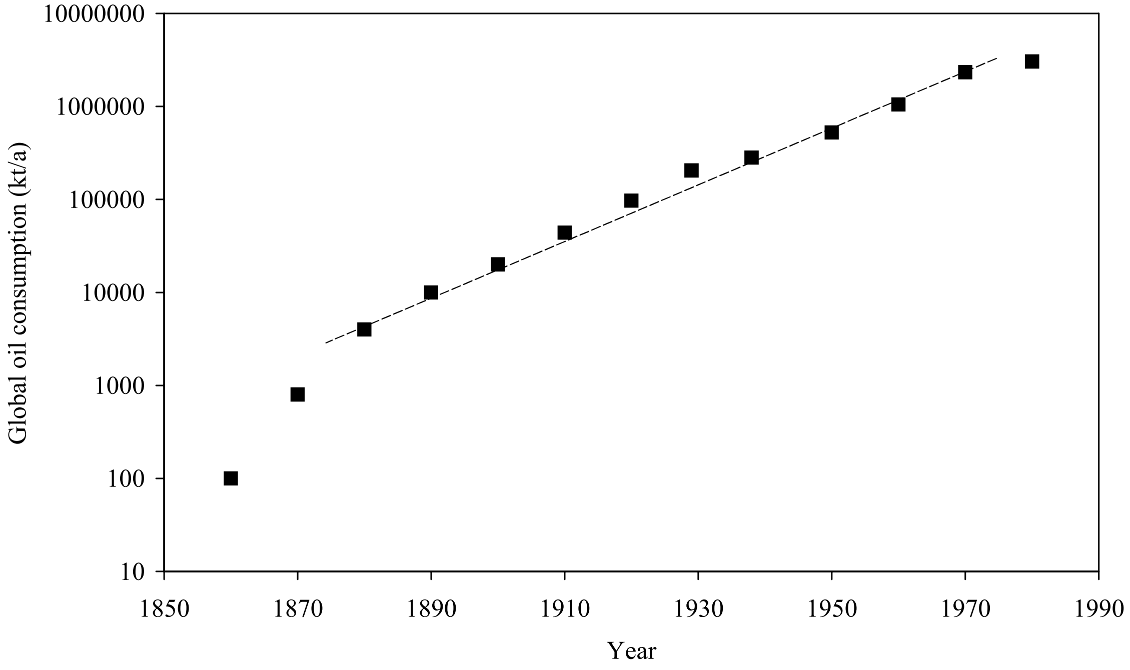

Figure 1. Global oil consumption for the period 1860-1980.

The problem faced by refiners at the beginning of the twentieth century was that the products obtained from the distillation of crude oil were not in the same ratio as required by the market. Furthermore, as the automobile manufacturing industry got going and later the aviation industry too, improvements in engine design required a better quality fuel to deal

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[c] Until 1910 all crude fractionation had been done by batch distillation. Only then did continuous-operating boilers appear. The first true distillation columns were only built in the 1920's.

[d] Historically it was Germany that played the key part in the development of the automobile, with the invention of the internal combustion engine by August Nikolaus Otto in 1872 and the pioneering work of Gottlieb Daimler and Karl Benz. Both Daimler and Benz realised that gasoline (petrol) would be a better fuel than gas and adapted the Otto-engine for such use. The spark-ignition system and water cooling for automobiles can both be credited to Benz (1885).

[e] Most European automobiles were built for sportsmen and enthusiasts, not for the ordinary man who just needed transport. Henry Ford had the insight to provide transportation for the common man and 15 million Ford model T's were sold between 1908 and 1927.

with the performance requirements of higher compression ratio engines. These two aspects, namely market requirements and fuel quality, were destined to become a recurring theme in crude oil refining. Upgrading crude oil by distillation only (a first generation refinery) was no longer enough and it heralded the start of the second phase in refinery development.

Markets had to be found for the heavier products from crude oil and methods had to be devised to change the properties of the products to meet the market demands. The second stage of refinery development is characterised by the introduction of reactive processes to change the nature of the crude oil. Although the development of refineries, catalysts and the chemical engineering discipline started off independently, they quickly came together to create second generation refineries. This period saw the development of many of the key technologies that are still being used in refineries today (Table 1).(4)(5)(6)(7)(8)(9)(10)(11)

Table 1. Historical development of some key refining technologies.

Year	Process	Catalyst
1920's	Hydrogenation	Ni-kieselguhr
1933	Paraffin isomerisation	$AlCl_3$
1934	Olefin oligomerisation (CatPoly)	Solid phosphoric acid (SPA)
1936	Catalytic cracking (Houdry)	Montmorillonite (acidic clay)
1940	Catalytic cracking improved	Amorphous silica-alumina (ASA)
1942	Paraffin alkylation	HF and H_2SO_4
1942	Fluid catalytic cracking	Amorphous silica-alumina (ASA)
1949	Reforming (Platforming)	Pt-Al_2O_3
1959	Hydrocracking	Ni/Mo- Co/Mo- silica-alumina
1964	Zeolite fluid catalytic cracking	Faujasite (Y)
1967	Multimetallic reforming	Pt/Re- Pt/Ir-Al_2O_3
1973	Etherification	Acidic resin (e.g. Amberlyst 15)
1970's	Zeolite based processes	ZSM-5, etc.

When the application of compression ignition engines became more widespread,[f] markets were found for diesel fuel and fuel oil. Fuel oil started replacing coal as energy source on ships in the 1900's.

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[f] Since the development of the compression ignition engine by Rudolf Diesel in 1893, it took some time before its use became widespread. Despite its better thermodynamic efficiency than a spark-ignition engine, a

The demand for high-octane aviation gasoline during the Second World War and transportation fuel in general, also prompted technological advances in crude oil refining. Yet, crude oil was cheap and despite increasing consumption, prices were low. Many refineries did not make use of all the technologies that were on offer and the new technologies that were being developed. Second generation refineries generally used a simple topping-reforming refinery flowscheme (Figure 2),(12) which sometimes included visbreaking[g] too. The refineries that exploited the market for high octane gasoline during the Second World War, were left long in octane once the demand for aviation gasoline dropped in the 1950's.

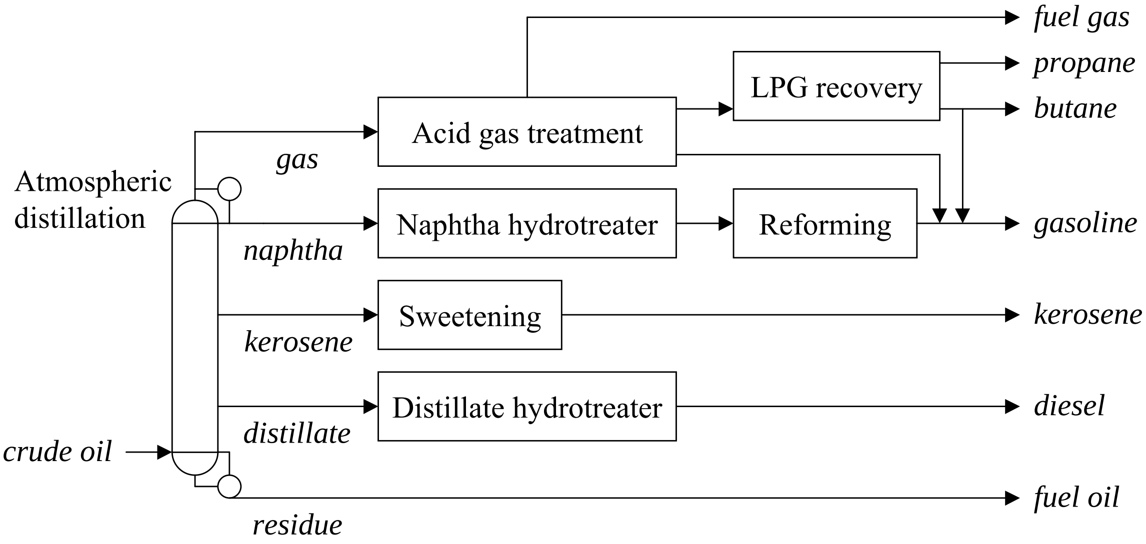

Figure 2. Topping-reforming flowscheme used by most 2nd generation refineries.

In the early 1970's crude oil prices were at their lowest, with a barrel of Arabian Light crude costing only US$ 1.80. This was to change quite dramatically with the Oil Crisis at the end of 1973,[h,(13)] when oil prices increased six-fold in a short period of time. In January 1974

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compression ignition engine is heavier and more expensive, which initially made its use for automobiles less attractive, but made it very attractive for heavy vehicles and ships.

[g] Visbreaking is a refinery process and the term is used to denote thermal cracking of residues. It is not the same as thermal cracking, which is a process used for the production of short chain olefins. The principle of operation is the same though.

[h] A small number of very large international oil companies informally working together, controlled most of the world's markets for oil in the 1950's. By 1959 these companies were under economic pressure from each other and outsiders. They therefore decided to reduce their tax commitments to the producing countries to boost their profits, by posting lower prices for the crude oil on which tax was calculated. The reaction was unexpectedly strong and one of the results was the formation of the Organisation of Petroleum Exporting Countries (OPEC) at the instigation of Venezuela. During the 1960's internal disagreements amongst member countries failed to result in any coherent collective action, but OPEC survived mostly as a result of the political solidarity felt by the Arab countries. It was this solidarity that caused the production cuts in 1973, since it was seen as a way to get back at the pro-Israel Western world after the Six Day War in 1967 and finally the Yom Kippur War that started on 6 October 1973.

a barrel of Arabian Light crude was around US$ 12, with another significant increase that were to take place at the end of the decade.(3) Since the residue fraction of most crude oils constitute close to 50% of the total volume of crude oil, the increase in oil price not only affected the price of white products (motor-gasoline, jet fuel and diesel), but also the price of fuel oil. This resulted in a drop in the use of fuel oil and a slowdown in the growth of white product consumption. Refiners now had to produce more white products and less fuel oil, while light crude oils were becoming scarcer and more costly. This gave rise to third generation refineries that included significant residue upgrading capacity (Figure 3).(12) Such refineries typically used topping-reforming-cracking or topping-reforming-cracking-visbreaking configurations and included a vacuum distillation column for residue fractionation.

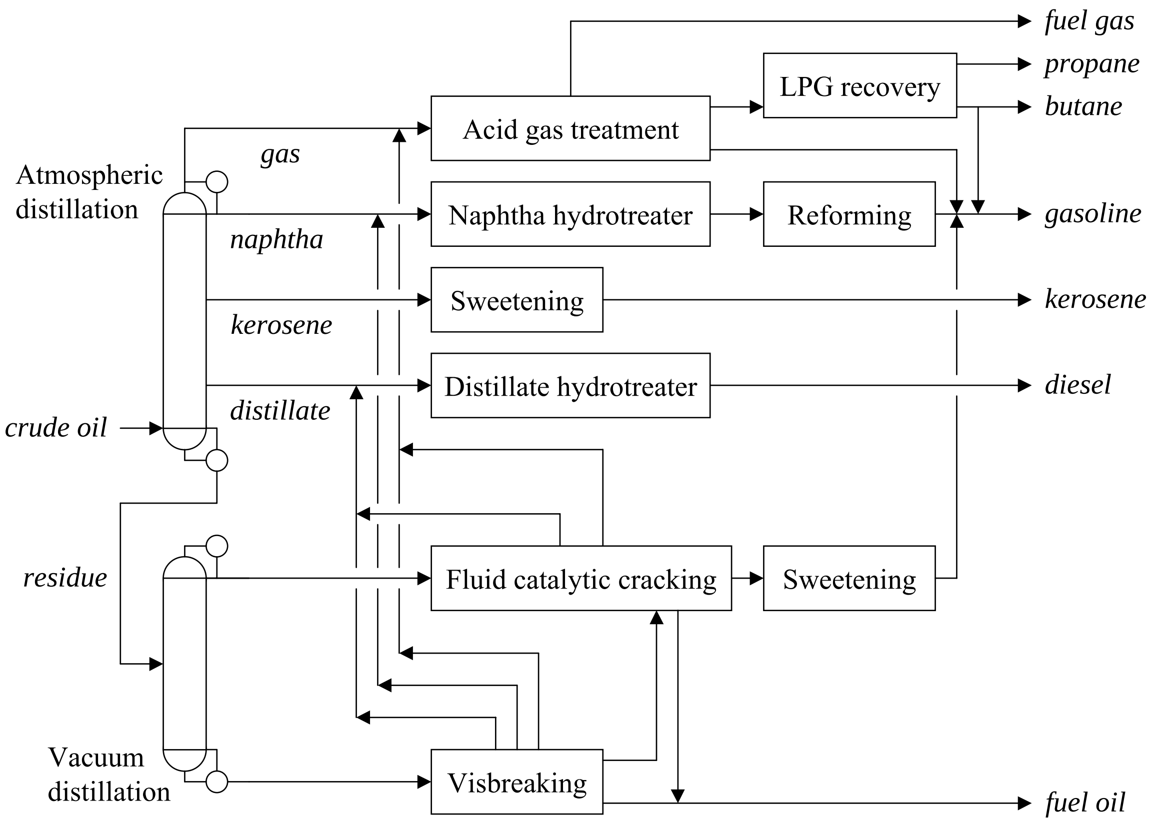

Figure 3. Topping-reforming-cracking flowscheme with vacuum distillation and optionally visbreaking of 3rd generation refineries.

In the same period, the introduction of unleaded motor-gasoline was lobbied.[i] This would remove the 5-7 octane number boost that refiners could rely on by adding tetra-ethyl lead (TEL) to the motor-gasoline.(14) Just as the Oil Crisis forced refiners to consider crude as an expensive feedstock from which the production of high value white products had to be maximised, the need to forgo the use of TEL forced refiners to have a serious look at the quality of the products being produced. This was not an immediate concern, since lead phase-out took some time.[j] Yet, time moved on and in the 1980's it was realised that taking out lead was not enough, sulphur content of fuel also had to be reduced.[k] Deeper hydrogenation of all cuts not only consumed more hydrogen, but also lowered the octane number of the motor-gasoline. This set the stage for the development of the next generation of refineries.

Refinery upgrades and new refineries planned to meet the need for high octane unleaded, low sulphur motor-gasoline had to modify their naphtha upgrading sections. It was quickly realised that paraffin quality was the key to meeting the octane demands and that isomerising C_4-C_6 paraffins provided a cheap and easy octane boost. It was also realised that the olefins produced by the high temperature residue upgrading units opened synthetic routes[l] for the production of high octane motor-gasoline. Fourth generation refineries (Figure 4), typical of the 1990's, used topping-reforming-cracking-visbreaking-alkylation-isomerisation schemes.(3) These schemes frequently include etherification too. The number and severity of the hydrotreating operations in a fourth generation refinery are also increased, especially with respect to the refining of heavier material that is rich in sulphur.

Not all refineries have opted to change with the times and intermediate product exchange agreements are often used to balance product properties with market demands. For example, of the 99 refineries in Europe there are still 16 refineries that have not added residue upgrading capacity(15) and are essentially still 2nd generation refineries.

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[i] The president of General Motors (GM), Mr. Cole, lobbied the introduction of unleaded gasoline. It started with a public announcement at the Society of Automotive Engineers (SAE) on 14 January 1970, which indirectly led to the Clean Air Act Amendments of 1970, signed by Pres. Nixon in November 1970. The distribution network and vehicles requiring unleaded gasoline were ready by end 1974.

[j] The phase-out of lead was a gradual process and in a country like the USA that prefers motor-gasoline to diesel powered vehicles, it took 20 years to complete. By the end of the 1980's leaded gasoline was essentially gone and by 1996 its use on highways became illegal in the USA.

[k] Ironically the reduction in sulphur was called for in parallel with the phasing out of lead, but to make the introduction of unleaded gasoline a success, its impact was downplayed.

[l] The three main synthetic motor-gasoline technologies based on olefins are alkylation, etherification and oligomerisation. Of these the alkylation of iso-butane with olefins is most often used. Etherification went through a boom-and-bust cycle in the USA for political reasons, but is still widely used in Europe. The use of oligomerisation is less widespread, mainly because it uses two moles of olefin per one mole of product, unlike alkylation and etherification that requires only one mole of olefin per one mole of product.

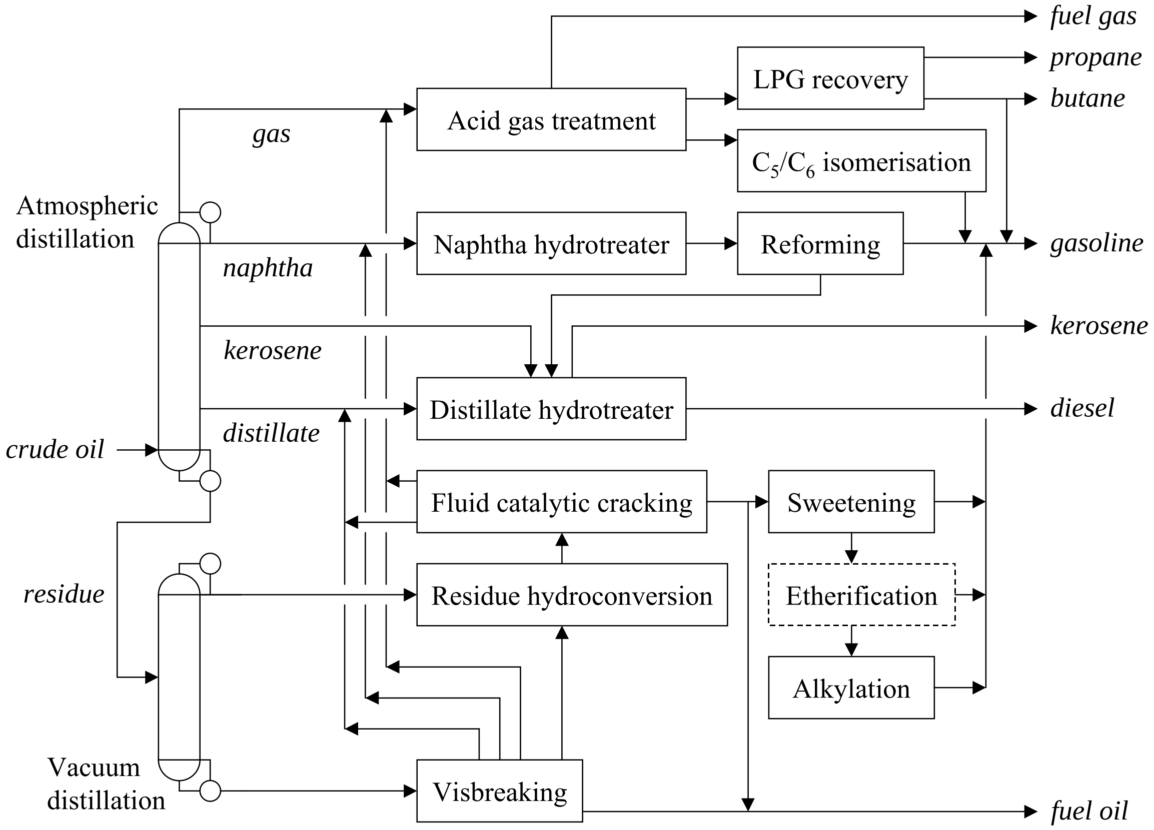

Figure 4. Topping-reforming-cracking-visbreaking-alkylation-isomerisation flowscheme, 4th generation refineries.

It will be appreciated that refineries are constantly changing and that they are subject to the same pressures that shape transportation fuel specifications. Oil refining will therefore be discussed in general terms, referring to the main separation and conversion processes needed to produce transportation fuels. This will serve as an introduction to crude oil refinery design and what factors need to be considered for grassroots refineries, including some future trends in refinery design.

2. Separation processes

Separation processes are associated with all refining units, but in the present context it refers to the primary crude oil separation that takes place at the front-end of a refinery (Figure 5).(12) The first step is *desalting*, which is mainly a corrosion and fouling prevention measure. During desalting the crude oil is washed with water and caustic (NaOH) to remove dissolved salts and to convert acid chlorides, such as $MgCl_2$ and $CaCl_2$, to NaCl (Equation 1) that is a neutral chloride. This prevents the formation of hydrochloric acid when residual chlorides enter the refinery.

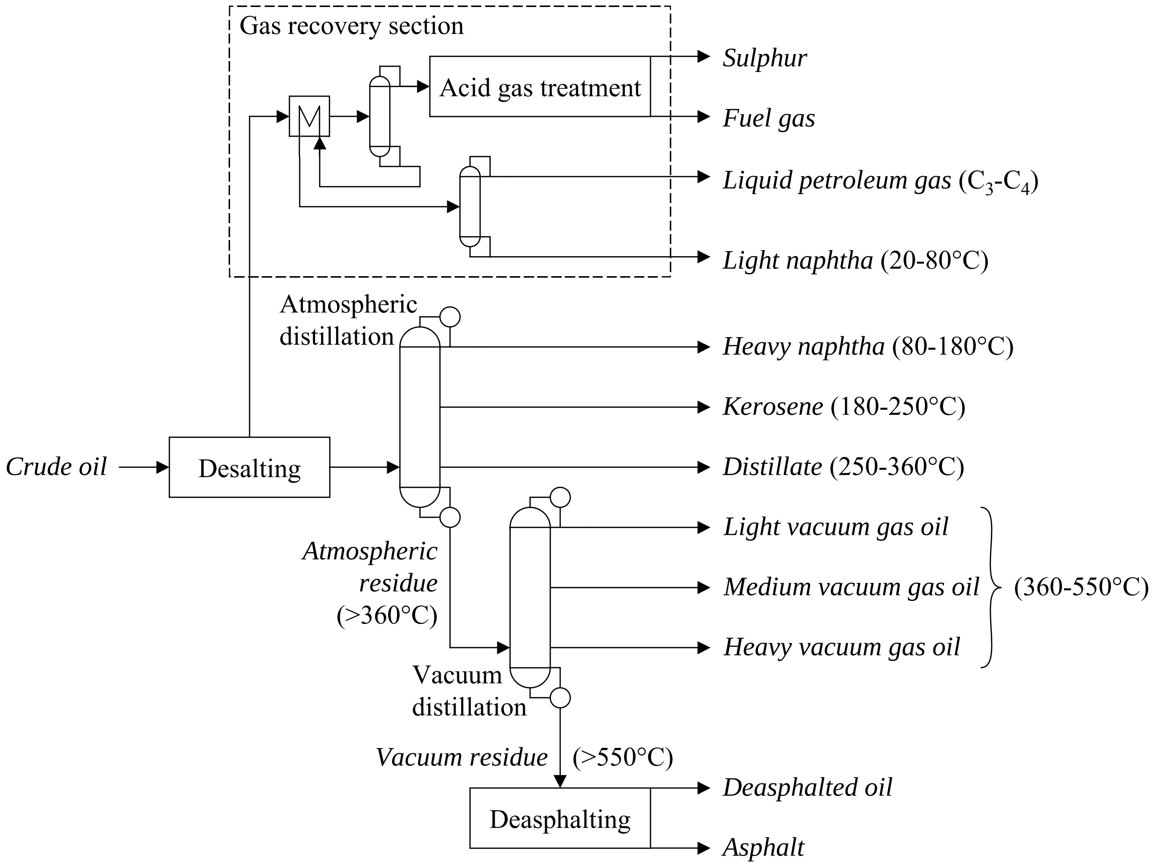

Figure 5. Generic separation scheme in crude oil refinery.

$$MgCl_2 \text{ (aq)} + 2\ NaOH \text{ (aq)} \rightarrow Mg(OH)_2 \text{ (aq)} + 2\ NaCl \text{ (aq)} \qquad \ldots (1)$$

During this process some naphthenic acids are also converted to their respective carboxylate salts (Equation 2) and are removed as part of the aqueous effluent.

$$RCOOH + NaOH \text{ (aq)} \rightarrow RCOONa \text{ (aq)} + H_2O \qquad \ldots (2)$$

This can sometimes be problematic though, because the carboxylate salts are surface active and can form stable emulsions. This hazard is reduced by coalescing and decanting the water droplets under the influence of an electric field.[m],(16)

The main separation step in any crude oil refinery is *atmospheric distillation unit* (ADU).[n] This column fractionates the crude into straight run naphtha, kerosene, distillate and atmospheric residue. This is a crucial refining step, since it routes the molecules to the

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[m] A field strength in the order of 700-1000 V·cm^{-1} is typically used.

[n] This is also referred to as the crude distillation unit (CDU).

appropriate conversion units in the refinery. The cut point of the atmospheric residue depends on the prevailing fuel specifications and crude slate used. It is typically set to satisfy the T90 specification of diesel fuel from the refinery and is usually in the range 360-375°C. The atmospheric residue is further processed in the vacuum distillation unit.

The cut points of the product fractions from the *vacuum distillation unit* (VDU) depend on the refinery configuration. The gas oil or vacuum distillate cuts range from 360-550°C and are typically used for lubricating oil production, but may also be converted to lighter cuts in the refinery. The heavy product from the VDU that has a boiling point above 550°C is called the vacuum residue. The vacuum residue contains most of the crude oil contaminants like metals, salts, heteroatom rich compounds and high molecular weight polycondensed aromatic structures. The vacuum residue may be further processed in the refinery, or serve as feed for the last separation process at the front-end of the refinery, namely deasphalting.

Deasphalting is a liquid-liquid extraction whereby the last of the molecules that can be refined to white products are extracted from the vacuum residue. Light hydrocarbons, like propane, butane and pentane are typically used as solvents. The yield of deasphalted oil increases with increasing molecular weight of the solvent, but its quality decreases, while the fluidity of the asphalt is likewise decreased with increasing molecular weight of the solvent (Table 2).(12)

Table 2. Effect of solvent on the quality and yield of deasphalted oil, as illustrated by deasphalting of the vacuum residue (>538°C) of a Heavy Arabian crude.

Properties	Type of solvent used for deasphalting		
	Propane	Butane	Pentane
Yield (mass %)	32	50	66
Density (kg·m^{-3})	945	963	985
Sulphur content (mass %)	3.8	4.5	4.9
Nitrogen content (mass %)	0.1	0.2	0.21
Ni+V content (μg·g^{-1})	6	24	67
Viscosity @ 100°C (cSt)	60	100	250

Dissolved gases and volatile hydrocarbons can be recovered after desalting or atmospheric distillation. The gas is typically separated into fuel gas, liquid petroleum gas (LPG) and light naphtha. The *gas recovery section* is used not only for the straight run gas, but also the gas produced during conversion processes. An important component of the gas recovery section is *acid gas treatment*, which entails the removal of hydrogen sulphide (H_2S) from the gas. The H_2S is typically dissolved in a solvent from which it can be recovered and converted to elemental sulphur in a Claus or similar type of unit.(17)

3. Conversion processes

Conversion processes are required to bridge the gap between feed properties and desired product properties. Numerous refining technologies exist, but for the most part the conversion processes can be classified under the following headings:

a) *Carbon number growth*. These are technologies that increase the average molecular mass of the carbon backbone of the molecule, such as oligomerisation. Due to the heavy nature of crude oil, there is seldom use for this class of technologies in processing straight run products, but it is used in upgrading gas from cracking units by processes like alkylation.

b) *Carbon number reduction*. These are technologies that decrease the average molecular mass of the carbon backbone of the molecule, such as cracking. Many residue upgrading technologies[o] fall into this category, because they transform molecules with a high boiling point to lower boiling products.

c) *Functionalisation*. Technologies that change the functional group to which a molecule belongs, fall in this category, like hydrodesulphurisation (HDS), reforming and etherification. One could say that hydrotreating technologies result in defunctionalisation, but the removal of heteroatom-based functional groups effectively changes the class of compounds to which a molecule belongs.

d) *Rearrangement*. This is a special class of technologies that can modify the structure of a molecule, without changing the carbon number or functional group of the molecule, like hydroisomerisation and double bond isomerisation.

Some technologies perform more than one function and can be classified into more than one of these categories. This form of process intensification(18) does not invalidate the

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[o] Residue upgrading technologies are also sub-divided into the classes “hydrogen addition” and “carbon rejection”. A secondary aim of residue upgrading is to enrich the hydrogen content of the lower boiling products. If this can be done by adding hydrogen, like in hydrocracking, which makes it a “hydrogen addition” technology, but hydrogen is a scarce commodity in a crude oil refinery. More often some of the carbon mass of the residue is sacrificed as coke or some other form of carbonaceous product to comparatively enrich the lighter products in hydrogen. Examples of such technologies are fluid catalytic cracking and coking, which make them “carbon rejection” technologies.

classification and in such cases the technology is classified according to its main aim. For example, hydrocracking is mainly a carbon number reduction technology, although it also results in heteroatom removal. This classification is important, because it describes the function of the conversion. It comes in handy to describe the type of conversion processes needed to deal with the various crude oil fractions, without immediately delving into the details associated with technology selection linked to the specifics of each refinery design.

3.1. Residue upgrading

It is appropriate to start with residue upgrading, since it is a source of lighter boiling fractions that need to be upgraded with the other straight run products. The upgrading can take two basic forms, either it aims to reduce the average carbon number of the molecules to be upgraded as transportation fuels, or it modifies the properties of the products to be used in non-fuel applications.

3.1.1. Conversion of residue to fuels

Residue upgrading technologies that have carbon number reduction as main objective are normally high temperature (>350°C) processes:

a) *Fluid catalytic cracking* (FCC). Typical products from FCC are gas (15-20%), naphtha in the 20-220°C boiling range (40-50%), light cycle oil in the 220-350°C boiling range (15-20%), heavy cycle oil and slurry in the >350°C boiling range (15-20%) and coke (5%).(8)

b) *Visbreaking*. Typical products from visbreaking are gas (1-5%), naphtha in the 20-165°C boiling range (5-10%), gas oil in the 165-350°C boiling range (10-25%) and residue in the >350°C boiling range (60-85%).(19)

c) *Coking*. Typical products from delayed coking are gas (5-10%), naphtha in the 20-195°C boiling range (10-25%), gas oil in the >195°C boiling range (30-65%) and coke (10-35%).(20)

d) *Hydrocracking*. Typical products from hydrocracking are gas (5%), naphtha in the 20-180°C boiling range (15-20%), kerosene in the 180-250°C boiling range (30-40%), gas oil in the 250-360°C boiling range (25-45%) and residue in the >360°C boiling range (0-20%).(7)

With the exception of hydrocracking, all the other technologies are carbon rejection processes. They also produce olefins, which is one of the main hydrocarbon classes required in naphtha upgrading, but that is not present in crude oil.

3.1.2. Non-fuels application of residues

Residues are not necessarily upgraded by conversion technologies. Some of the main non-fuel related applications of residues rely mostly on separation processes to achieve the desired product characteristics:(21)

a) *Lubricants*. There are numerous special lubricant types and applications, but most lubricants can be classified as either oil or grease. Lubricating oil is generally aliphatic in nature, with solvent extraction of the aromatics being used to improve the viscosity index and solvent dewaxing being used to remove linear paraffins to improve the cold flow properties. Lubricating grease is a semi-solid material that is obtained by dispersing a gelling agent in a lubricating oil.

b) *White oils*. This is a term used for highly refined lubricating oils, principally where the oil has been significantly dearomatised. These white oils were previously made from light oil cuts treated with oleum to remove the aromatics, but presently deep catalytic hydrodearomatisation (HDA) is more often used.

c) *Paraffins and waxes*. These are by-products from solvent dewaxing and are used in numerous applications ranging from food packaging to polishes and cosmetics.

d) *Bitumen*. There are many grades of bitumen that differ in hardness and flow properties. It can be produced as vacuum residue or by deasphalting of vacuum residue. Air oxidation, typically at temperatures higher than 200°C, is often employed to modify the structure and to produce hard grades of bitumen. By increasing the oxidation temperature, air contact time or air pressure the hardness can be increased.(22) Applications of bitumen include waterproofing, fillers, insulation materials and road binders. Cracked residue does not make a good feed material for bitumen production.(23)

e) *Coke*. Although coking has been discussed as a conversion process to produce fuels, it also produces coke. The quality of the coke determines its application possibilities, for example graphite, pigments, electrodes or reducing agents in the metallurgical industry.

3.2. Diesel and jet fuel upgrading

Diesel and jet fuel have many specification characteristics in common and will therefore be treated together. The straight run kerosene and distillate have the right carbon number distribution and mainly requires a reduction in sulphur content and aromatic content (functionalisation) to meet fuel specifications. This can be achieved by *hydrotreating*.[p]

Depending on the crude oil, the product might still contain linear paraffins, which is good for diesel cetane, but could be detrimental to diesel cold flow properties and cause the jet fuel to fail the freezing point specification. The linear paraffins can either be modified by hydroisomerisation (rearrangement), or the linear paraffins can be removed by *solvent dewaxing*. The other fuel properties that may be lacking can be fixed by fuel additives.

It is clear that the upgrading of crude oil derived straight run kerosene and distillate is not complicated. Since the requirements for jet fuel and diesel are almost the opposite of that required for motor-gasoline, it is anticipated that naphtha upgrading will be much more involved.[q]

3.3. Naphtha and gas upgrading

The upgrading of naphtha and gas to motor-gasoline is unit-wise by far the most intensive refining operation. The main adjustments that have to be made to the properties of the fuel are related to the sulphur content and octane number (functionalisation and rearrangement), as well as the average molecular mass when dealing with gas (carbon number growth). Getting rid of the sulphur is not difficult, since naphtha range material contains mostly mercaptans and other easy to remove sulphur containing compounds, which can be removed by mild *hydrotreating* or sweetening. Meeting the octane number specification is more difficult. Crude oil derived straight run naphtha typically has a low octane number (LSR from Arabian Light crude has a RON of about 60 and the heavy naphtha has a RON of less than 25)(16) and increasing the octane number requires a complex refinery scheme.

The main sources of octane are aromatics and oxygenates (ethers and alcohols), but the volume of these compounds are limited by motor-gasoline specifications. Roughly half

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[p] Hydrotreating to meet diesel fuel specifications will automatically ensure that the mercaptan specification of jet fuel is met. Previously this would not necessarily have been the case and the kerosene cut would have to go through a sweetening process.

[q] It may seem that the increased refining complexity required for motor-gasoline production compared to diesel fuel production is another reason to nudge the market in the direction of increased diesel fuel use. Surprisingly, from a refining perspective this is not true. Catalytic reforming is the main source of refinery hydrogen and is linked to motor-gasoline production. Furthermore, since transportation fuels are sold by volume, motor-gasoline effectively commands a higher price than diesel fuel on account of its lower density.

of the motor-gasoline has to be paraffinic and it is the quality of the paraffins in the fuel pool that determines the refining needs (as discussed in Chapter II). As a rule of thumb, the required minimum octane number of the paraffins can be calculated by a simple formula (Equation 3) based on the octane specification (RON_{spec}) and the volume fractions (V_i) and octane numbers (RON_i) of the various compound classes:

$$\mathrm{RON_{paraffin}} \geq [\mathrm{RON_{spec}} - (\mathrm{RON{\cdot}V})_{\mathrm{aromatic}} - (\mathrm{RON{\cdot}V})_{\mathrm{oxygenate}} - (\mathrm{RON{\cdot}V})_{\mathrm{olefin}}]/\mathrm{V_{paraffin}} \quad \text{... (3)}$$

Most modern crude oil refineries use *catalytic reforming*.[r] The reformer is not only the main source of aromatics for the motor-gasoline, but also the main source of hydrogen in the refinery. The octane number of aromatic rich reformate can be manipulated by varying the severity of the operating conditions of the reforming unit, but in practise reformate generally has a RON of 96-102, with an aromatic content of around 70%.(9)

Not all refineries have etherification units and with present pressure on fuel ethers in the USA, many refiners are forced to use ethanol instead. Nevertheless, ethanol has a RON of 120,(24) while the typical fuel ethers have a slightly lower octane number. Olefin oligomerisation, which typically yields a RON of about 96, is practised in some refineries, but FCC derived olefins are more often used for etherification and aliphatic alkylation.

Using Euro-4 specifications as reference, aromatics can be blended to 35%, olefins to 18% and ethers and alcohols to 10-15%. If typical, realistic refinery values are substituted into Equation 3,[s] the paraffin RON required to make 95 octane motor-gasoline can be calculated for scenarios with and without oxygenates and olefins (Equations 4-7):

$$\mathrm{RON_{paraffin}} \geq [95 - (98{\cdot}0.5)_{\mathrm{aromatic}} - (120{\cdot}0.1)_{\mathrm{oxygenate}} - (96{\cdot}0.15)_{\mathrm{olefin}}]/(0.25)_{\mathrm{paraffin}} \geq 79 \quad \text{... (4)}$$

$$\mathrm{RON_{paraffin}} \geq [95 - (98{\cdot}0.5)_{\mathrm{aromatic}} - (120{\cdot}0.1)_{\mathrm{oxygenate}} - (0)_{\mathrm{olefin}}]/(0.4)_{\mathrm{paraffin}} \geq 85 \quad \text{... (5)}$$

$$\mathrm{RON_{paraffin}} \geq [95 - (98{\cdot}0.5)_{\mathrm{aromatic}} - (0)_{\mathrm{oxygenate}} - (96{\cdot}0.15)_{\mathrm{olefin}}]/(0.35)_{\mathrm{paraffin}} \geq 91 \quad \text{... (6)}$$

$$\mathrm{RON_{paraffin}} \geq [95 - (98{\cdot}0.5)_{\mathrm{aromatic}} - (0)_{\mathrm{oxygenate}} - (0)_{\mathrm{olefin}}]/(0.5)_{\mathrm{paraffin}} \geq 92 \quad \text{... (7)}$$

It is clear that even when oxygenates and olefins are added to the fuel, some paraffin upgrading is required to increase the octane number of the straight run naphtha. The

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[r] A catalytic reformer will typically not be found in refineries that do not produce on-specification motor-gasoline as a final product. In such refineries hydrogen is produced by other means, for example steam reforming of methane.

[s] Since reformate is not a pure aromatic stream, but contains about 70% aromatics at a RON of 98, 50% of the motor-gasoline can be made up of reformate without violating the 35% maximum aromatic specification.

following upgrading pathways can be considered, assuming that a source of olefins is available from residue conversion units in the refinery:

a) *Etherification*. Depending on the branched olefins being available and the preferred alcohol, the typical fuel ethers produced are 2-methoxy-2-methylpropane (MTBE, methyl tertiary butyl ether), 2-ethoxy-2-methylpropane (ETBE, ethyl tertiary butyl ether) and 2-methoxy-2-methylbutane (TAME, tertiary amyl methyl ether). These ethers all have a RON in the range 115-118.(24) It is also possible to directly etherify light FCC gasoline,(25)(26) yielding a product with a calculated blending RON of 110.(27) However, it has been shown that most C_6 and heavier ethers have poor octane numbers, unless the source olefin is highly branched.(28)

b) *Olefin oligomerisation*. There are various technologies available for olefin oligomerisation,(29) but when the focus is on unhydrogenated motor-gasoline, the octane values from many processes fall in a narrow band around RON 92-97 and MON 79-82. Olefinic motor-gasoline is therefore close to octane neutral, albeit somewhat MON constrained.

c) *Aliphatic alkylation*. The alkylation of iso-butane with olefins to produce alkylate, is often used as a source of high octane paraffins; RON 92-97 and MON 90-94.(30)(31)(32) Although the product is highly desirable, current commercial processes are all based on either sulphuric acid (H_2SO_4), or hydrofluoric acid (HF). Much effort has been spent on the development of more environmentally friendly solid acid catalysed processes, but with limited success.(33) It can be argued that aliphatic alkylation is essential to meet the requirements for high octane paraffins, but environmental concerns keep looming in the background.

d) *Hydroisomerisation*. The skeletal isomerisation of paraffins in the C_4-C_6 range is often practised. Butane isomerisation typically provides a source of iso-butane for aliphatic alkylation when it is used in the refinery, while hydroisomerisation of LSR (C_5-C_6) is routinely employed to produce an isomerate with RON 78-92, depending of the recycle configuration of the technology.(10) The hydroisomerisation of C_7 and heavier fractions is actively researched, but has met with little success.(34)(35)

It can therefore be said that all naphtha and gas upgrading sections of a crude oil refinery has a hydrotreater to remove sulphur and reformer to produce aromatics. In addition to these units, one or more paraffin upgrading units needs to be present, namely aliphatic alkylation and hydroisomerisation, with optionally etherification and olefin oligomerisation.

An external source of alcohols is required to produce motor-gasoline blends that require oxygenates.

4. Future crude oil refineries

4.1. Change drivers in crude oil refining

Based on the historical development of crude oil refineries, it does not take a huge leap of faith to predict that crude oil refineries will continue to change. The drivers for change are inherent to the purpose of a refinery, namely to transform a raw material into a more valuable end product that meets market demands. These are:

a) *Crude oil availability and cost*. Although it is unlikely that crude oil will run out in the short term, it is a finite resource and some of the more sought after types of crude oil may become scarcer more quickly. This underpins two threats to a refinery, namely the availability and the cost of the raw material.

b) *Refinery capital and operating cost*. To turn the raw material into a more valuable product, the market must be willing to buy the product at a higher price than the cost of upgrading it. To process cheaper more readily available raw materials (lower quality heavy crudes), will require capital to be invested in residue upgrading units and result in an increase in the operating cost. Refiners are also under pressure to keep their environmental footprint small and processing heavier crudes is environmentally speaking a move in the wrong direction. The decision to modify a refinery to deal with cheaper difficult crudes, is therefore not such a clear-cut investment decision.(36) Furthermore, there is a rising cost associated with environmental conservation and the refinery upgrades needed to keep within legislated emission levels.[t,(37)] The underlying threat is that more efficient, more environmentally friendly or even alternative technologies for the production of transportation fuel may come along to undermine the profitability of investments in refining infrastructure. Conversely there is the threat that in times of high profit, governments might impose a “windfall” tax on refiners, as has indeed happened in the past.(38)(39)

c) *Market demands*. To sell transportation fuel, the fuel must comply with the fuel specifications that have been changing to require increasingly refined products. This places strain on the refiner, because the environmental concerns giving rise to more stringent fuel specifications, translate into a larger environmental footprint of the refinery. This reality is not always appreciated by the politicians and the lawmakers. Furthermore, the market for refined products is not homogeneous and grows at different rates in different regions. In general market demand for fuel oil is decreasing and market demand for white products are increasing,(3) but this says nothing about the substructure of white product demand. Product price also affects the overall market demand and may selectively suppress the use of some fuel types when the price is too high, or stimulate their demand when the price is low. This gives rise to fears about over-investment in refining capacity, as well as under-investment in refinery flexibility to deal with market swings.

4.2. Changes in crude oil refining

The impact of the change drivers will be seen both in refinery design, as well as in the transportation fuel industry. In refineries, effects will most likely be seen in the following areas:(40)

a) *Residue upgrading*. More efficient residue upgrading is key to refining economics. This is driven by the lower demand for heavy products like fuel oil and the price differential between expensive light crude oils and cheap heavy crude oils.(3)(12)(41) The need for molecules from residue upgrading units, especially olefins,(42) is also becoming more apparent with the need for high octane paraffinic blending components for motor-gasoline production. This further emphasises the importance of residue upgrading in future. The nature of the residue upgrading capacity that is added has one natural side-effect, namely that it influences the motor-gasoline to distillate ratio produced by the refinery. In Europe this is a serious concern and may cause the significant swing from motor-gasoline to diesel to slow down and reach a natural refinery driven equilibrium.[u],(15) Any technology breakthrough in residue upgrading technology, for example novel technology to improve or supersede FCC, will have a tremendous impact on future crude oil refinery flowschemes.

b) *Hydrogen production*. The drive to produce more ultra low sulphur transportation fuels will increase the need for hydrogen in the refinery. The increase in hydrogen demand is exacerbated by the lowering of the maximum aromatics content in fuel, which decreases the

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[t] In many European countries the cost of compliance to environmental legislation increased between 400-2500% from 1985 to 1993.

[u] In Europe many refiners are already having difficulty meeting diesel fuel demand and quality. This problem is most acute in refineries having FCC's (57 refineries), which represent 76% of the European refining capacity. It is not clear to what extent the political landscape will change to cope with this challenge.

hydrogen production in the refinery. Additional hydrogen will also be required if residue upgrading increasingly employs hydrogen addition, rather than carbon rejection.(12)(43) This may necessitate investment in on-purpose hydrogen production units.(3) At this stage hydrogen production is costly and chances of a "hydrogen economy" bleak,(44) but advances in technology may make refineries more hydrogen rich in future.

c) *Refinery complexity and cost.* As fuel specifications drive the fuel composition further away from the crude oil composition, more units will be required to make final products. This has implications for refinery complexity and cost, increasing the minimum refinery size that makes economic sense. To offset the cost, refineries may increasingly opt for co-generation of power,(3) as well as to co-produce chemicals. With increasing focus on residue upgrading and hydrogen production, chemicals like propylene from FCC(45) and aromatics from reforming(46) are natural choices for co-production.

d) *Renewable fuel.* If the inclusion of bio-derived components in transportation fuel becomes mandatory, it will be impossible for a crude oil refinery to produce on-specification fuel with only crude oil as raw material. At present, most fuels that include a bio-derived component are only blends, but there are already investigations dealing with possible co-processing.[v]

e) *Synthetic fuel.* The need for hydrogen in a refinery can be addressed by investing in on-purpose hydrogen production, which may entail gas reforming (water-gas shift). This would not only make hydrogen available, but could potentially also make synthesis gas (H_2 + CO) available to the refinery. If this happens, crude oil refineries may in future become integrated with synthesis gas based synthetic fuel technologies, such as Fischer-Tropsch(48) and Syngas-to-methanol.(49) The benefit of CO_2 capture to enhance oil production(50) in addition to the use of Fischer-Tropsch technology to produce fuels, have also been advocated.(51) Although it should be noted that the possibility of using CO_2 for enhanced oil recovery, is very location specific. Furthermore, gasification technology could be a convenient sink for excess coke production from residue upgrading by delayed coking, since the coke can be employed as gasifier feedstock. This approach has previously been explored in the Exxon Donor Solvent (EDS) process for direct coal liquefaction.(52) The EDS process

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[v] It is interesting to speculate on the political ramifications of this situation. Big oil companies may want to buy into agriculture, which is arguably then an essential part of their business. Since bio-fuels are subsidised, the oil companies would be subsidised, an issue that is already boiling up with the 2007 Tyson-ConocoPhillips deal. According to this deal, a "renewable" diesel fuel will be produced from animal fat by co-processing the animal fat with crude oil derived hydrocarbons in a thermal depolymerisation (cracking) unit.

was combined with the gasifier section from an Exxon Flexicoker(20) to convert the coal residue into hydrogen, which is needed for coal liquefaction.

4.3. Future crude oil refineries

Translating trends in crude oil refining into a futuristic flowscheme is fraught with the same obstacles encountered in devising any generic refinery flowscheme. Views on future crude oil refineries should therefore not be seen as a concrete entity, but rather as an expression of philosophy, with very different pictures emerging.

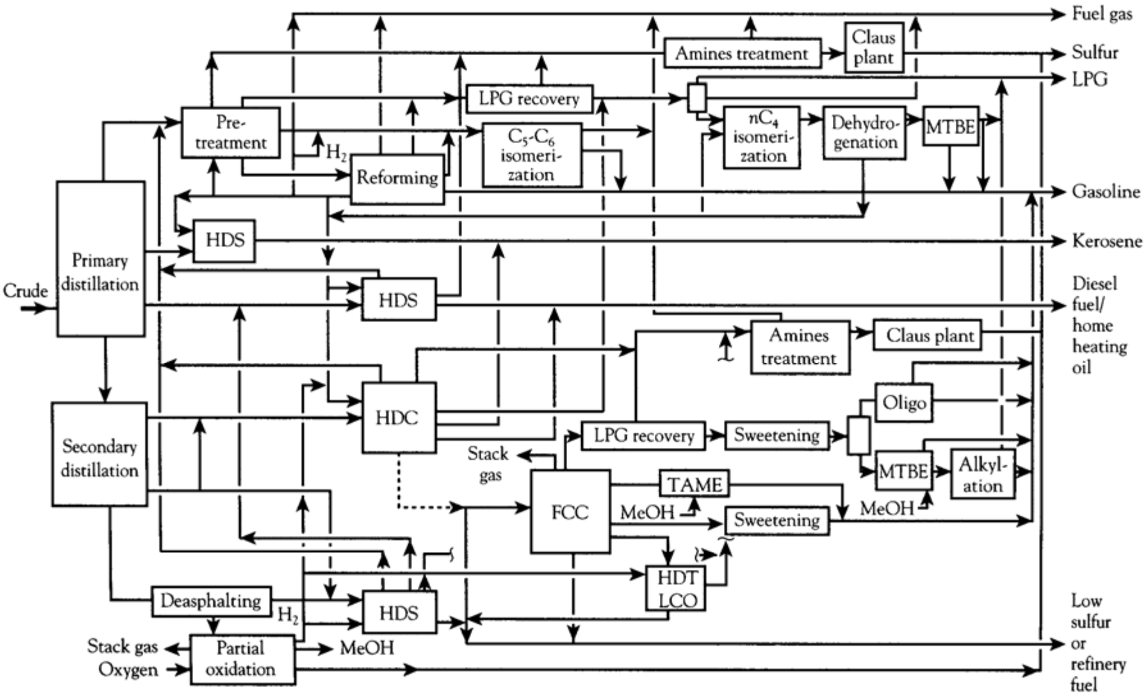

Figure 6. Future crude oil refinery concept developed along traditional lines. (This figure has been reproduced directly from Ref.(12) and is copyright protected).

A fairly traditional approach is presented by Heinrich from the Institut Français du Pétrole (Figure 6).(12) The intensity of residue upgrading and the need for additional hydrogen in the refinery is reflected in the addition of a hydrocracker and partial oxidation unit. Although it is not explicitly indicated, the partial oxidation unit is coupled with some form of syngas-to-methanol technology, making the refinery self-sufficient in terms of methanol for etherification. A lot of emphasis has been placed on etherification for the production of high octane oxygenates, a view that is questionable in USA context, but probably still valid for Europe. The appearance of an olefin oligomerisation unit is interesting, since it implies a much more olefin rich refinery. The increase of olefins is a consequence of the intensification of residue upgrading, but also a means to reduce the hydrogen requirements.[w] Of the five trends identified in the previous section, only the inclusion of renewable fuel is not reflected and it can be argued that it shouldn't be, since it does not require co-refining, only blending.

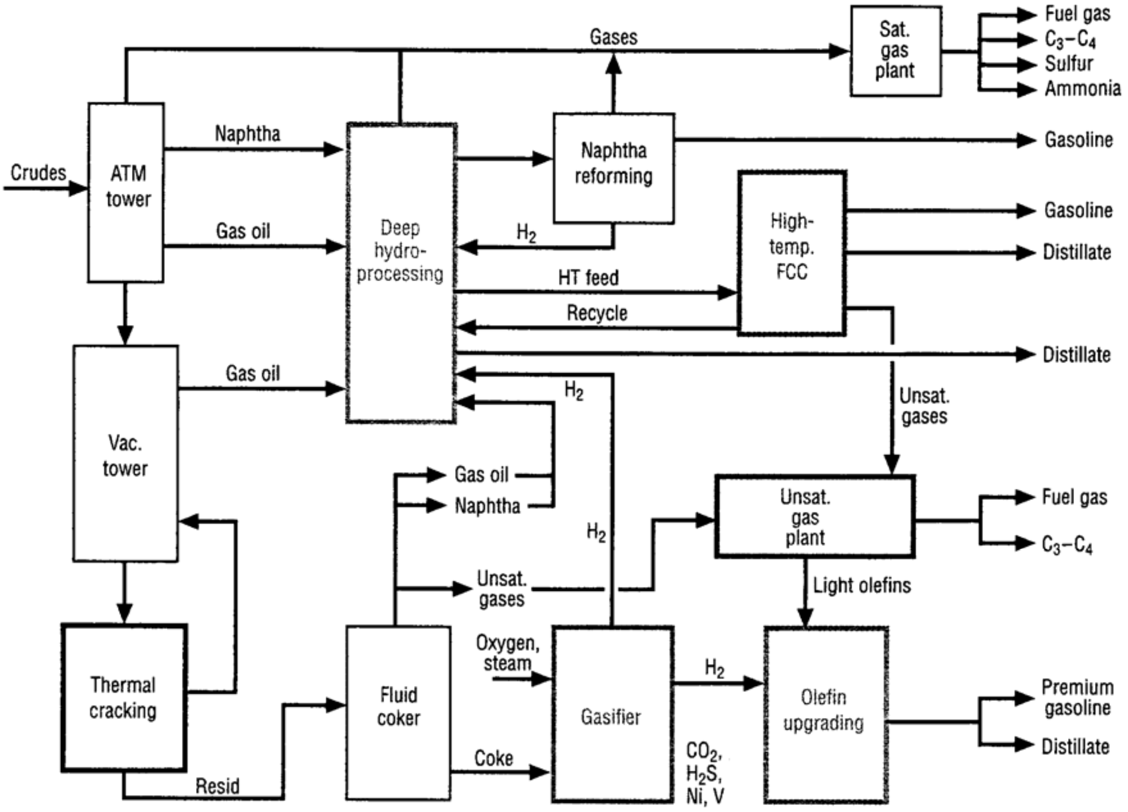

Figure 7. Future crude oil refinery concept based on environmental friendliness of the refining units. (This figure has been reproduced directly from Ref.(42) and is copyright protected).

A much more radical approach, focussing on the environmental impact of the refining units, is presented by Chen from ExxonMobil (Figure 7).(42) The flowscheme is not always technology specific, with technology classes being grouped together, like olefin upgrading and deep hydroprocessing. This hides the increased complexity of the refinery. The intensity of residue upgrading and hydrogen production is reflected by the use of a thermal cracker, fluid coker, high temperature FCC and gasifier. The gasifier also enables the production of synthetic fuels by other means, like Fischer-Tropsch. In general there is a clear fuel synthesis focus and "the heart of this new scheme resides in olefin upgrading technologies". The

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[w] If C_8 is taken as a representative carbon number for motor-gasoline, the ability to include octenes (C_8H_{16}) from olefin oligomerisation, rather than octanes (C_8H_{18}) in the fuel pool, saves about 10% hydrogen for that fraction.

exclusion of aliphatic alkylation and hydrocracking is interesting. The exclusion of the former is understandable from an environmental perspective and the latter is excluded purely as result of the proposed configuration. Again four of the five refining trends are embodied in the flowscheme, with only renewable fuel not being shown.

The consequence of the trends in crude oil refining is that future crude oil refineries will become more hydrogen and olefin rich and have the capacity to integrate synthesis gas based synthetic fuel. It is also expected that peak oil production, that is likely to be reached soon,(53)(54) will have a significant impact on transportation fuel production. The emergence of hybrid crude oil refineries that co-process alternative materials like tar sands or coal might fundamentally change the way in which crude oil refining is approached in future.

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CHAPTER V

Fischer-Tropsch Syncrude

The composition of Fischer-Tropsch derived syncrude is discussed and related to the mechanism of Fischer-Tropsch synthesis. Syncrude is differentiated based on the operating temperature of the Fischer-Tropsch synthesis between high temperature (HTFT) and low temperature (LTFT) syncrude. The main compound classes in syncrude are hydrocarbons (paraffins and olefins, as well as aromatics in HTFT) and oxygenates (alcohols, aldehydes, carboxylic acids, esters and ketones). The products are mostly linear, with a high n-paraffin and α-olefins content. Minor compound classes have been listed and the presence of metal carboxylates has been noted. A comparison with crude oil in general is made showing differences in composition and release during refining. Syncrude is rich in paraffins, olefins and oxygenates, while crude oil is rich in paraffins and aromatics, with sulphur, nitrogen and oxygen as heteroatoms. Syncrude is more reactive than crude oil due to its high olefin and oxygenate content. These differences suggest differences in refinery design.

1. Introduction

On 22 July 1925 the German scientists Franz Fischer and Hans Tropsch patented a process for the catalytic conversion of carbon monoxide and hydrogen to heavier hydrocarbons.[a,(1)] Fischer-Tropsch syncrude is a term that is used to collectively describe the products that are obtained by this means. Like crude oil, there are numerous types of syncrude and the composition of each type is dependent on many variables, including the nature of the Fischer-Tropsch catalyst, reactor type and operating conditions. The metals that are Fischer-Tropsch-active, are iron, cobalt, nickel and ruthenium.(2) Of these, only iron and cobalt are of commercial interest, since ruthenium[b] and nickel[c] both have small useful Fischer-Tropsch operating windows. Fischer-Tropsch catalysis will not be discussed in depth, but where

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[a] The Kaiser Wilhelm Institute for Coal Research was established in 1913 in Mülheim in the Ruhr, Germany. The aim of the research of Fischer and Tropsch was to find a way of making fuels and chemicals from coal-derived gas. Their work only started to yield positive results in the 1920's and the first commercial application of their technology was in 1935 in an atmospheric fixed bed reactor, 10 years after the process was patented.

[b] Ruthenium is also too expensive and scarce to be considered for industrial applications.

[c] Nickel is difficult to use industrially, because nickel is lost as nickel carbonyl, $Ni(CO)_4$.

possible, variations in syncrude composition will be related to the Fischer-Tropsch process and catalyst.

It is important to discuss syncrude properties in generic terms, since syncrude composition influences refining in much the same way that crude oil does. A comparison is also made to highlight the differences between syncrude and crude oil, as well as to show why refining of syncrude should be approached differently to crude oil refining. Emphasis is placed on olefins and oxygenates, because it is these compound classes that differentiate syncrude from crude oil.

Although Fischer-Tropsch plants are often classified in terms of feed material as coal-to-liquids (CTL), gas-to-liquids (GTL), or biomass-to-liquids (BTL) plants, the feed material does not determine the type of Fischer-Tropsch technology or the syncrude composition. The feed material only influences the gasifier type(3) and once the feed has been converted to synthesis gas,[d] the gas loop can be configured to suit the Fischer-Tropsch technology. One exception is low temperature gasification. These gasifiers produce pyrolysis products in addition to synthesis gas. Although the co-production of pyrolysis products has no impact on Fischer-Tropsch synthesis, there are benefits associated with processing these pyrolysis products too. The composition of coal pyrolysis products will not be discussed.

2. Fischer-Tropsch catalysis

The Fischer-Tropsch reaction is initiated by the adsorption of carbon monoxide (CO) on the catalyst surface (Figure 1). Once that has happened, chain propagation and chain termination can take place by various routes. The main products are paraffins, olefins and oxygenates.

From the simplified reaction network shown in Figure 1, some general deductions can be made about what would influence product selectivity. The main chain termination reactions leading to final products are hydrogenation and desorption. Any catalyst properties or operating conditions that would favour these termination steps, would therefore result in a lighter product. Conversely, any catalyst properties or operating conditions that would favour CO adsorption would increase the concentration of adsorbed species and thereby the chance of chain propagation, resulting in a heavier product. It can also be seen that paraffins, olefins, primary alcohols, carboxylic acids and aldehydes are all primary Fischer-Tropsch products.

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[d] Strictly speaking this is true only if the trace components in the synthesis gas are ignored. Depending on the trace components, further cleaning steps may be required to ensure adequate Fischer-Tropsch catalyst lifetime.

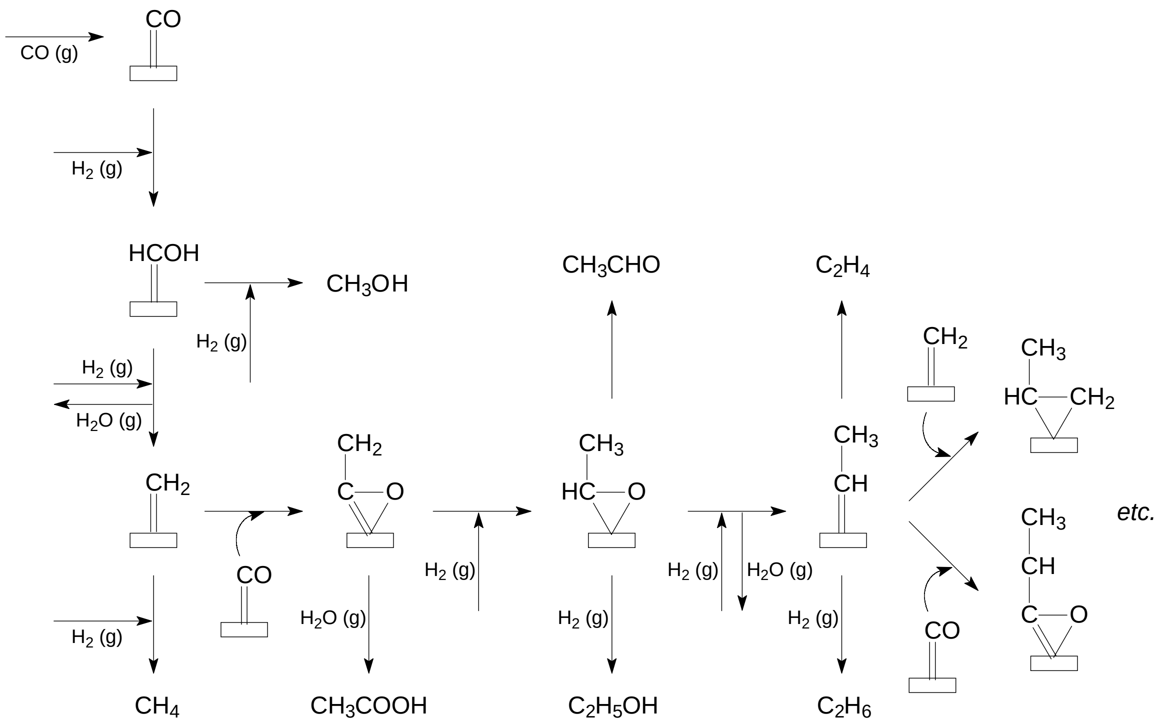

Figure 1. Simplified mechanism of the Fischer-Tropsch reaction showing the formation of the primary products, namely paraffins, olefins, alcohols, aldehydes and carboxylic acids.

Re-adsorption of the oxygenates compete with CO adsorption and at high enough temperature oxygenate interconversion reactions are at equilibrium (Equations 1 and 2).[e,(4)]

$$C_2H_5OH + H_2O \rightleftharpoons CH_3COOH + H_2 \qquad \text{... (1)}$$

$$C_2H_5OH \rightleftharpoons CH_3CHO + H_2 \qquad \text{... (2)}$$

Of the main oxygenate classes found in the Fischer-Tropsch product, only ketones, esters and *sec*-alcohols seem to be secondary products. The ketones seem to be secondary products from carboxylic acid decomposition.(5) This would be analogous to ketone formation by metal carboxylate decomposition[f,(6)] and temperature is expected to be important, since subsequent decomposition to produce CO_2 can also take place. Since most of the ketones are methyl ketones, acetic acid plays an important role in ketone formation. The *sec*-alcohols are produced by hydrogenation of the ketones.

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[e] At 610 K (337°C) the equilibrium and observed values for Equation 1 are both 0.14 and at 600 K (327°C) the equilibrium and observed values for Equation 2 are 0.22 and 0.21 respectively. At 510 K (237°C) neither of these reactions are at equilibrium. (All data for Fe-FT catalysts and equilibria calculated at exit conditions).

[f] Thermal analysis of iron(iii)propionate decomposition indicates the following sequence: $Fe(C_2H_5COO)_3.3H_2O \rightarrow Fe(C_2H_5COO)_3$ at 170°C → $Fe(C_2H_5COO)_2$ at 230°C → $Fe_2(CO_3)_3$ at 370°C → α-Fe_2O_3 at 570°C. The thermogravimetric data suggests a continuous loss of mass from about 230°C as the carboxylate decomposes to form a ketone.

Internal olefins are secondary products, since the chain growth mechanism depends on the terminal carbon being adsorbed onto the catalyst. An interesting inverse relationship was found between the selectivity to internal olefins and carboxylic acid production. It has been postulated that the same sites responsible for double bond isomerisation of α-olefins to internal olefins can be converted to sites responsible for carboxylic acid formation.(7) This inverse relationship between internal olefins and carboxylic acids seems to generally hold true, irrespective of the catalyst type. It is speculated that this relationship is not due to specific sites on the catalyst, but rather that it is related to the acid decomposition pathway leading to the formation of ketones, then *sec*-alcohols and finally dehydration to produce internal olefins.

It should be noted that the actual mechanism of Fischer-Tropsch synthesis is not yet resolved and there may even be a possibility that the mechanism over iron and cobalt is different from each other.(8) The kinetic description of the Fischer-Tropsch reaction is likewise still being disputed. For example, recent work(9) provided compelling evidence for the omission of the water partial pressure from the kinetic description of iron-based LTFT synthesis.

2.1. Catalyst properties

2.1.1. Probability of chain growth

The carbon number distribution obtained during Fischer-Tropsch synthesis is determined by the probability of chain growth on the catalyst, which is also called the α-value of the catalyst. Apart from the influence of the catalyst itself, other variables also affect the observed α-value, like operating conditions, feed gas composition and reactor type.(4) However, if the environment is kept constant, a relative comparison of α-values would be a direct measure the likelihood that a Fischer-Tropsch catalyst would catalyse chain propagation, rather than chain termination.

There is a well-defined interrelationship between the carbon number distribution of the products formed during Fischer-Tropsch synthesis and the probability of chain growth over the catalyst. The molar fraction of carbon number n (x_n) in the product is related to the carbon number (n) and probability of chain growth (α) by the Anderson-Schultz-Flory (ASF) equation (Equation 3).(5)

$$\log x_n = n.\log\alpha + \log\frac{(1-\alpha)^2}{\alpha} \qquad \text{... (3)}$$

The probability of chain growth can therefore be calculated from experimental data by taking the molar ratio of any two carbon numbers in the product (Equation 4).(5) It can be determined more accurately from the slope of a logarithmic plot of the molar fractions against carbon number.

$$\frac{x_i}{x_j} = \alpha^{i-j} \qquad \text{... (4)}$$

In practise Fischer-Tropsch catalysts that produce a considerable amount of heavier hydrocarbons (>C_{20}), do not have a single α-value, but two. The first α-value (α_1) describes the carbon number distribution from C_3 to C_{12}, while the second α-value (α_2) describes the distribution of the C_{20} and heavier fraction.(4) This seems to be a mathematical convenience, since the α-value seems to slowly increase with chain length. Some attribute this to short chain olefin incorporation during chain growth,(2) but this can only account for the deviation at low carbon numbers. It is more likely that these deviations occur due to differences in the microscopic kinetic environment that cannot be kept the same at all sites during actual synthesis conditions.(10) It should also be noted that C_1 and C_2 never fit the ASF distribution. Methane is generally higher than predicted, while C_2 is lower.

An exciting new development has been the model description by Botes(11) that accounts for both the paraffin to olefin ratio of C_2 and heavier hydrocarbons and the carbon number distribution, inclusive of C_1 and C_2. It states that the rates of hydrogenation and chain growth are independent of chain length, but that the chain length determines the rate of desorption. This has been rationalised by arguing that chain growth and hydrogenation takes place at the active endpoint, which is not significantly influenced by the inductive effect of the length of the alkyl chain attached to it. Conversely the alkyl chain may be adsorbed on the catalyst, making desorption dependent on the strength of adsorption that increases with increasing alkyl chain length. The probability of further reaction is consequently increased as the chain length of the adsorbed species is increased.

2.1.2. Hydrogenation activity

The different metals active for the Fischer-Tropsch reaction have different hydrogenation propensities. Iron is the least active for hydrogenation, followed by cobalt, nickel and ruthenium. Nickel and ruthenium are both very active methanation catalysts and produce heavy hydrocarbons only at low temperatures.(4) Due to the difference in hydrogenation activity the products from iron based Fischer-Tropsch synthesis are in general more olefinic than those from cobalt based synthesis.

2.1.3. Water gas shift activity

A significant difference between iron and cobalt based Fischer-Tropsch catalysts is the ability of an iron based catalyst to catalyse the water gas shift (WGS) reaction (Equation 5), while cobalt based Fischer-Tropsch catalysts virtually have no WGS activity.(4)

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \text{... (5)}$$

The WGS reaction allows the interconversion of carbon monoxide, carbon dioxide, hydrogen and water, which implies that CO_2 is a final product for cobalt Fischer-Tropsch catalysts, but not for iron catalysts. It also implies that cobalt based catalysts would be more sensitive to the H_2:CO ratio in the feed than iron based catalysts, because the latter can shift H_2 or CO to change the balance.

2.1.4. Sensitivity to promoters

One way in which the inherent properties of the Fischer-Tropsch active metal can be changed, is by adding promoters that act as modifying agents to the catalyst. Cobalt Fischer-Tropsch catalysts are not sensitive to promoters during high pressure operation,(4) nor sensitive to the support being used.(12) Iron Fischer-Tropsch catalysts are significantly affected by promoters and the addition of strong alkaline salts of Na and K are required for successful catalysts. Alkali promotion increases amount of CO adsorbed. With increasing alkaline addition activity passes through a maximum, while the α-value and oxygenate selectivity increases.(4) This happens because iron is not very hydrogenating and by increasing the CO adsorption, the probability of chain growth and CO incorporation to form oxygenates is higher.

2.2. Influence of operating conditions

2.2.1. Synthesis gas composition

During the Fischer-Tropsch reaction, hydrogen and carbon monoxide are consumed in a certain ratio that is dependent on the products being formed (Table 1). As the products become heavier, the usage ratio approaches 2, irrespective of the compound class being formed.

Ideally the synthesis gas composition of the feed should match this ratio, because if it does not, the H_2:CO ratio would change during synthesis and lead to the production of unwanted side-reactions. For example, if the H_2:CO becomes very high, the rate of methanation will increase, while when the H_2:CO becomes very low, the rate of coke formation on the catalyst will increase.

In this respect iron based catalysts are less sensitive to the synthesis gas composition, because it has WGS activity (Equation 5). At high enough temperatures the WGS reaction is in equilibrium and deficiencies in either H_2 or CO can be compensated for. The same is not true for cobalt-based Fischer-Tropsch catalysts that have little WGS activity. For low temperature synthesis, the usage ratio of cobalt Fischer-Tropsch catalysts is 2.05-2.15, while that of an iron Fischer-Tropsch catalyst is about 1.65.⁽⁴⁾

Table 1. Usage ratio of H_2:CO in various Fischer-Tropsch reactions.

Product	Reaction	H_2:CO usage	H_2:CO usage for *n* equal to				
			2	4	10	25	50
Methane	$CO + 3\ H_2 \rightarrow CH_4 + H_2O$	3	3	3	3	3	3
Paraffins	$n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$	(2n+1)/n	2.5	2.25	2.1	2.04	2.02
Olefins	$n\ CO + 2n\ H_2 \rightarrow C_nH_{2n} + n\ H_2O$	2	2	2	2	2	2
Alcohols	$n\ CO + 2n\ H_2 \rightarrow C_nH_{2n+1}OH + (n-1)\ H_2O$	2	2	2	2	2	2
Aldehydes	$n\ CO + 2n\ H_2 \rightarrow C_nH_{2n}O + (n-1)\ H_2O$	(2n-1)/n	1.5	1.75	1.9	1.96	1.98
Acids	$n\ CO + 2n\ H_2 \rightarrow C_{n-1}H_{2n-1}COOH + (n-2)\ H_2O$	(2n-2)/n	1	1.5	1.8	1.92	1.96

2.2.2. Pressure

The reactor pressure and feed gas composition determine the partial pressure of the reagents, hydrogen and carbon monoxide. Since CO is more strongly adsorbed on the catalyst than H_2, the concentration of CO on the catalyst surface is increased when the pressure is increased. High CO concentration on the catalyst surface promotes chain growth and increases the observed α-value of the catalyst. A high CO concentration also favours CO incorporation and consequently the production of oxygenates.

2.2.3. Temperature

Temperature affects the desorption rate of products on the catalyst surface. Desorption is an endothermic reaction and an increase in temperature consequently increases the desorption rate and thereby chain termination. The rate of hydrogenation, which can also cause chain termination, is increased by an increase in temperature too. These two temperature effects lower the α-value and higher temperatures consequently result in more shorter chain products. If the increase in hydrogenation rate with temperature is faster than the increase in the rate of olefin desorption, it will cause the product from a specific Fischer-Tropsch catalyst to become more paraffinic.

All reaction rates increase with an increase in temperature. At higher temperatures aromatics start appearing in the product and the influence of temperature is especially apparent in the reactions of oxygenates:

a) Interconversion of aldehydes, alcohols and carboxylic acids reach equilibrium.
b) Ketone formation by the decomposition of carboxylic acids increases.
c) Iso-alcohol formation by hydrogenation of ketones increases.
d) Alcohol dehydration to produce olefins increases.

The reactor technology is dependent on the operating temperature too, which is why commercial Fischer-Tropsch technologies are classified either as low temperature (LTFT)(13) or high temperature (HTFT).(14)

3. Syncrude composition

Syncrude is produced from synthesis gas and the compounds that can be produced by a Fischer-Tropsch process must therefore be limited to those containing the elements hydrogen, carbon and oxygen. Consequently, Fischer-Tropsch products are either hydrocarbons, or oxygenates. This is reflected in literature on Fischer-Tropsch(4)(15)(16) that list hydrocarbons (paraffins, olefins and aromatics) and the main oxygenate classes (alcohols, aldehydes, carboxylic acids and ketones) as the only constituents of syncrude. In practise syncrude is more complex than it would appear from the discussion thus far and many isomers and minor compound classes can be identified (Figure 2). Some compound classes not normally associated with Fischer-Tropsch synthesis, such as cyclic dienes and alkynes, are indeed found in low concentration in the syncrude.

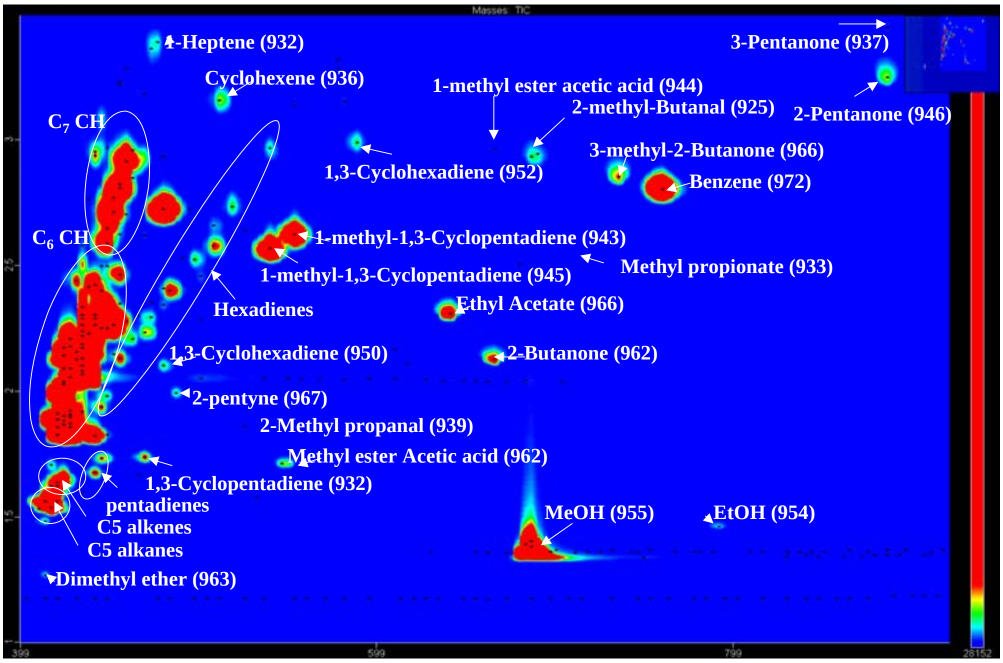

Figure 2. Two dimensional GC-GC-TOFMS chromatogram of C_6/C_7 HTFT derived stabilised light oil. Compound identification is based on similarity index (given in brackets) compared to the mass spectra of known compounds. Separation on the vertical axis is based on boiling point, while separation on the horizontal axis is based on polarity. In this way many compound classes that would normally co-elute during chromatographic separation can be resolved and identified. (Unpublished results)

3.1. Hydrocarbons

Syncrude can potentially contain all the hydrocarbon compound classes, but only the following classes are major constituents:

a) *Paraffins*. The saturated hydrocarbons are mostly *n*-paraffins, especially the high molecular weight products, like waxes. Branched paraffins are present too and are more prevalent in HTFT processes than in LTFT processes. A mathematical description of chain branching in Fischer-Tropsch synthesis has been given by Weitkamp, et al.(17) that describes data for short chain hydrocarbons well, but the assumptions on which it is based do not hold true for longer chain hydrocarbons. The probability of chain branching does not remain constant, but decreases with increasing chain length and monomethyl branches, randomly situated along the chain, exceed all other forms of branching by an order of magnitude.(18) Syncrude also contains cyclo-paraffins (naphthenes) in low concentration, typically in the order of 0.1-1% of the total paraffin content.

b) *Mono-olefins*. Like the paraffins, the olefins are mostly *n*-olefins, with linear α-olefins being especially prevalent. Linear internal, branched and cyclo-olefins are also found. The branching properties are similar to that of paraffins, but even amongst the branched olefins, the double bond is often in the α-position. Fischer-Tropsch catalysts that have a very high α-olefin content in the product, also have a high carboxylic acid make, while the converse is also true.(7)

c) *Aromatics*. Aromatics are produced in HTFT processes and are mainly mono-nuclear aromatics that include benzene,[g] as well as alkylbenzenes, like toluene. Dinuclear and polynuclear aromatics are formed too, but in low amounts. In HTFT products about 10% of the alkylbenzenes have unsaturated alkylchains, like styrene, and there are also significant quantities of indanes and indenes present (Figure 3).(19) Syncrude derived from LTFT processes are almost devoid of aromatics.(4)

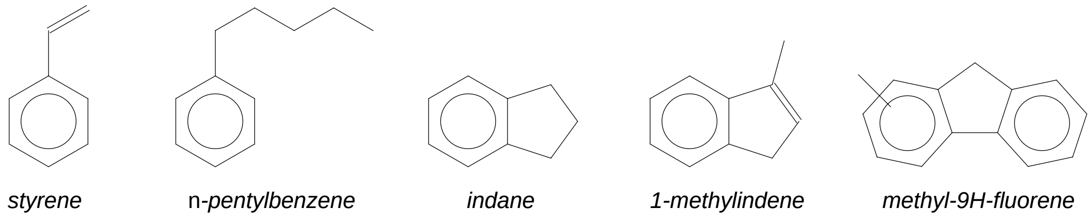

Figure 3. Examples of typical aromatic hydrocarbons present in HTFT syncrude.

During HTFT some *dienes* are produced, but these are minor components, with a concentration of less than 0.1% in the hydrocarbon product. The diene content becomes less with increasing carbon number. The formation of *alkynes* is not generally associated with Fischer-Tropsch, although trace quantities of alkynes have been identified in HTFT syncrude.(20)

3.2. Oxygenates

The oxygen containing functionality of most oxygenate classes renders it polar. The polarity of the molecules decrease with increasing carbon number, as the aliphatic component of the molecules become more dominant. The short chain oxygenates are therefore mainly found in

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[g] Benzene produced during Fischer-Tropsch synthesis is only about 1% of the total aromatics.

the aqueous product phase, while the longer chain oxygenates are exclusively found in the organic phase. Partitioning between the aqueous and organic phases change with increasing carbon number and despite the high polarity of molecules like acetic acid, the organic phase is never devoid of such highly polar oxygenates.

It has already been shown that alcohols, aldehydes and carboxylic acids are primary Fischer-Tropsch products, with ketones being formed as a secondary product during carboxylic acid decomposition. Although esters are often not included in discussions on the Fischer-Tropsch mechanism, it is a significant secondary product.(21) The main oxygenate classes are (Figure 4):

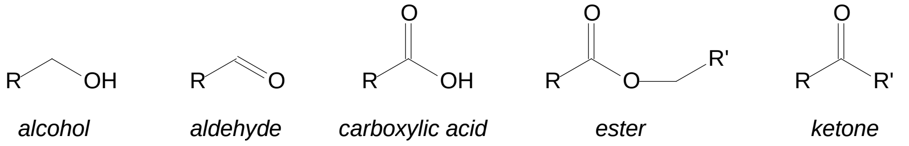

Figure 4. Major oxygenate classes found in Fischer-Tropsch syncrude.

a) *Alcohols*. The alcohols are mainly linear 1-alcohols. Branched alcohols are also formed, but just like the hydrocarbons, branching is mostly methyl branching. The branched alcohols are also predominantly 1-alcohols. Secondary alcohols are formed by hydrogenation of ketones and are therefore secondary products. Hydration of olefins is a minor reaction, if it happens at all, since dehydration of alcohols to olefins is more likely to occur.(4) Almost all alcohols have only an aliphatic chain and only trace amounts containing a phenyl group (phenols excluded) are found in HTFT products.(19) Most of the short chain alcohols (C_1-C_5) are found in the aqueous product phase. The organic product contains some C_2-C_5 alcohols, but it is predominantly the C_6 and heavier alcohols that partition in the organic product phase.

b) *Aldehydes*. The aldehydes are mainly linear, but have the same branching pattern and content as found in the hydrocarbons and alcohols. This is expected, since the formation of aldehydes occur by the same route as the other primary products, it is just the method of chain termination that imparts a different functionality to it. The organic product contains C_4 and heavier aldehydes, with the aqueous product containing C_4 and lighter aldehydes, as well as a minor amount of the heavier aldehydes.

c) *Carboxylic acids*. Like the other primary Fischer-Tropsch products, the carboxylic acids are mainly linear, with a decreasing degree of branching with increasing carbon number. The aqueous phase contains mainly C_2-C_6 acids, but these and heavier acids are also found in the organic phase, despite their high polarity.

d) *Esters*. The esters seem to be mostly linear aliphatic compounds and do not seem to follow an ASF distribution. Heavier esters are quite prevalent in HTFT syncrude, indicating that they are likely to be formed by the condensation of carboxylic acids and alcohols, or possibly even by the condensation of alcohols. The esters are mainly found in the organic product.

e) *Ketones*. It has already been mentioned that most ketones are methyl ketones with the carbonyl group on the β-carbon. The remainder of the ketones has the carbonyl on the γ-carbon. This indicates that decomposition reactions invariably involve acetic and propionic acid. Considering the chain length of the ketones observed in HTFT syncrude, it is unlikely that this is the product of long chain carboxylic acid decomposition per se.[h] LTFT syncrude contains little ketones, since carboxylic acid decomposition is a thermal reaction favoured by high temperature. Interestingly enough, HTFT syncrude also contains trace amounts of aromatic ketones.(19) The partitioning of ketones is such that the organic product contains a fraction of all ketones, including about 10% of the acetone. The aqueous product contains only acetone and methyl ethyl ketone in significant quantities, with the heavier ketones being less prevalent.

Other oxygenate classes that are also found in syncrude in much lower concentrations are *acetals*, *ethers*, *furans* and *phenols* (Figure 5).(19)

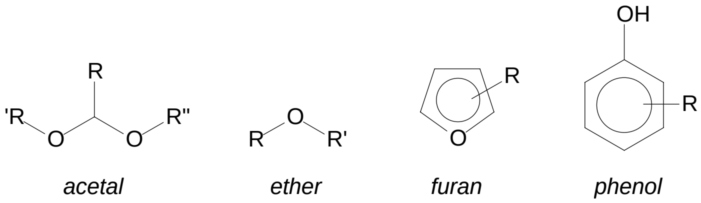

Figure 5. Minor oxygenate classes found in Fischer-Tropsch syncrude.

3.3. Metal containing compounds

One would not expect metal containing products from the feed material to end up in the syncrude product, since the feed consists only of purified synthesis gas. However, carboxylic acids are a primary product from Fischer-Tropsch synthesis. At high temperature the short

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[h] The low concentration of heavier than C_8 carboxylic acids in HTFT syncrude, as well as the low reincorposation tendency of longer chain hydrocarbons in the FT product, ref.(2), argues against preferential readsorption of long chain carboxylic acids to produce heavy ketones. It could rather be that adsorbed intermediates, which have not yet desorbed as products and that could lead to the formation of long chain carboxylic acids are decomposed in the presence of short chain acids (acetic acid and propionic acid), or their intermediates to yield heavy ketones.

chain carboxylic acids are very aggressive and can lead to corrosion of processing equipment and leaching of catalysts.(22) Fischer-Tropsch syncrude therefore contains *metal carboxylates* that are produced by carboxylic acid attack on metal or metal oxide containing surfaces.

4. Properties of commercial syncrudes

There are an infinite number of syncrude compositions that can be achieved by Fischer-Tropsch catalysis. It is nevertheless instructive to look at the composition of some commercial syncrudes. At present there are six commercial Fischer-Tropsch processes in operation globally (Table 2), using four different types of Fischer-Tropsch catalyst.

Table 2. Commercial Fischer-Tropsch processes currently in operation in the world.

Type	Catalyst	Reactor-type	Technology	Operator	Location
HTFT	Fused Fe	Fluidized bed	Synthol	PetroSA	Mossel Bay, South Africa
HTFT	Fused Fe	Fluidized bed	SAS	Sasol	Secunda, South Africa
LTFT	Precipitated Fe	Fixed bed	ARGE	Sasol	Sasolburg, South Africa
LTFT	Precipitated Fe	Slurry bed	SSBP	Sasol	Sasolburg, South Africa
LTFT	Co-SiO_2	Fixed bed	SMDS	Shell	Bintulu, Malaysia
LTFT	Co-Al_2O_3	Slurry bed	SSBP	Sasol	Ras Laffan, Qatar

SAS = Sasol advanced Synthol
ARGE = Arbeitsgemeinschaft Ruhrchemie-Lurgi
SSBP = Sasol slurry bed process
SMDS = Shell middle distillate synthesis

The α-values for Fischer-Tropsch catalysts that are used in HTFT fluidized bed applications are limited to <0.71, because higher α-values would lead to the formation of products that condense at the operating conditions. Product condensation would cause catalyst particle agglomeration and eventual de-fluidisation of the catalyst bed. The α-values used for LTFT catalysts in fixed bed or slurry bed applications are generally above 0.90 (Figure 6).(4)(23)

The properties of some commercial syncrudes are given in Table 3.(4)(24)(25) From this it is clear that catalyst pretreatment and reactor type play significant roles, since a similar catalyst is used in the LTFT ARGE and LTFT SSBP reactors.(26) However, these are not the only parameters differentiating ARGE and SSBP.

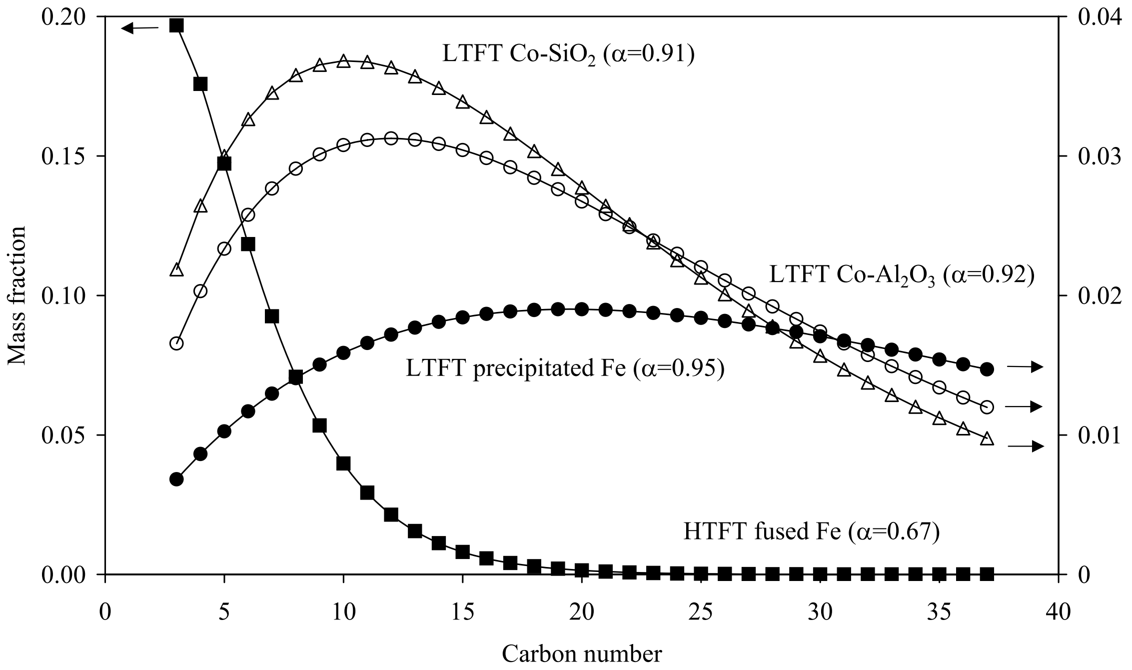

Figure 6. Carbon number distribution of some commercial Fischer-Tropsch technologies.

Table 3. Composition of straight run syncrude naphtha and distillate from various commercial Fischer-Tropsch processes (mass %).

Process	Cut	Olefin	Paraffin	Aromatic	Oxygenate	α-Olefin	*n*-Paraffin
Fe-HTFT	Naphtha	70	13	5	12	49	8
SAS	Distillate	60	15	15	10	34	9
Fe-LTFT	Naphtha	64	29	0	7	61	28
SSBP	Distillate	50	44	0	6	47	42
Fe-LTFT	Naphtha	32	60	0	8	30	57
ARGE	Distillate	26	66	0	8	24	61
Co-LTFT	Naphtha	35	54	0	11	32	49
SSBP	Distillate	15	80	0	5	14	76

5. Comparison of crude oil and syncrude

The composition of crude oil and syncrude differs in some crucial aspects (Table 4). There are obvious differences, with syncrude containing large amounts of olefins and oxygenates, but no sulphur or nitrogen compounds, while crude oil contains no olefins and mostly heavier oxygenates, as well as significant amounts of sulphur and nitrogen compounds. LTFT syncrude contains no aromatics, which is also different to crude oil, while syncrude in general has comparatively little naphthenes compared to crude oil. The nature of the metal containing compounds is different and although crude oil may contain associated water, it is a major by-product from Fischer-Tropsch synthesis. The physical properties of crude oil(27) and that of syncrude(28) are also very different.

Table 4. Comparison of the compound classes present in crude oil and iron-based Fischer-Tropsch derived syncrude. The LTFT syncrude from Co-based Fischer-Tropsch synthesis contains less olefins and oxygenates.

Compound class	Crude oil	HTFT syncrude	LTFT syncrude
Acyclic paraffins	major component	> 10%	> 30%
Naphthenes	major component	< 1%	< 1%
Olefins	none	> 60%	> 20%
Aromatics	major component	5-10%	none
Oxygenates	< 1% O (heavies)	5-15%	5-15%
Sulphur compounds	0.1-5% S	none	none
Nitrogen compounds	< 1% N	none	none
Metal containing compounds	phorphyrines, Cl^-	carboxylates	carboxylates
Water	0-2%	major by-product	major by-product

Syncrude is consequently a much more reactive feed than crude oil due to the high concentration of olefins and oxygenates in syncrude. Syncrude is also a “cleaner” feed, since heteroatoms are limited to oxygen, while crude oil contains nitrogen and sulphur compounds too. This makes syncrude refining easier and more environmentally friendly in terms of separation complexity and dealing with off-gas from refining operations.(29)(30)

Something that is less obvious from the comparison in Table 4 is the impact this has on hydrotreating in the refinery. Not only is the focus of hydrotreating different, but also the heat release during hydrotreating.(31)(32)(33) Crude oil has a hydrodesulphurisation (HDS) and a hydrodenitrogenation (HDN) focus, while syncrude has a hydrodeoxygenation (HDO) and olefin saturation focus. The energy associated with the different compound classes is very different (Tables 5 and 6).(34) Hydrotreating a sulphurous atmospheric residue typically has a heat release of around 450 $kJ \cdot kg^{-1}$, while hydrotreating a HTFT naphtha has a heat release of around 1000 $kJ \cdot kg^{-1}$, more than double that of a difficult to hydrotreat crude oil. Heat management during Fischer-Tropsch syncrude refining is consequently much more of an issue than during crude oil refining. This can be viewed in a positive light, since it implies scope for beneficial heat recovery to improve the overall thermal efficiency of a Fischer-Tropsch refinery. This can be extended to the CO_2 footprint of the refinery, which becomes smaller when the high heat release associated with Fischer-Tropsch syncrude refining is beneficially used.

Table 5. Generalised standard heats of hydrogenation (ΔH_r) of selected aliphatic bond types.

Aliphatic class	Hydrogenation reaction type	ΔH_r	
		kJ·mol^{-1}	kJ·g$_{\text{heteroatom}}^{-1}$
Hydrocarbon	CH_2=CH-R → CH_3-CH_2-R	-126	-
	cis R-CH=CH-R → R-CH_2-CH_2-R	-119	-
	trans R-CH=CH-R → R-CH_2-CH_2-R	-113	-
Oxygen containing	R-CH_2-OH → R-CH_3 + H_2O	-92	-5.7
	R-CHO → R-CH_3 + H_2O	-162	-10.1
	R-COOH → R-CH_3 + 2 H_2O	-134	-4.2
	R-O-CO-R' → R + CH_3-R' + 2 H_2O	-208	-6.5
	R-CO-R → R-CH_2-R + H_2O	-130	-8.1
Sulphur containing	R-CH_2-SH → R-CH_3 + H_2S	-61	-1.9
	R-CH_2-S-CH_2-R → 2 R-CH_3 + H_2S	-106	-3.3

Table 6. Standard heats of hydrogenation (ΔH_r) of selected aromatic compounds.

Aromatic class	Hydrogenation reaction type	ΔH_r	
		kJ·mol^{-1}	kJ·g$_{\text{heteroatom}}^{-1}$
Hydrocarbon	Benzene → cyclohexane	-206	-
	Naphthalene → tetrahydronaphthalene	-148	-
Oxygen containing	Phenol → cyclohexane + H_2O	-268	-16.7
Sulphur containing	Thiophene → butane + H_2S	-262	-8.2
Nitrogen containing	Pyrrole → butane + NH_3	-280	-20
	Pyridine → pentane + NH_3	-333	-23.8
	Aniline → cyclohexane + NH_3	-256	-18.3

Based on these fundamental differences between syncrude and crude oil composition, one would expect that Fischer-Tropsch syncrude refineries would be different from crude oil refineries.

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CHAPTER VI

Fischer-Tropsch Refineries

The historical development of commercial Fischer-Tropsch refineries is documented. The German technology (1930-1940's), Hydrocol (1940-1950's), Sasol 1 (1950's), Sasol 2 and 3 (1970-1980's), Mossgas (1980-1990's), Shell Bintulu (1980-1990's) and Oryx GTL (2000's) are all discussed in terms of their Fischer-Tropsch synthesis, gas loop and refinery designs. The evolution of the commercial refineries that are still in operation is also described to show how external factors influenced modifications to the refinery design. It is shown that the same change drivers that affect crude oil refineries also affect Fischer-Tropsch refineries, but that different variables are introduced by options like feedstock choice (GTL or CTL), gasification technology (tar products or not), Fischer-Tropsch synthesis (HTFT or LTFT), product slate (fuels, chemicals or both) and market (final or intermediate products).

1. Introduction

The development of Fischer-Tropsch refineries should be seen in historical context. The German LTFT refineries, the USA Hydrocol HTFT refinery and the South African Sasol 1 HTFT-LTFT combination refinery were built before the 1970's, in the time when most crude oil refineries were still 2nd generation topping-reforming type refineries. It should further be noted that Fischer-Tropsch catalyst development is much like oil exploration and generally takes place in isolation, not being sensitive to its impact on refining. Fischer-Tropsch refinery designs are therefore truly a reflection of the transformations that were needed to convert syncrude into products that met the market demands of their time.

Few Fischer-Tropsch technologies were developed to the point where either a demonstration scale pilot plant, or a commercial Fischer-Tropsch refinery was built. The Fischer-Tropsch refineries that will be described are all commercial facilities. During the discussion, reference will be made to the Fischer-Tropsch technology and the syncrude composition, since it is pertinent to the refinery design. The basis for the Fischer-Tropsch technology selection, as well as the design philosophy for the refinery will be highlighted.

Apart from the Sasol refineries in South Africa, all other Fischer-Tropsch refineries that were built before the 1990's are no longer in operation. Unlike the post-1990 refinery designs and those of the period 1930-1950 that are mainly of historical interest, discussion of the refinery designs of the 1950-present period presents a moving target. The older Fischer-Tropsch refineries that are still operational, had to evolve to keep pace with changes in the market and the legislation governing transportation fuels. The evolution of these refineries will be dealt with separately from the description of the original design.

It is highly likely that existing Fischer-Tropsch refineries will continue to change and that future refineries will be different to those constructed since the 1990's. Predictions about the future of Fischer-Tropsch refining is more difficult to make than for crude oil refining, because it presents such a small sample. This topic will nevertheless be briefly discussed to serve as an introduction to the chapters on technology selection and refinery design.

2. German technology (1930-1940's)

German Fischer-Tropsch research focussed mainly on iron, cobalt and thorium,[a] while studies using ruthenium and nickel were limited to initial laboratory work.(1)(2) Although the initial work was done with iron, cobalt proved easier to develop and all commercial German Fischer-Tropsch plants were based on cobalt catalysts.[b,(1)(3)] Interest in iron based Fischer-Tropsch was revived only during the Second World War, when cobalt became increasingly scarce.

Two processes were developed based on the Fischer-Tropsch catalyst: a normal-pressure (<0.1 MPa) process and a medium-pressure process (1-2 MPa). The German Fischer-Tropsch plants were all built in the period 1935-1938 and initially made use of the normal-pressure process. Development of the medium-pressure process started in 1937 and was tested on large scale in 1939 by Lurgi in the Hoesch plant.(5) Conversion of a further two commercial scale plants were reportedly planned. Ruhrchemie further developed the medium-pressure process, but in 1944, before conversion of the Holten Sterkrade plant to medium pressure operation could be completed, it was destroyed by bombing.(2) In a more recent summary of the German FT production capacity these conversions were indicated,

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[a] The thorium based Fischer-Tropsch catalysts were selective for short chain branched products and it was called the "Iso-synthesis" process. This made it ideal for high octane gasoline and research on this process was reportedly begun in 1941 at the Kaiser Wilhelm Institut für Kohlenforschung. Other oxides and combinations thereof could also be used, but required the complete absence of iron-group metals, even in trace quantities.

showing seven normal-pressure and four medium pressure plants spread among the nine German Fischer-Tropsch production sites.(6) (Literature seems to be contradictory).

Work on Fischer-Tropsch technology continued in Germany after the Second World War and amongst other things led to the development of the first slurry bed technology in 1953.(7) A detailed history and description of the German Fischer-Tropsch developments has recently been published by Davis.(8)

2.1. Normal-pressure cobalt Fischer-Tropsch synthesis

The flow diagram of a German normal-pressure Fischer-Tropsch synthesis plant is given in Figure 1.(4) Not all plants used the same synthesis gas production methodology, but due to the sulphur sensitivity of the Fischer-Tropsch catalyst, all were required to purify the gas before use. A H_2:CO ratio of 2:1 was required for synthesis and a water gas shift-reactor was used to adjust the H_2:CO ratio of the purified gas.

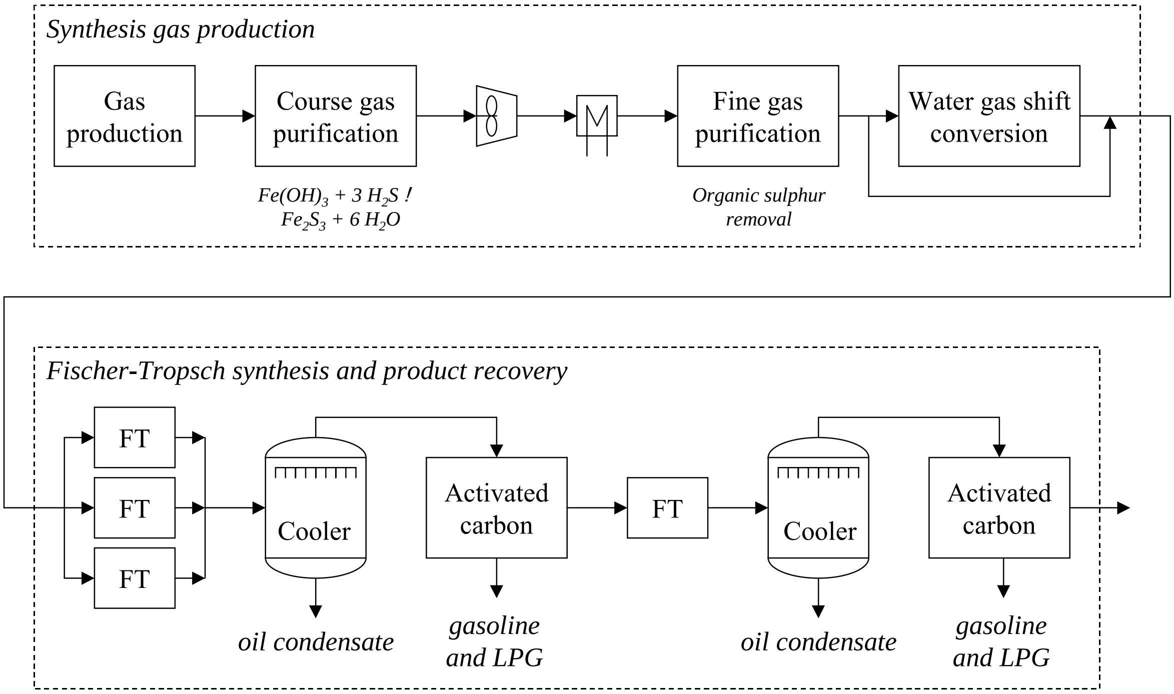

Figure 1. Flow diagram of a German normal-pressure Fischer-Tropsch synthesis plant.

The normal-pressure Fischer-Tropsch reactors were about 5 m long, 2.5 m wide and 1.5 m high. Each reactor consisted of tubes and heat transfer plates, with the catalyst being loaded on the shell-side between the heat transfer plates (Figure 2).(2)(4) Water was circulated

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[b] The precipitated cobalt Fischer-Tropsch catalyst used in German technology consisted of a mixture of cobalt-thoria-magnesia-kieselguhr in 100:5:10:200 ratio.

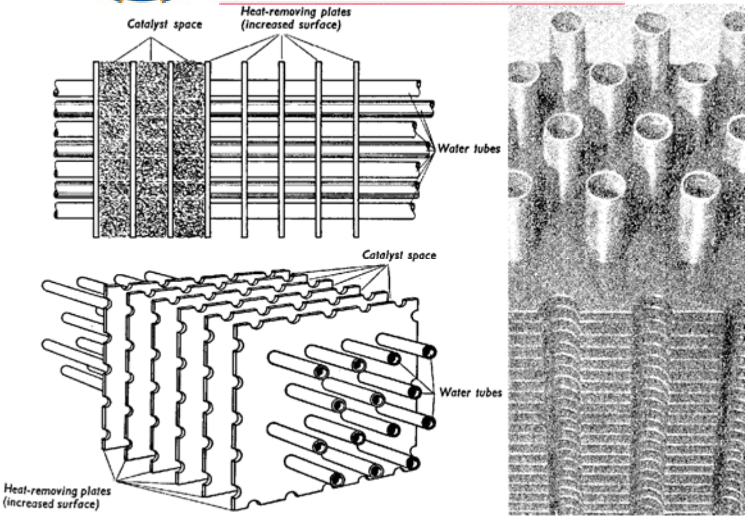

Figure 2. Internals of a normal-pressure Fischer-Tropsch reactor. (These figures have been reproduced directly from Refs.(2) and (4), and are copyright protected).

in the tubes to regulate the temperature. The catalyst bed was typically operated 5-8°C higher than the temperature in the tubes and in practise the reactor temperature could be controlled to within 1°C in the range 170-200°C by regulating the water pressure, using a boiler principle.[c] The synthesis gas pressure in the reactor was around 30 kPa.(4) The German normal-pressure Fischer-Tropsch technology can therefore be classified as a low temperature Fischer-Tropsch (LTFT) process.

In order to achieve a reasonable synthesis gas conversion,[d] normal-pressure plants used two or three Fischer-Tropsch synthesis stages in series. The German cobalt Fischer-Tropsch catalyst typically had a lifetime of 4-6 months, but temporary deactivation due to blockage by wax required "regeneration" every 700 hours. This entailed catalyst washing by spraying it with kerosene (180-230°C boiling range) to extract the wax. The product thus obtained was called catalyst wax.

A product recovery section followed each synthesis stage. The product was cooled down by spray-condensers to ambient conditions to yield an oil fraction, before the uncondensed gas was passed over a bed of activated carbon. The gaseous hydrocarbons were adsorbed on activated carbon from which it was recovered batch-wise by steaming (Figure 3).(4) The desorbed product was then stabilised by pressure distillation to yield an active carbon gasoline and liquid petroleum gas (LPG). The composition of the syncrude fractions from such a normal-pressure process is given in Table 1.[e],(4) In addition to the hydrocarbon

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[c] In the German design the tubes could withstand a pressure of 3 MPa. The heat release during Fischer-Tropsch synthesis is about 150 kJ·m^{-3} synthesis gas, which is equivalent to about 1.5 MJ·kg^{-1} of product.

[d] Conversion on average yielded in the order of 0.1 kg product per 1 m^{3} of gas.

[e] The kerosene (180-230°C) was called Kogasin I, while the diesel (230-320°C) was called Kogasin II.

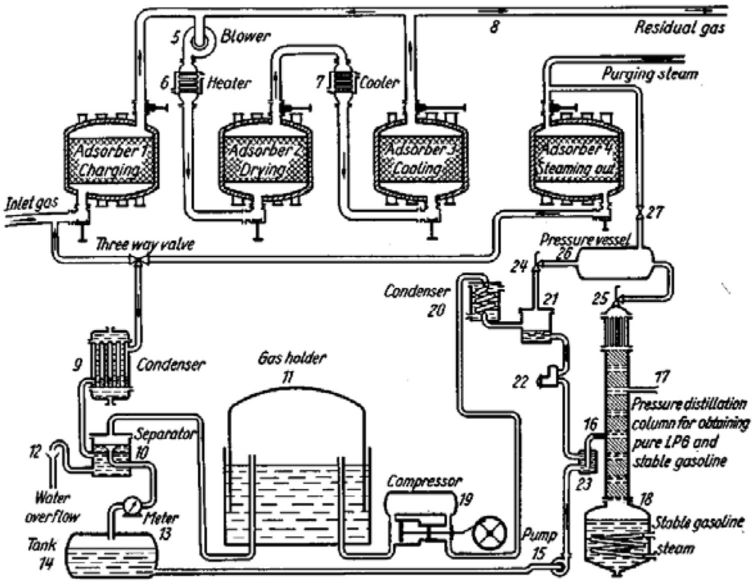

Figure 3. Activated carbon product recovery section after each Fischer-Tropsch synthesis stage. (This figure has been reproduced directly from Ref.(4) and is copyright protected).

products, the syncrude also contained oxygenates, mostly alcohols and carboxylic acids, which gave it a characteristic smell.

Table 1. Syncrude composition from German normal-pressure Co Fischer-Tropsch synthesis.

Description	Catalyst wax	Condensate oil	Carbon gasoline ‡	Crude LPG	Olefin content
Mass of total product (%)	2	40	50	8	
CO_2				10-30	
CO				1-3	
H_2				2-4	
methane				2-3	
ethane and ethylene				1-2	
propane and propylene			1	15-20	43
C_4 hydrocarbons			5-15	20-40	
C_5 hydrocarbons			15-20	10-20	37
C_6-180°C fraction		1-3	20-25	3-5	
180-230°C fraction (Kogasin I)		35-40			18
230-320°C fraction (Kogasin II)		30-35			8
320-460°C fraction (Slack wax)	20-30	20			0
>460°C fraction (Hard wax)	70-80	1			0

‡ In the source reference the carbon gasoline does not add up to 100%, since the remainder is mainly gaseous products.

2.2. Refining of normal-pressure syncrude

The German normal-pressure Fischer-Tropsch process was originally considered a motor-gasoline synthesis process and product work-up was directed exclusively to this end. The reason behind this thinking is clear from the product distribution of the commercial processes (Table 2).(4) The light olefins (C_3-C_4) were converted to chemicals, like alcohols, while the low octane motor-gasoline and high cetane distillate fractions were used as fuel blending components.(2) It was later recognised that the middle distillate paraffins can also be used for substitution reactions and that the slack wax has value as starting material for lubricating oil production, as well as products from autoxidation.(2)(4)

Table 2. Product distribution from the Rheinpreussen plant in Germany.

Product	Mass %
Liquid petroleum gas, LPG (C_3 and C_4)	10
Motor-gasoline (C_5-180°C)	52.2
Diesel fuel (180-320°C)	26.5
Soft paraffin wax (320-460°C)	7.6
Hard paraffin was (>460°C)	3.7

The Fischer-Tropsch refineries used in conjunction with the German normal-pressure Fischer-Tropsch process differed mostly in the processing of the heavier fractions and the sequence of the processing steps. A basic flow-diagram showing the main conversion steps is given in Figure 4. This does not represent any specific German Fischer-Tropsch refinery, but rather a general refinery configuration.

Table 3. Liquid phosphoric acid oligomerisation of Fischer-Tropsch derived propylene at 180-200°C and 4-6 MPa, as practised by I.G. Farbenindustrie during the Second World War in Germany to produce hydroformylation feed.

Description	Boiling range (°C)	Yield (mass %)
Dimers	60-130	15-20
Trimers	130-180	35-40
Tetramers	180-200	29
Higher olefins	200-260	16

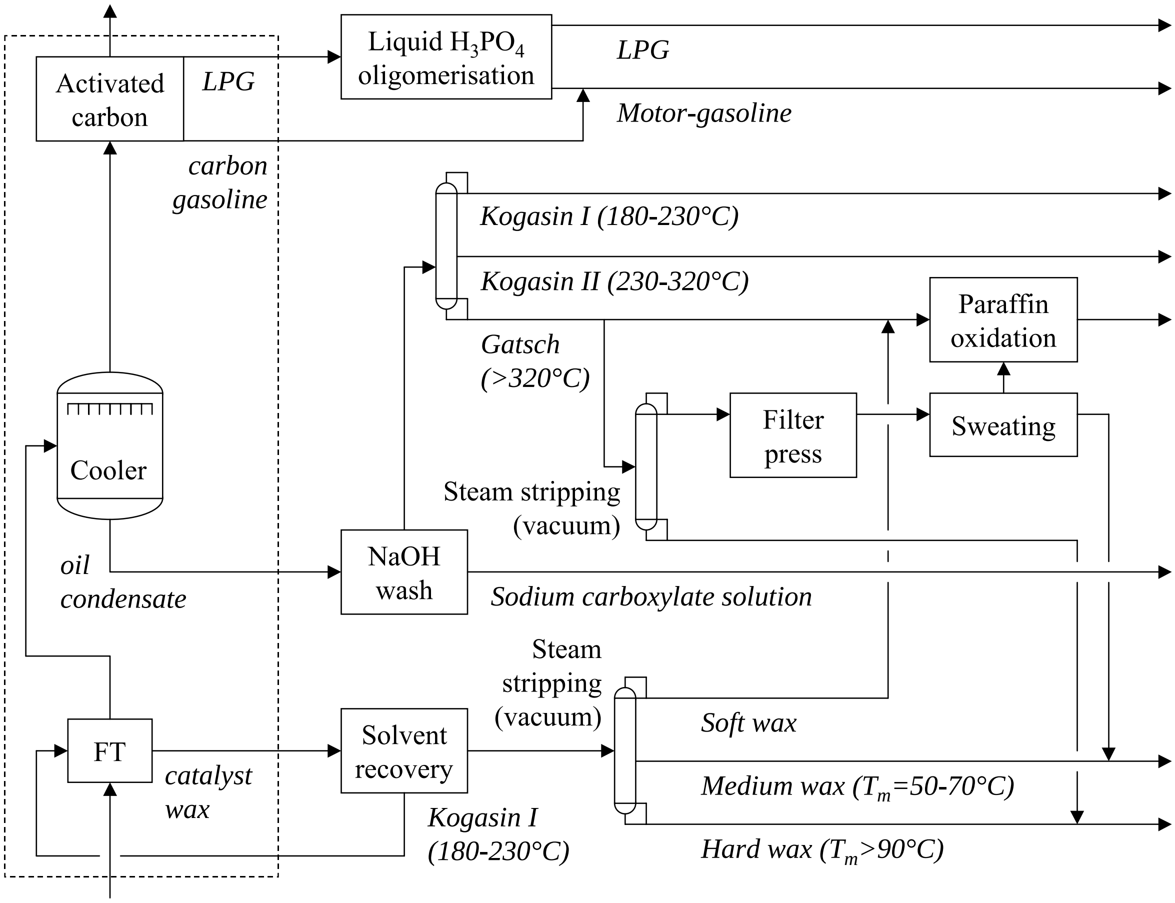

Figure 4. Generic German normal-pressure Fischer-Tropsch refinery.

The light olefins were converted by either a phosphoric acid oligomerisation, or aluminium chloride based oligomerisation processes. Liquid phosphoric acid oligomerisation was chiefly employed to produce dimers, trimers and tetramers of propylene and butenes that could be hydroformylated[f] and hydrogenated to detergent range alcohols. The method practised in Germany used a reactor consisting of three silvered tubes connected in series in a single water-cooled reactor,[g] yielding an oligomeric product in the desired range (Table 3).(9) Aluminium chloride oligomerisation was used to produce synthetic lubricants. The feed to this process was not only obtained from the LPG fraction, but also from cracking. Ruhrchemie used the Kogasin II fraction and thermally cracked it in the presence of steam at 550-600°C, before oligomerising it over $AlCl_3$ (Figure 5).(9)(10) A variation of this was practised by Établissements Kuhlmann in France starting with Fischer-Tropsch gasoline.(9)

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[f] Alcohol manufacture was typically done by the OXO process, discovered by Otto Roelen of Ruhrchemie in 1938, which is the hydroformylation of olefins with CO and H_2 to produce aldehydes.

[g] Each tube was 5 m high and had a diameter of 0.18 m. Each tube was loaded with 40 kg of acid and 70 kg of oligomer to about one third of its height. The olefinic feed was pumped through the tubes with an inlet pressure of 6 MPa and outlet pressure of 4 MPa. Reaction took place at 180-200°C and olefin conversion of 90% was typically achieved. Entrained phosphoric acid was separated from the product and recycled.

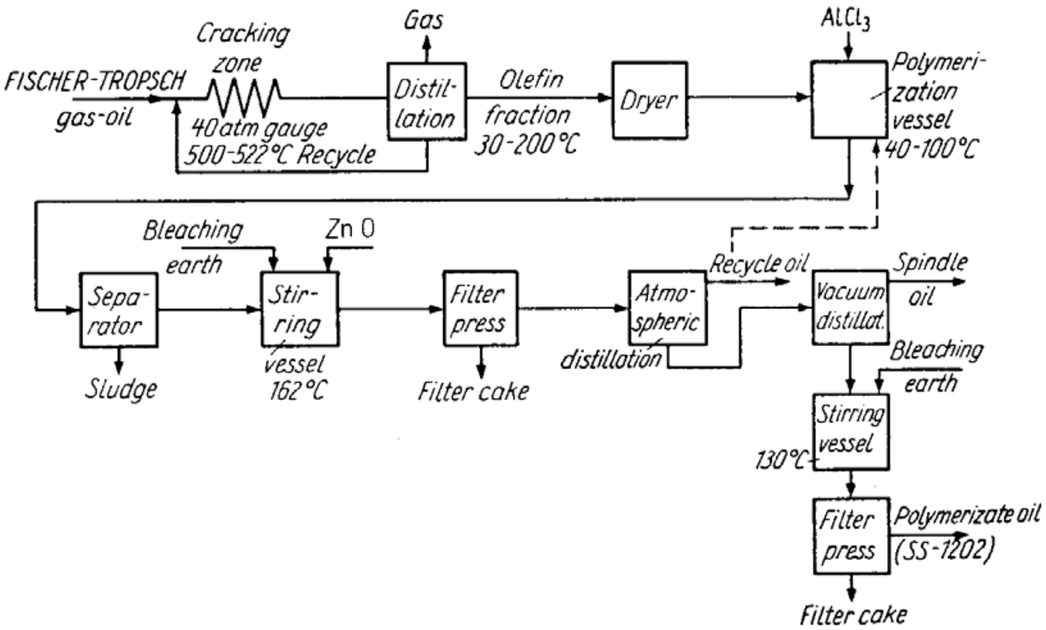

Figure 5. Cracking of Kogasin II and $AlCl_3$ oligomerisation to produce lubricating oil. (This figure has been reproduced directly from Ref.(4) and is copyright protected).

The straight run motor-gasoline from the Fischer-Tropsch process had a low octane number, with the 30-110°C cut having a MON of 67 and the 30-140°C a MON of 62.(2) Initially, in 1938, the octane value was improved by mixing it with aromatics and alcohol, but later Ruhrchemie added two True-Vapour-Phase processes[h] with gas recycle to convert the higher boiling fractions to gasoline with a much higher octane number, for example the 30-165°C fraction had a MON of 75.(11) The construction of a catalytic cracking plant to produce C_3-C_5 olefins from C_7+ Fischer-Tropsch fractions to be oligomerised to motor-gasoline (by phosphoric acid catalysis) was abandoned in mid-1944.(2) An evaluation of the products from such a process was done before the Second World War.(12)

Condensate oil contained some carboxylic acid that was removed by a caustic wash. The aqueous wash solutions contained sodium carboxylates in addition to hydrocarbons, iron[i] and other impurities.(1) The carboxylates were recovered and used for greases, soaps, etc. The acid-free organic product was distilled to produce various fractions. The Kogasin I fraction was combined with the heavy gasoline and used as diesel fuel.[j] It was a quite light diesel (155-250°C), with good cetane number (75-78) and low density (743-749 kg·m^{-3}), but according to Weil and Lane(2) it did not make a very good diesel fuel, although no specific

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[h] Thermal cracking and oligomerisation of the short chain olefins. Operating conditions of 540°C and 0.3-0.5 MPa, with a residence time of 100-200 s.

[i] Since a cobalt based Fischer-Tropsch catalyst was used, it is likely that the iron was due to acid corrosion.

[j] The motivation behind the use of heavy gasoline in the diesel is not known with certainty, but probably due to a lack of motor-gasoline octane improving technologies in the Fischer-Tropsch refinery and the need to use the molecules in the detergent range (C_{12}-C_{15}) for detergents. Ref.(2)

reasons were given.[k] A detailed analysis of the diesel fuel from the Carrières Kuhlmann FT plant at Harnes in France showed a heavier product (195-310°C) consisting of Kogasin I and Kogasin II, with a density at 20°C of 768 kg·m^{-3} and cetane number of 80.(13) The diesel contained 2% oxygenates, mostly alcohols, carbonyls and carboxylic acids, but it also contained some esters and phenolic compounds.

The Kogasin II fraction was used as feedstock for thermal cracking to make lubricating oils(14) when not used as diesel fuel. The bottom fraction from distillation (gatsch or slack wax) was either being used as feedstock for paraffin oxidation and fatty acid manufacture, or steam stripped to produce medium and hard wax products. The hard wax had a small market as ceresin wax, but in general had little use, while the medium wax could be used for candles, etc. The catalyst wax was also steam stripped to produce a soft, medium and hard wax fraction. The characteristics of these wax products have been reported.(15)(16)

3. United States technology (1940-1950's)

Subsequent to the Second World War, much technical information about the German Fischer-Tropsch technology became available in the United States. During this period Hydrocarbon Research Inc. developed an American version of the Fischer-Tropsch process, called the Hydrocol process.(17) This process used an iron based Fischer-Tropsch catalyst in a fixed fluidized bed reactor.(4) The process was piloted at Olean, New York, and led to the construction of the first commercial scale Fischer-Tropsch plant in the USA at Brownsville, Texas by the Carthage Hydrocol Co. This plant was in operation during the period 1951-1957 and was shut down mainly due to economical reasons.(20) A second plant was planned by Standolind Oil and Gas Co. for Hugoton, Kansas, but was never built.(21)(22) Around the same time Philips Petroleum Co. also started development of an iron based fluidised bed Fischer-Tropsch process, which was piloted at their research facilities in Bartlesville, Oklahoma, but this process was never commercialised.(23)(24) Various other companies also had research programmes and some are still active in the field of Fischer-Tropsch research.(8)

Apart from the commercial interest in Fischer-Tropsch technology in the United States, the strategic value of this technology was recognised at government level. Prior to the Second World War, Fischer-Tropsch research was funded by the United States government.

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[k] It is speculated that the evaluation was performed on a comparative basis without compensating for the low density and viscosity of the Fischer-Tropsch product. This would result in lower power output, as was indeed reported elsewhere. Ref.(6)

This process was accelerated when the U.S. Bureau of Mines was tasked by the United States Congress[l] to find an alternative to crude oil as source for transportation fuel.(22) Fischer-Tropsch and coal liquefaction were investigated in parallel, since it was unclear which of these technologies were the most economical. Although demonstration scale operation was terminated in 1953, after substantial new oil reserves were discovered in the United States, Canada and Middle East, pilot plant studies were continued at the Pittsburgh Energy Technology Centre.(25) Work on Fischer-Tropsch has been continuously sponsored by the United States Department of Energy.

3.1. Hydrocol Fischer-Tropsch synthesis

The Hydrocol plant made use of natural gas as feedstock for the production of synthesis gas by partial oxidation of the methane with oxygen.[m] The basic flow diagram of the Hydrocol process is given in Figure 6.(17) The first step is separation of the condensable liquids from the natural gas. This is followed by synthesis gas production. The synthesis gas was not purified after production, but was directly used for Fischer-Tropsch synthesis, despite the presence of sulphur compounds in the synthesis gas. The omission of a gas purification step was nevertheless possible, because the design of the Fischer-Tropsch reactor allowed the replacement of deactivated Fischer-Tropsch catalyst on-stream,[n] not because of the low sulphur content of the natural gas.

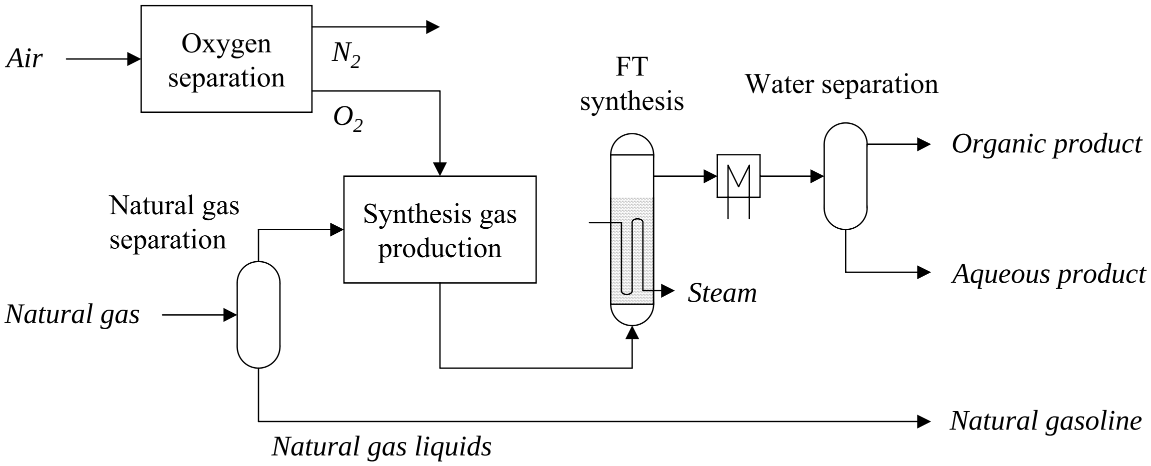

Figure 6. Flow diagram of the Hydrocol synthesis section.

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[l] On 5 April 1944 the "Synthetic Liquids Fuels Act" was passed by the United States Congress.
[m] The oxygen plant that was erected, was the largest in the world at that time.
[n] This ability proved to be more theoretical than practical.

The Fischer-Tropsch catalyst used in the Hydrocol process was a fused iron catalyst that was also used for ammonia synthesis, consisting of 97% Fe_3O_4 (magnetite), 2.5% Al_2O_3 and 0.5% K_2O. It was later replaced with a natural magnetite containing 0.5% K_2O. The catalyst was ground to a fine powder (0.045-0.45 mm) and was completely reduced at 350-460°C in hydrogen before use.$^{(4)}$ The synthesis gas was produced from non-catalytic combustion of natural gas with oxygen to produce a synthesis gas with H_2:CO ratio of approximately 2:1.$^{(18)}$ The Hydrocol plant used two 5 m diameter synthesis reactors.$^{(19)}$ The synthesis reactors were of a two phase fixed fluidised bed design with a heat exchanger suspended in the bed to control the temperature by producing 2.1-2.8 MPa steam. The surface of the fluidised catalyst bed remained fairly smooth during operation, although local eruption of bubbles could be seen. Little catalyst was carried away with the product gas.. The reactor was operated in the range 305-345°C and 2.8-4.5 MPa,[o] with a linear gas velocity of 0.2 $m \cdot s^{-1}$.$^{(4)(20)}$. This technology is therefore classified as a high temperature Fischer-Tropsch (HTFT) process.

The product from Hydrocol synthesis consisted mainly of motor-gasoline range products (Table 4).$^{(18)}$ The production of heavy products had to be avoided, since they would cause product condensation, catalyst agglomeration and then bed slumping in the synthesis reactor. This is a general restriction imposed on the α-value of Fischer-Tropsch catalysts used in technologies making use of fluidised bed reactors.

Table 4. Composition of the synthesis product from the Hydrocol process.

Description	Mass %	Olefinicity (%)
Liquid petroleum gas, LPG (C_3 and C_4)	32	82
Naphtha (C_5-204°C)	56	85-90
Distillate	8	75-85
Residue	4	-

The hydrocarbons produced by the Hydrocol process were rich in linear α-olefins and in general the products had a low degree of branching (Table 5),$^{(4)(18)}$ with the methyl branched products being mainly 2-methyl isomers.$^{(26)}$ In addition to the hydrocarbon products, oxygenates were also produced. The water-soluble oxygenates were mainly ethanol and acetic acid, with lesser amounts of acetone, acetaldehyde and higher alcohols

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[o] Conversion of about 90% was achieved, with about 0.15 kg C_3+ hydrocarbons per 1 m^3 of synthesis gas being produced. The overall reactor productivity was around 180 $kg \cdot h^{-1}$ per m^3 of catalyst.

being produced. With increasing carbon number, more oxygenates are found in the organic phase (Table 6).(4)(27) Since it is an HTFT process, aromatics were also produced.

Table 5. Degree of branching in the products from the Hydrocol process.

Carbon number	Linear	Methyl branched	Dimethyl branched	Cyclic
C_4	89.4	10.6	-	0.0
C_5	80.9	18.8	0.0	0.3
C_6	75.9	20.0	0.4	3.7
C_7	60.2	29.3	1.7	8.8
C_8	55.4	36.6	2.4	5.6

Table 6. Distribution of compound classes in the oil fraction of Hydrocol syncrude (mass %).

Carbon number	Distillation range (°C)	Paraffins (%)	Olefins (%)	Aromatics (%)	Oxygenates (%) ‡
C_3		20.2	79.8	-	-
C_4		15.5	84.5	-	-
C_5	15-40	15.4	81.8	0	2.8
C_6	40-75	13.2	80	0.2	6.6
C_7	75-104	10.5	80.2	2.1	7.2
C_8	104-138	9.6	76.2	6	8.2
C_9	138-162	1.8	79	6.2	13
C_{10}	162-187	6	79.3	7.2	7.5
C_{11}	187-200	9.3	74	5.8	10.9
C_{12}	200-220	5.4	76.5	3.6	14.5

‡ Oxygenates were calculated by difference.

3.2. Refining of Hydrocol syncrude

The aim of the Hydrocol process was to produce high-octane motor-gasoline with a better than 80% yield of the syncrude. This is an important statement of intent, since it requires the refining steps to produce a product that could meet the octane requirements of the 1950's after the addition of tetraethyl lead (TEL). Apart from normal oil product separation, the refinery had to include conversion and separation steps that addressed issues specific to the Hydrocol process,(2) namely:

a) Removal of the unwanted oxygenates from the organic product and especially the carboxylic acids that were known to cause problems.(28)

b) Increase the octane number of the straight run syncrude (RON=62, MON=68)(18) to a higher value that could be upgraded to meet an 80 MON specification by TEL addition.[p]

c) Convert the gaseous olefins (C_3-C_4) to liquid products, since it constituted about one third of the product from Hydrocol synthesis.

d) Recover the alcohols and other valuable oxygenates dissolved in the aqueous product to be sold as chemicals.(26)

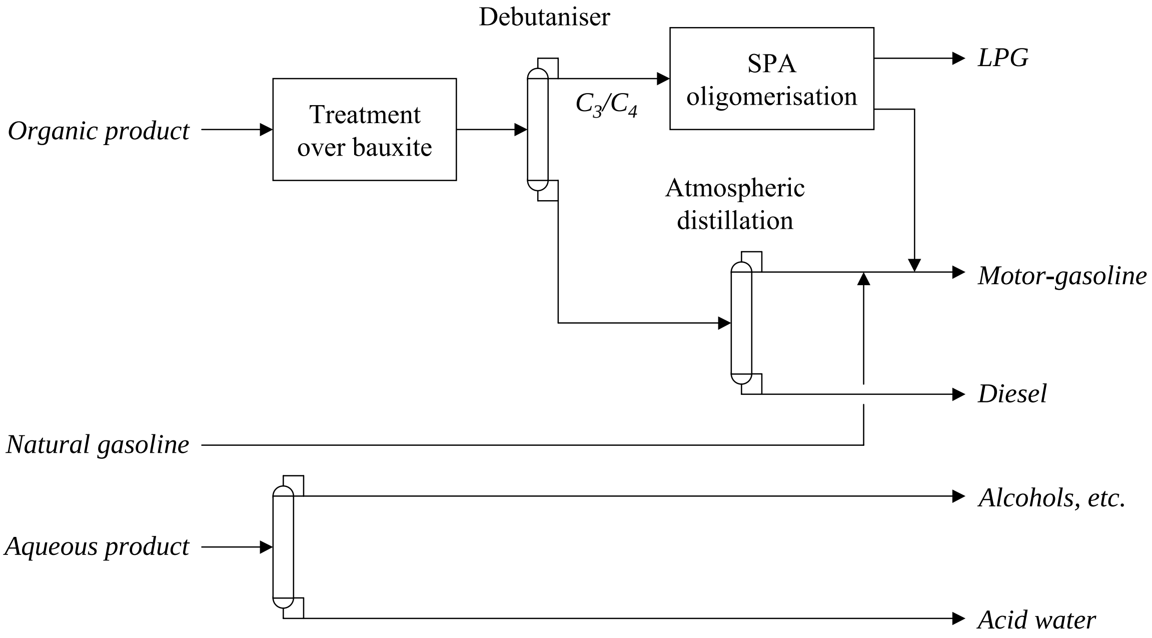

Figure 7. Flow diagram of the HTFT Hydrocol refinery.

The flow diagram of the Hydrocol refinery is shown in Figure 7. The first organic phase processing step involved oxygenate removal over bauxite at a temperature around 400°C.(18)(28) Bauxite is a natural silica-alumina consisting of 30-75% Al_2O_3, 2-9% SiO_2, 3-25% Fe_2O_3, 1-3% TiO_2 and 9-31% H_2O.(29) This bauxite treatment step was a commercial process, called the Perco-process, which was used as a sulphur removal step in oil refineries.(30) It was also used for oxygenate removal from the syncrude produced in the Philips Petroleum HTFT pilot plant.(24) Very good results were obtained with this process, since it not only removed the oxygenates, but also increased the octane number of the naphtha (RON=87 and MON=76).[q] The improvement in octane number is mainly due to

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[p] With the addition of 3 ml TEL per gallon of straight run Hydrocol syncrude, the RON=84 and MON=74.
[q] With the addition of 1 ml TEL per gallon of bauxite treated Hydrocol syncrude, the RON=93 and MON=80.

double bond isomerisation of the α-olefins to internal olefins and a more detailed description of the reactions involved in this process is given elsewhere.(31)

The C_3-C_4 olefins were converted to polymer gasoline over a solid phosphoric acid catalyst in the UOP CatPoly process(32) at 205°C, 3.5 MPa and LHSV of 1.15 h^{-1}.(18) The unhydrogenated motor-gasoline from such a process is fairly insensitive to the feed material and operating conditions used(33) and had a RON=95 and MON=82.(18)

The Hydrocol refinery also included cross-platform integration, since the natural gas derived naphtha (natural gasoline) was blended with the Fischer-Tropsch derived synthetic motor-gasoline. The distillate fraction was not upgraded any further and reportedly had a cetane number of 45-50 and pour point of less than –15°C.(2) It was nevertheless shown that this product could be upgraded by hydrogenation to have a cetane number of 71 and a pour point of –1°C.(34)

The upgrading of the aqueous product was investigated, but it was soon realised that many of the carbonyls and alcohols formed azeotropes on distillation.(26) The chemical potential of HTFT was therefore realised in principle, but required extensive investigations to be realised in practise, mainly due to the absence of binary and ternary phase diagrams.

4. Sasol 1 technology (1950's)

The Fischer-Tropsch work of P. C. Keith[r] of Hydrocarbon Research Inc., which formed the basis for the Hydrocol process, also interested Anglovaal. In 1945 Anglovaal officially informed the South African government of its intentions to build a coal-to-liquids plant in South Africa. Although a licence to produce synthetic fuels was officially given to Anglovaal in 1949, it became apparent that a venture of this magnitude would be difficult to finance without government support. It was also realised that such a venture was in national interest. This led to the formation of a new company called Sasol in 1950.[s]

During this period the technology selection for the synthetic fuels process was already under way. Five proposals were considered, of which only the proposals of the Arbeitsgemeinschaft Ruhrchemie-Lurgi (Arge) in Germany and Kellogg in the United States were found to be technically sound enough. It was realised that the HTFT Kellogg proposal would be much cheaper to implement, but that the LTFT Arge proposal brought all the

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[r] P. C. Kieth originally worked for M. W. Kellogg before forming the Hydrocarbon Research Inc. company and the Hydrocol process was a variant of the HTFT Kellogg technology.

German commercial experience to the table and the latter was therefore a much safer option. Eventually both proposals were accepted and Sasol 1 was constructed using two thirds American and one third German technology. Initially it was thought to run the processes in parallel, but separately, but in order to exploit the synergism between the HTFT Kellogg and LTFT Arge technologies, the two processes were integrated.(35)

Construction of the Sasol 1 facility started in the middle of 1952 at the place now called Sasolburg, which is about 100 km south of Johannesburg. Commissioning of the air separation plant, power generation plant and Lurgi gasifiers started in 1954, but the synthesis section and refinery were only commissioned in 1955.[t] Although the subsequent discussion will deal primarily with the original Sasol 1 design, it is noteworthy that some of the original units in the Sasol 1 facility are still operational more than 50 years later.

4.1. Kellogg Fischer-Tropsch synthesis

The Kellogg Synthol[u],(36) HTFT design made use of a fused iron catalyst that was operated in a circulating fluidised bed (CFB) reactor (Figure 8). These reactors had been developed by

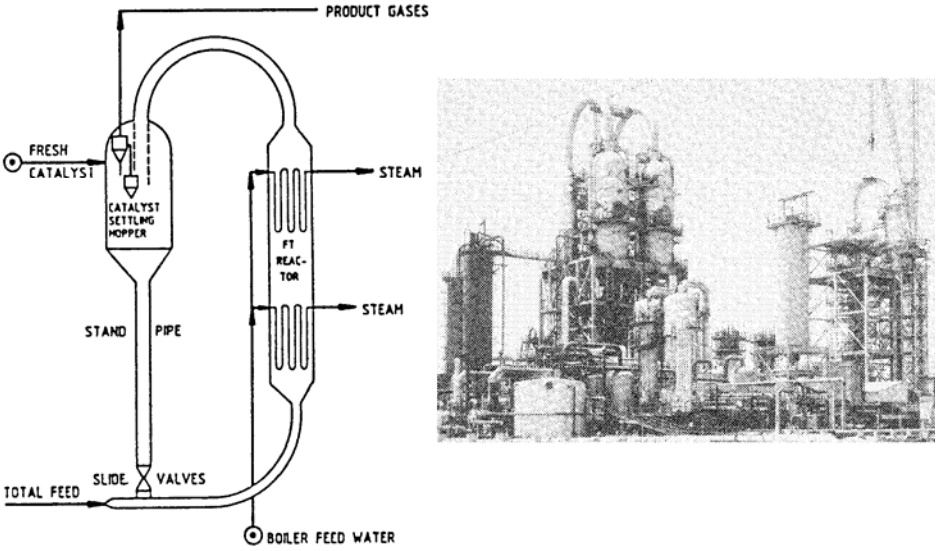

Figure 8. Kellogg circulating fluidised bed (CFB) reactors at Sasol 1. (These figures have been reproduced directly from Refs.(37) and (35), and are copyright protected).

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[s] On 26 September 1950 the "Suid-Afrikaanse Steenkool, Olie- en Gaskorporasie Beperk" became a public company, with Dr. P. E. Rousseau as managing director.

[t] The Kellogg HTFT section was commissioned on 23 August 1955 and the Arge LTFT section on 26 September of the same year. By 1 November 1955 the refinery already produced petrol for the local market.

[u] The HTFT circulating fluidised bed (CFB) reactor technology that was installed in Sasol 1 will be referred to as "Kellogg" to differentiate it from the modified "Synthol" CFB reactor technology developed by Sasol in the 1970's. It should be noted that the word "Synthol" has been in colloquial use since the 1940's. Ref.(2)

Kellogg and had only been tested on a 0.1 m diameter pilot plant scale. This design was scaled up to 2.3 m diameter, 46 m high units for use at the Sasol 1 facility(19)(38)(39) and each Kellogg reactor had a designed production capacity of 2000 bpd.(40) Typical operating conditions proposed by Kellogg for Fischer-Tropsch synthesis were 290-340°C and 1.9 MPa.(41) One of the design advantages cited for the use of a CFB reactor was the ability to change catalyst while the unit is in production.[v],(41) Although this was the design intent, the Kellogg reactor technology did not live up to this promise and the operating procedure was eventually changed to campaign mode operation to make the technology work.(35) The run length was limited by carbon build-up on the catalyst and each run lasted about 50 days before the reactor had to be unloaded, cleaned and fresh catalyst was loaded.(42) This placed a serious constraint on equipment availability and in 1960 a third CFB reactor was installed.

Although the Kellogg CFB reactors proved to be flexible in terms of dealing with fluctuations in flow rate, composition, temperature and pressure of the synthesis gas, the design had serious operational difficulties associated with the catalyst circulation rate. There was a small operating window that allowed stable performance. At high catalyst flow rates the intercooler tubes of the reactor were plugged, resulting in a loss of heat transfer and increased erosion in the tubes that were not plugged. At low catalyst flow rates bridging of the catalyst in the standpipe occurred, causing an interruption in production.(43)

The process used a fused iron catalyst made from a magnetite ore (Allenwood ore),(44) similar to that for Hydrocol. However, the Hydrocol operation was a fixed fluidised bed, not a CFB and the fused catalyst supplied by Kellogg was not without its own problems.(35) During CFB operation the catalyst is turbulently transported at linear velocities of several meters per second. The mechanical strength of the catalyst is therefore of paramount importance. If the catalyst is not robust enough, catalyst attrition will result in excessive fines formation that would cause increased catalyst loss, as well as a change in the fluidisation behaviour.(42)(45)

The Sasol Research department was established in 1957 and spent much time in understanding the behaviour and requirements of fused iron Fischer-Tropsch catalysts. The suitability of local sources of magnetite was investigated and mill scale from the nearby Vanderbijlpark Iscor steelworks was used to replace the imported Allenwood ore. The preparation of fused iron catalyst and the influence of chemical promoters (e.g. K_2O) and structural promoters (e.g. MgO, Al_2O_3) have been described in literature.(38)(42)(44) After

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[v] The catalyst recirculation rate was estimated at more than 4000 $t{\cdot}h^{-1}$, with a loss due to fines of about 0.0015%.

production and milling of the catalyst to the correct particle size distribution, it is reduced with hydrogen in a fixed bed reactor at 350-450°C over a period of 2 days. The unreduced catalyst has a surface area of only 1 $m^2 \cdot g^{-1}$, but on reduction this could be increased from 2 to 30 $m^2 \cdot g^{-1}$, depending on the type of promoters that were used.

The product distribution from the Kellogg HTFT synthesis is given in Table 7.(46) When this is expressed in terms of only C_3+ hydrocarbons, it amounts to 32% C_3-C_4 LPG, 53% naphtha, 8% diesel and 7% residue. As expected, the Kellogg syncrude is very similar to that of Hydrocol syncrude (Table 4). The product is quite olefinic and being an HTFT technology, the syncrude contains aromatics too (Table 8).(46) The oxygenates partition between the aqueous and organic product phases. Most of the lighter oxygenates end up in the aqueous product and are classified as either non-acid chemicals, or as carboxylic acids (Table 9).(40) The non-acid chemicals are typically aldehydes, ketones and alcohols. It should be noted that the product composition in Table 7 is not exactly the same as that obtained with present fused iron catalysts.[w]

Table 7. Fischer-Tropsch syncrude composition from the Sasol 1 HTFT Kellogg circulating fluidised bed reactors.

Compound	Mass %
Methane	10
Ethylene	4
Ethane	6
Propylene	12
Propane	2
Butenes	8
Butanes	1
C_5-C_{12}	39
C_{13}-C_{18}	5
C_{19}-C_{21}	1
C_{22}-C_{30}	3
C_{31} and heavier products	2
Non-acid chemicals	6
Carboxylic acids	1

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[w] The Kellogg CFB reactors at Sasol 1 has been decommissioned in the 1990's, but fused iron catalysts are used in the more modern versions of this technology too.

Table 8. Compound classes in Kellogg HTFT syncrude.

Product fraction	Paraffins (%) ‡	Olefins (%)	Aromatics (%)	Alcohols (%)	Carbonyls (%)
C_5-C_{10}	13	70	5	6	6
C_{11}-C_{14}	15	60	15	5	5

‡ The *n*-paraffin content of the paraffin fractions are 55% (C_5-C_{10}) and 60% (C_{11}-C_{14}).

Table 9. Non acid chemicals and carboxylic acids in the aqueous product of Kellogg HTFT synthesis.

Compound	Mass %
Non-acid chemicals ‡	
Methanol	1.4
Ethanol	55.6
1-Propanol	12.8
2-Propanol	3.0
1-Butanol	4.2
2-Butanol	0.8
2-Methylpropanol	4.2
1-Pentanol	1.2
2-Pentanol	0.1
Other alcohols	0.6
Acetaldehyde	3.0
Propionaldehyde	1.0
Butyraldehyde	0.6
Pentanal	0.2
Acetone	10.6
Butanone (MEK)	3.0
Pentanones	0.8
Carboxylic acids	
Acetic acid	70
Propionic acid	16
Butyric acid	9
Other acids	5

‡ The non-acid chemical composition in the source document does not add up to 100%.

4.2. Arge Fischer-Tropsch synthesis

The Arge LTFT design used a precipitated iron catalyst and synthesis is performed in a multi-tubular fixed bed reactor (Figure 9). Five Arge reactors were installed in the Sasol 1 plant with a design capacity of 550 bpd per reactor.[x],(40) Every Arge reactor contains 2052 tubes and each tube is 12 m long with a 50 mm internal diameter.(41)(47)(48) The reaction temperature is controlled and maintained almost isothermally by regulating the pressure at which the boiler feed-water is allowed to evaporate on the outside of the reactor tubes. Typical operating conditions of Fischer-Tropsch synthesis during start up are 200-230°C and a gas inlet pressure of 2.5-2.7 MPa. During operation the temperature is increased by 25-30°C before end-of-run conditions is reached.(41) The process has been designed to use a H_2:CO ratio of 1.7-1.8:1.(41)

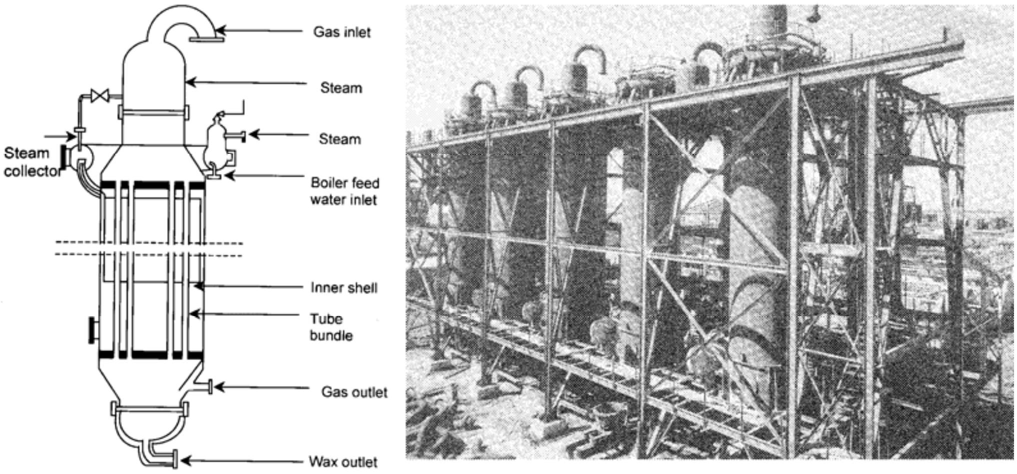

Figure 9. Arge multi-tubular fixed bed reactors at Sasol 1. (These figures have been reproduced directly from Refs.(19) and (35), and are copyright protected).

The precipitated iron catalyst is produced on site by dissolving iron in nitric acid and precipitating it by adding sodium carbonate. The potassium promoter is added before drying and extrusion to produce extrudates (about 3 mm diameter and 10 mm long). The catalyst is reduced at around 220°C and is coated in wax to prevent re-oxidation before being loaded in the reactor. Commissioning of the reactor is conducted under a hydrogen atmosphere to prevent the formation of iron carbonyl, which is volatile.(44)

The Arge LTFT syncrude composition (Table 10)(46) is typical of a high α-value Fischer-Tropsch product. The product contains less olefins and no aromatics, because it is

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[x] Arge reactor production capacity is approximately 18 000 tons per year per reactor. Ref.(40)

LTFT technology (Table 11).(46) The oxygenates are rich in alcohols, with little carboxylic acids and ketones being produced, as is expected from low temperature operation. Although the Arge reactors at Sasol 1 are still in production, the catalyst has been improved over the years and the precipitated iron catalyst presently used has a higher α-value.

Table 10. Syncrude composition from Arge LTFT synthesis.

Compound	Mass %
Methane	5
Ethylene	0.2
Ethane	2.4
Propylene	2
Propane	2.8
Butenes	3
Butanes	2.2
C_5-C_{12}	22.5
C_{13}-C_{18}	15
C_{19}-C_{21}	6
C_{22}-C_{30} (medium wax)	17
C_{31} and heavier products (hard wax)	18
Non-acid chemicals	3.5
Carboxylic acids	0.4

Table 11. Compound classes in Arge LTFT syncrude.

Product fraction	Paraffins (%) ‡	Olefins (%)	Aromatics (%)	Alcohols (%)	Carbonyls (%)
C_5-C_{12}	53	40	0	6	1
C_{13}-C_{18}	65	28	0	6	1

‡ The *n*-paraffin content of the paraffin fractions are 95% (C_5-C_{12}) and 93% (C_{13}-C_{18}).

4.3. Sasol 1 gas loop

The Sasol 1 plant has been designed to use coal as feed material. The coal is gasified in nine Lurgi high-pressure moving bed gasifiers in the presence of oxygen and steam. The temperature is kept low enough to prevent the ash from fusing to form clinker(49) and the gasifiers were designed to operate with coal having a high ash content.[y] The gasifiers were operated in the range 700-850°C reaction temperature, 300-650°C product gas outlet temperature and 2-3 MPa pressure.(50) When the Sasol 1 gasifiers were built, they were the largest in the world. To distinguish the original design from improved versions, these gasifiers were called Lurgi Mark I gasifiers.[z]

In terms of gasifier design it would be an over-simplification to classify gasifiers only by operating temperature, but in terms of refining this is a useful classification. The main difference from a refining perspective between low and high temperature gasification is that low temperature gasifiers, like those installed at Sasol 1, co-produces coal pyrolysis products with the raw synthesis gas. These products must be separated from the raw synthesis gas (Figure 10).(50) Separation of the neutral oil, gas liquor and tar is based on liquid density differences. The liquid product also contains dissolved light hydrocarbons, ammonia and carbon dioxide. The de-gassed coal pyrolysis product is rich in aromatics, phenols, tar acids and creosotes and can be refined to produce fuels and chemicals.

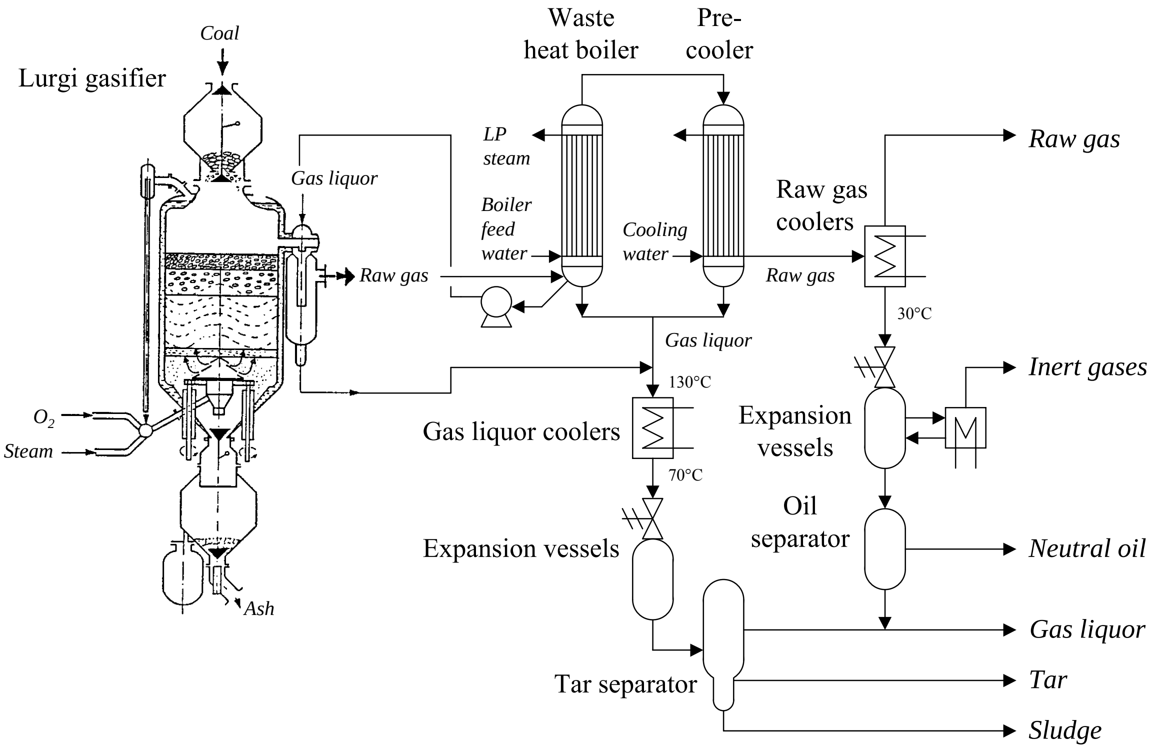

Figure 10. Low temperature Lurgi gasification and coal pyrolysis product separation at Sasol 1.

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[y] Coal samples from Coalbrook with an ash content of 30% were successfully tested in Germany in 1951 using Lurgi gasifiers.

[z] After commissioning of the gasifiers, only 80% of the design capacity could be achieved. Design capacity on the Lurgi Mark I gasifiers were only achieved at the end of 1957, while unit availability was only 78% (design unit availability was 89%).

The raw gas contains the synthesis gas components, CO and H_2, as well as significant quantities of methane, CO_2, H_2S and N_2 (the oxygen plant delivered O_2 at 99.1% purity to the gasifiers).(49) Since H_2S and organic sulphur containing compounds are Fischer-Tropsch catalyst poisons, these compounds had to be removed from the raw gas. This was done in a Rectisol unit, which uses methanol under pressure at cryogenic conditions to remove all sulphur containing compounds, in addition to removing about 98% of the CO_2.(49) The Rectisol process consists of three steps (Figure 11):(51) a) a pre-wash that removes hydrocarbons, oxygenates and organic sulphur compounds from the gas; b) a main wash that liquefies the CO_2 and removes most of the COS and CS_2 in addition to 95% of the CO_2; and c) a fine wash that removes the remaining sulphur components (COS and H_2S) in addition to some further CO_2 removal. The pure gas that contains at most 0.04 $mg{\cdot}m_n^{-3}$ sulphur, is then sent to the Fischer-Tropsch synthesis reactors. The Rectisol process was a new process in 1955(52) and the unit at Sasol 1 was the first commercial installation. It consisted of three identical scrubbing trains followed by a common regeneration section.(49) A more detailed description of the Rectisol process can be found elsewhere.(53)(54)

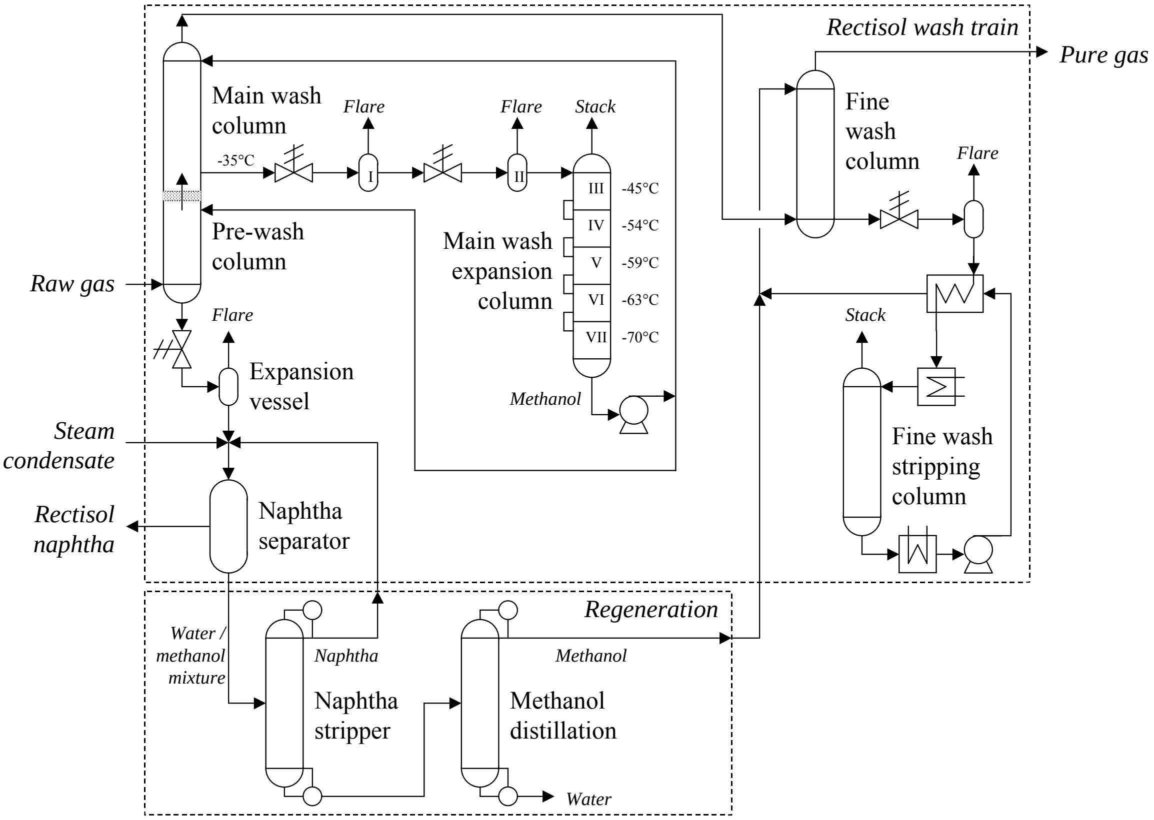

Figure 11. Rectisol process flow diagram.

The original Sasol 1 gas loop design is especially interesting, because it combined LTFT and HTFT synthesis reactors operating at different temperatures and pressures, with different H_2:CO ratios into a single gas loop (Figure 12).(41)(49) The Arge LTFT reactors required a higher pressure and had lower synthesis gas conversion than the Kellogg HTFT reactors. The tail gas from Arge synthesis was partly recycled to the Arge reactors to ensure the correct H_2:CO ratio (LTFT internal recycle), and partly sent to the gas reformer in the HTFT gas loop to convert the methane to synthesis gas and increase overall conversion. The tail gas from Kellogg synthesis was partly recycled to the Kellogg reactors (HTFT internal recycle) and partly sent to the gas reformer (HTFT external recycle). In this way the high CO conversion during HTFT synthesis was used to convert the unreacted CO from LTFT synthesis.

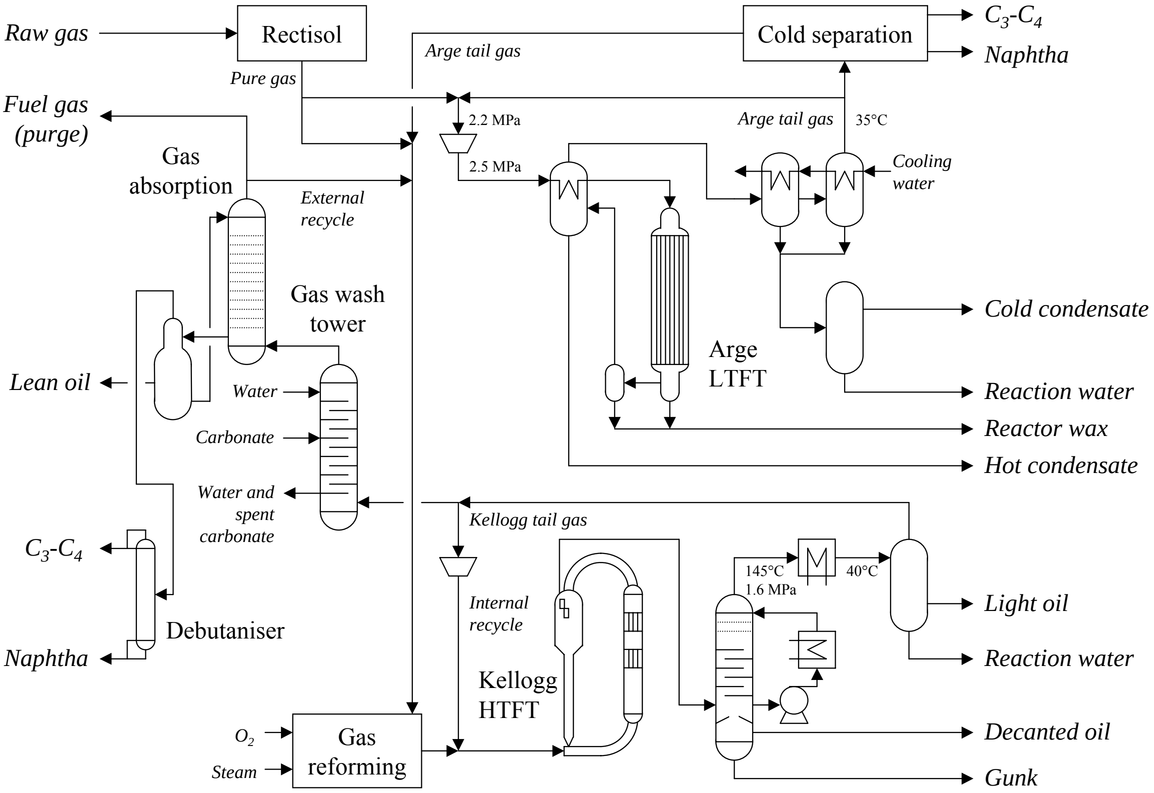

Figure 12. The Sasol 1 gas loop.

The flowscheme of the original Sasol 1 gas loop is clearly very complex. The feed material being sent to the refinery originates from gasification (coal pyrolysis products), Rectisol (aromatic naphtha) and the two types of syncrude produced during HTFT and LTFT synthesis.

4.4. Sasol 1 refinery

The original Sasol 1 refinery consisted of four different refineries, namely tar work-up, Kellogg oil work-up, Arge oil work-up and chemical work-up (Figure 13). Tar work-up refined the products from low temperature coal pyrolysis that were separated from the raw synthesis gas in the gasification section, as well as during gas purification in Rectisol. Such a tar refinery can also be found in coking plants or any other process that involves coal pyrolysis.[aa] The tar work-up section is consequently not really part of the Fischer-Tropsch refinery, but a by-product of the gasification technology that was selected. Upgrading of coal liquids is a specialised topic in its own right(55) and will only be superficially treated for the sake of completeness.

The Kellogg, Arge and chemical work-up sections together constitute the Fischer-Tropsch refinery. It is interesting that the design had very little refinery integration, apart from common aqueous product work-up and transfer of the C_3-C_4 fraction from Arge oil work-up to Kellogg oil work-up. This is in marked contrast to the approach that was followed during the gas loop integration.

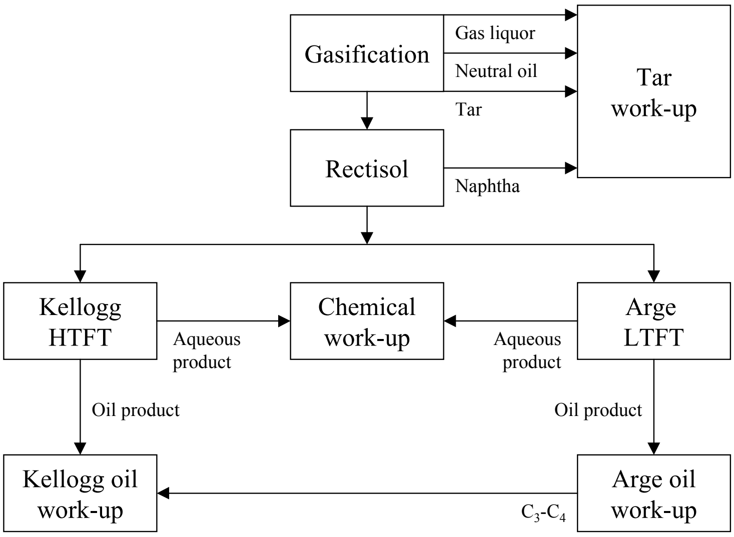

Figure 13. Sasol 1 refinery showing the feed origin for the various work-up sections.

[aa] Steel manufacturers may also have an associated tar refinery to work-up the products from their coking plant. Refining of these products has much more in common with direct coal liquefaction than with Fischer-Tropsch.

4.4.1. Sasol 1 tar work-up

The coal pyrolysis products are rich in aromatic and phenolic material. The basic Sasol 1 tar refinery flowscheme is shown in Figure 14. The gas liquor had an average concentration of 0.85% dissolved ammonia and 0.18% tar acids (phenolics). In the Phenosolvan process, the phenolic material is selectively extracted with butyl acetate at a pH of 8.5 to produce a crude phenol containing 40% phenol, 30% cresols, 7% xylenols and 23% higher boiling tar acids.(56) The ammonia was steam stripped from the phenol-lean gas liquor and converted into ammonium sulphate fertiliser.

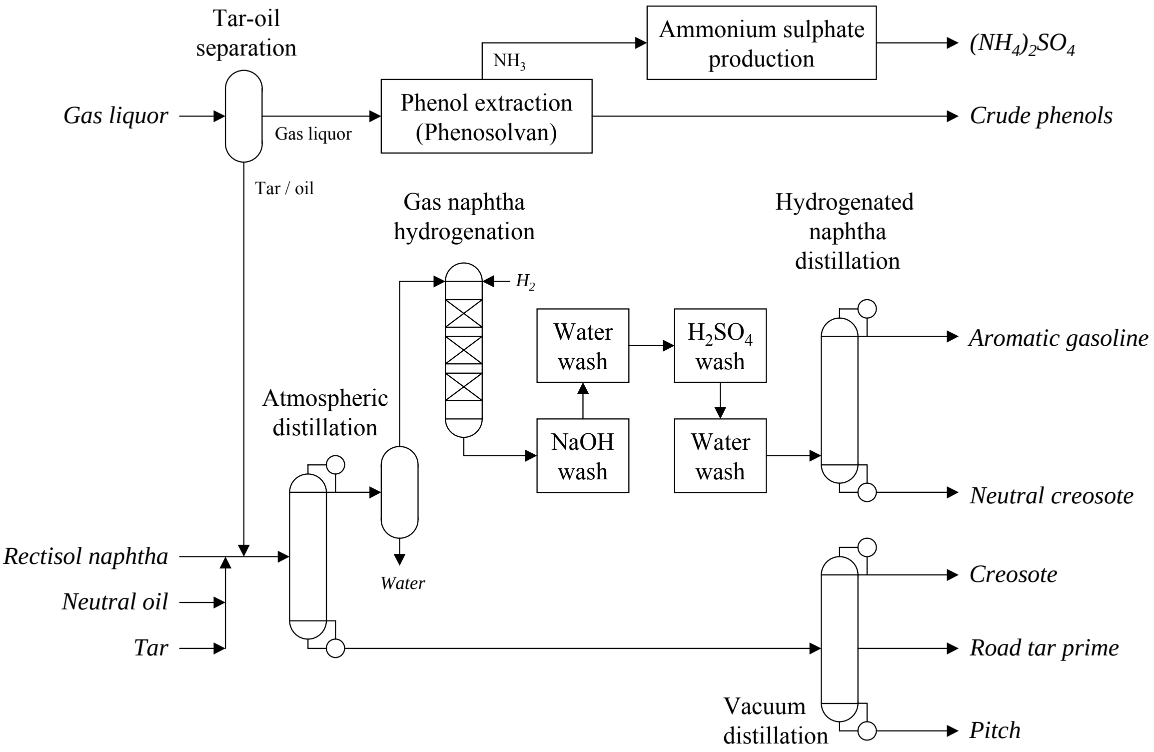

Figure 14. Sasol 1 tar work-up section.

The naphtha fraction from distillation of the Rectisol naphtha, neutral oil and tar, has been hydrogenated in a fixed bed reactor at 315-370°C and 5 MPa to remove gum forming substances and phenols, as well as to removed sulphur as H_2S. The hydrogenated product is cleaned by alkali and acid washing, before being distilled. Although only the fractionation scheme for aromatic motor-gasoline has been shown, the hydrogenated naphtha can also be fractionated in benzene, toluene, xylene, neutral oil and heavy naphtha fractions for the solvent market.(56) Most products from the tar refinery can in principle be sold as chemicals.

4.4.2. Sasol 1 Kellogg oil work-up

The HTFT Kellogg product refinery consisted of two conversion units, namely a clay-treater and a catalytic polymerisation unit (Figure 15).(57) The clay-treater used a silica-alumina acid-catalyst[bb] operated at 425°C to remove oxygenates and to improve the octane number of the α-olefin rich Kellogg syncrude by double bond isomerisation. In this respect it has a very similar function to the Bauxite treatment unit used in the Hydrocol process, but due to the more acidic nature of the catalyst and higher operating temperature, it also resulted in catalytic cracking of the feed. The clay-treater produced cracked gas that was routed to the feed from the gas absorber with the product from the gas wash tower (Figure 12), where the C_3-C_4 fraction was recovered and returned to the Kellogg work-up section.

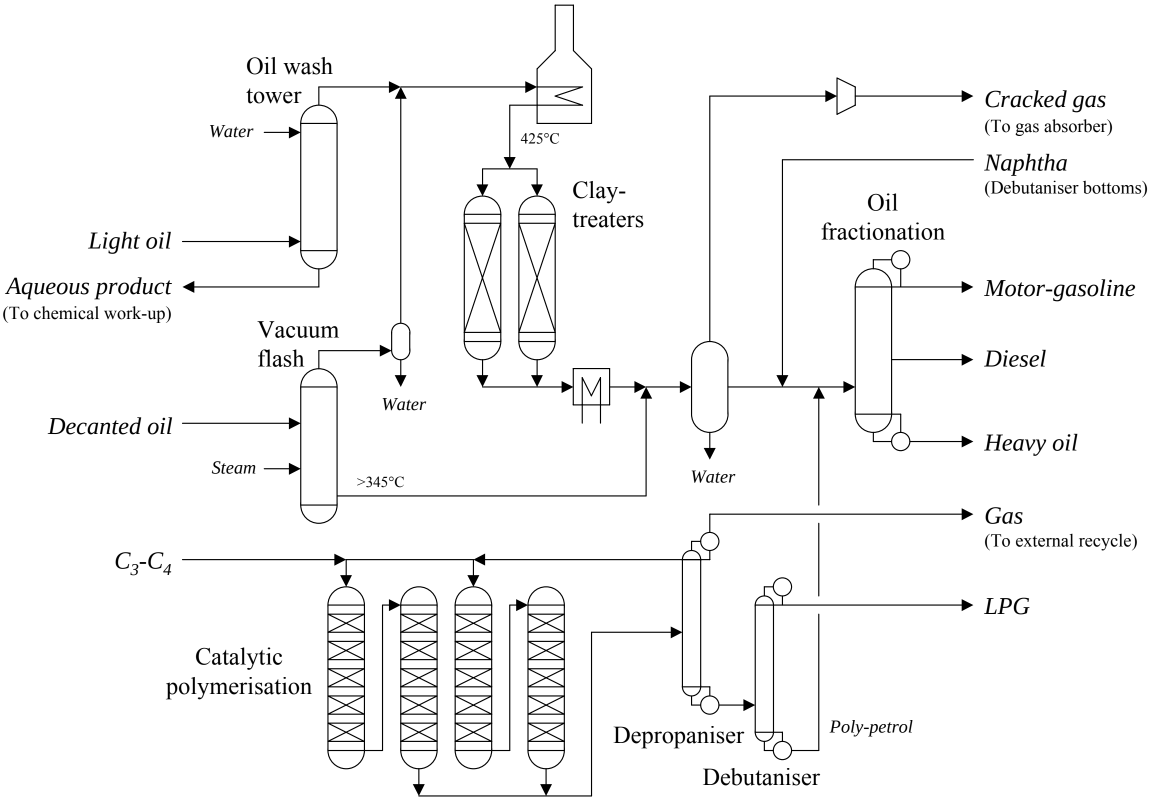

Figure 15. Sasol 1 Kellogg work-up section.

All C_3-C_4 molecules in the Sasol 1 plant were routed to the catalytic polymerisation unit, which oligomerised the gas that contained 60-70% olefins to produce a high octane olefinic motor-gasoline and some distillate. The olefin lean product gas (propane and butane rich) was used as fuel gas in the factory or sold as LPG. The oligomerisation technology

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[bb] The acidic clay was likely to be acidified montmorillonite, $H_x.aH_2O(Al_{4-x},Mg_x)^{oct}(Si_8)^{tet}O_{20}(OH)_4$, or beidellite, $H_x.aH_2O(Al_4)^{oct}(Si_{8-x}Al_x)^{tet}O_{20}(OH)_4$, which are naturally occurring zeolites. Ref.(58)

originally selected for the Sasol 1 refinery was that of the Polymer Corporation, which employed a copper pyrophosphate and charcoal catalyst.[cc],(59)(60)(61)(62) There were four reactors, each 1.2 m in diameter and 7.6 m high, containing five catalyst beds with inter-stage quench capability.[dd] Part of the feed was compressed to 6-7 MPa and pre-heated to 220°C before being introduced to the reactors, while the remainder of the feed was used as reactive inter-stage quenches. The reactors were configured to operate as a pair of two reactors in series. When fresh catalyst was loaded in one of the reactors, the reactor with fresh catalyst was always configured to be the second reactor in series to boost conversion, but prevent temperature excursions.(57)

The bottom product from the two debutaniser columns (Figures 12 and 15), the steam stripped decanted oil and the de-gassed product from clay-treatment were combined and used as feed to the oil fractionator. This produced motor-gasoline, diesel and fuel oil cuts as final products.

4.4.3. Sasol 1 Arge oil work-up

There are three conversion units in the Arge work-up section, namely Bauxite treatment, catalytic cracking and wax hydrogenation (Figure 16).(57) Bauxite treatment, which is similar to that used in the Hydrocol refinery, converts the oxygenates and double bond isomerises the olefins to produce a higher octane motor-gasoline as final product. The feed is obtained from the Arge tail gas, which is purified in the gas loop to remove the light hydrocarbons (Figure 12). Only the C_5-C_7 fraction is converted over the Bauxite, because that is the only fraction where the final product had a high enough octane number to be used as final product. The process was operated at 400°C, slightly lower than the clay-treaters in the Kellogg work-up, but the aim of both processes were the same. The reason for having a separate Bauxite treatment unit in Arge work-up and not routing it to the Kellogg work-up, like the C_3-C_4 stream, is not clear.

The Paraformer, or paraffin reformer plant, is a thermal cracker that converts the hard wax to medium and soft wax, as well as the waxy oil fractions to diesel and motor-gasoline.(57) The conversion and product selectivity is controlled by varying the temperature, which is typically above 500°C.(63) The C_3-C_4 gas is sent to Kellogg work-up, while the

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[cc] This was probably done because Kellogg introduced a process based on this type of catalyst. Ref.(9)

[dd] This reactor design is very similar to that used for the UOP CatPoly and cumene processes that employ a solid phosphoric acid catalyst.

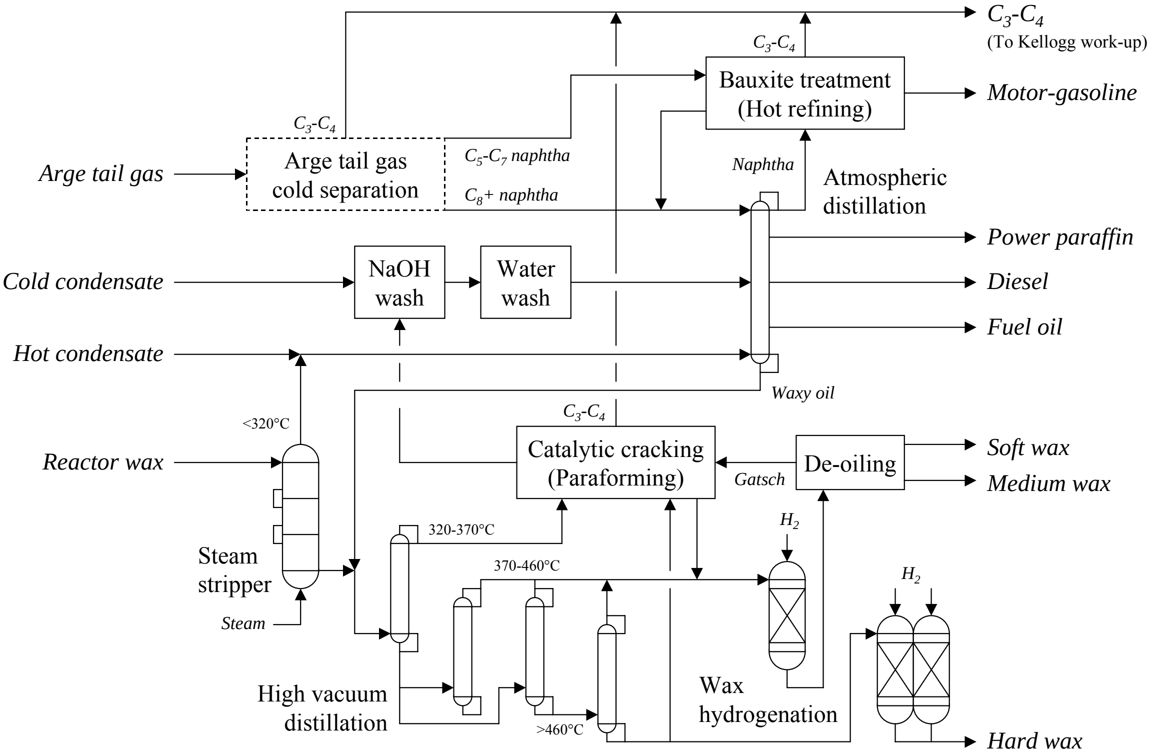

Figure 16. Sasol 1 Arge work-up section.

naphtha and distillate range product is caustic washed with the cold condensate before being distilled with the hot condensate into naphtha, power paraffin (kerosene), diesel, fuel oil and waxy oil fractions. The kerosene, diesel and fuel oil are final products, while the naphtha is first Bauxite treated before becoming motor-gasoline as final product.

Waxy oil and reactor wax are steam stripped to remove the lighter than 320°C material, before it is deep vacuum distilled to produce soft, medium and hard wax fractions. The waxes contain small amounts of olefins and oxygenates that has to be removed by hydrogenation. Hydrogenation was done at 260°C, 5 MPa and LHSV of 0.3-0.5 h^{-1}.[ee] Three reactors were used, two for hard wax hydrogenation and one reactor to hydrogenate the lighter fractions.(57)

The de-oiling of the wax was done by dissolving the wax in a suitable solvent at 60°C and then slowly cooling it down in a scraper cooler.(57) The wax fractions that crystallised could be recovered by filtration. Details of solvent dewaxing, which is typically performed with methyl ethyl ketone as solvent, can be found in literature.(65)

[ee] Although the catalyst type has not been specified in literature, it is stated that it is a “highly-active” catalyst. It is likely that it was an unsulphided nickel hydrogenation catalyst. For background on Fischer-Tropch wax hydrogenation see ref.(64).

4.4.4. Sasol 1 chemical work-up

The aqueous product from both Kellogg and Arge synthesis reactions contained about 6% oxygenates dissolved in the reaction water and was refined in the chemical work-up section (Figure 17).(57) The chemical work-up section consisted of two parts, chemical recovery and solvent recovery.

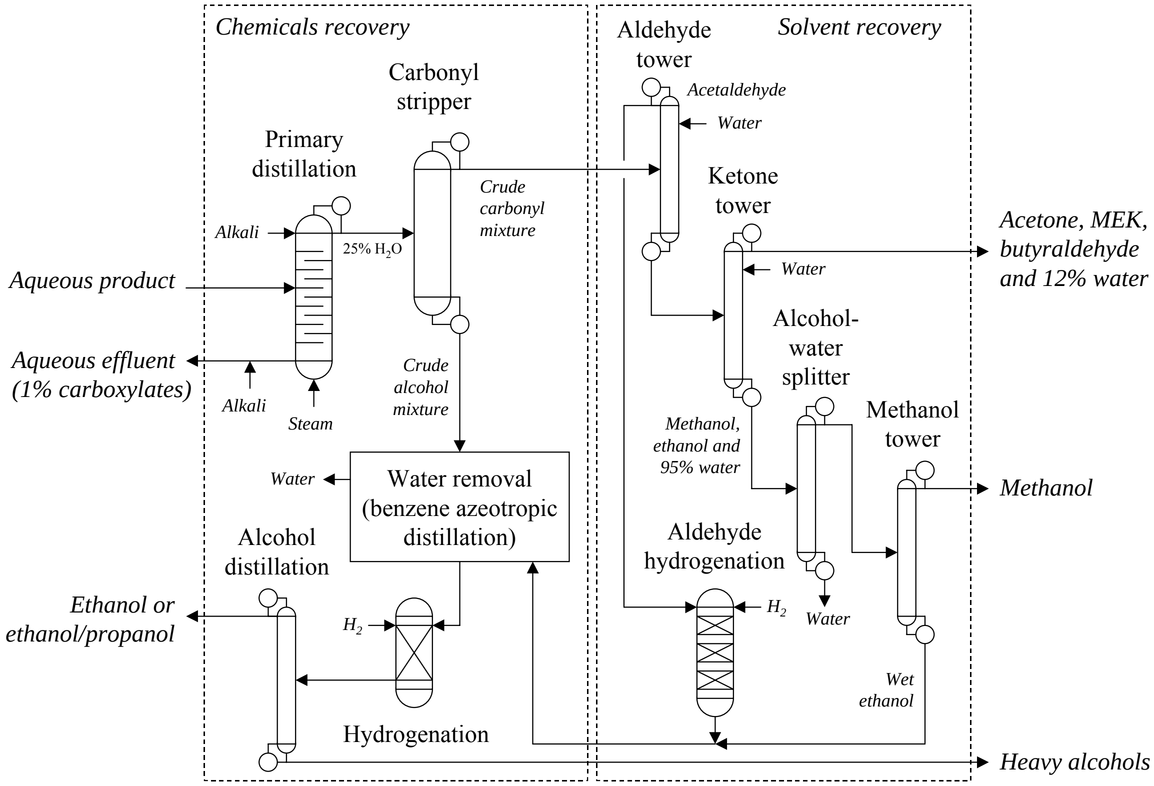

Figure 17. Sasol 1 chemical work-up section.

The aqueous product was first distilled in the primary distillation column, which was stainless steel lined on account of the carboxylic acids in the feed. To prevent any carboxylic acids from distilling into the overheads product, an alkali solution was injected on two trays near the top of the column. The bottoms product from the column was also treated with alkali to neutralise the carboxylic acids (Equation 1).

$$NaOH\ (aq) + RCOOH\ (aq) \rightarrow RCOONa\ (aq) + H_2O \qquad \text{... (1)}$$

The overheads product from primary distillation was rich in oxygenates and contained 25% water. The carbonyl stripper was used to effect a crude separation between the alcohols and carbonyls. The overheads product contained mostly carbonyls (aldehydes and ketones), esters and methanol, while the bottoms product contained mostly water, ethanol and the heavier alcohols. The stripper overheads product was further refined in the solvent recovery section, while the alcohols were further purified in chemical recovery. The first step was water removal by azeotropic distillation with benzene, which is a textbook purification (Keyes process).(66) The water-free alcohol stream was then mildly hydrotreated to convert the residual aldehydes and ketones into alcohols. The final alcohol purification step was either used to produce ethanol or an ethanol-propanol mixture as fuel alcohols. The heavy alcohols were not enough to be purified by continuous distillation and the mixture was sent to the solvent recovery section where the alcohols were separated by batch distillation, which is not shown in Figure 17.

The overheads product from the carbonyl stripper was distilled in various steps to successively remove acetaldehyde, mixed carbonyls (mainly acetone, methyl ethyl ketone and butyraldehyde), water, methanol and ethanol. Of these, only methanol was a final product. The acetaldehyde was hydrogenated to ethanol at 150°C and 3.8 MPa over a nickel catalyst in a reactor with three catalyst beds and inter-stage quenching. It is interesting to note that preheating of the acetaldehyde was done in the presence of hydrogen, presumably to prevent aldol condensation reactions. The product was then combined with the wet ethanol from the methanol tower and processed with the other alcohols in the chemical recovery section. The mixed carbonyls, like the heavy alcohols, were further separated by batch distillation.

The aqueous effluent that contained about 1% carboxylates was concentrated in an evaporator to yield a 50% salt solution. The alkali was regenerated from this solution, but the acids were not recovered, although this intent was expressed.(56)

5. South African Sasol 2 and 3 technology (1970-1980’s)

The Sasol 2 and 3 facilities are children of the 1973 oil crisis. The South African government requested Sasol on 30 November 1973 to investigate the technical and economic viability of building one or more coal-to-liquid facilities in the Republic of South Africa. The study was completed by early January 1974 and on 3 December 1974 the construction of Sasol 2 was publicly announced. In December 1978 the request was repeated and in January 1979 the government was provided with a report detailing the cost of doubling Sasol 2 (then still known as the Sasol 2 expansion project). In Iran the regime of the Shah was toppled and by February 1979 the decision to proceed with Sasol 3 was taken.(67)

Sasol 2 and 3 were grassroots facilities just like Sasol 1 and were erected about 100 km east of Johannesburg at the place presently called Secunda. Construction of Sasol 2 started in 1976 and commissioning of the steam plant took place early in 1979. In the same year, 1979, construction of Sasol 3 commenced. The synthesis and refining sections of Sasol 2 were commissioned in 1980,[ff] although the last Fischer-Tropsch Synthol-train was only commissioned in January 1981. Design production capacity of Sasol 2 was reached in 1982.

Commissioning of Sasol 3 took place in parallel with the start-up of Sasol 2 and already commenced in 1981, with the synthesis and refinery sections being commissioned in 1982.[gg] Design production capacity of Sasol 3 was reached on 16 February 1983.

The discussion of Sasol 2 and 3 will deal with the original designs. The design of the Sasol 2 and Sasol 3 refineries were similar, except for the addition of a high pressure creosote hydrogenation section (360 kta) to the tar refinery of Sasol 3, which processed creosote from both facilities.(67) Other minor improvements were also made to units based on lessons learnt from Sasol 2 and will be pointed out only where these led to significant differences between the Sasol 2 and Sasol 3 facilities.

5.1. Sasol Synthol Fischer-Tropsch synthesis

The Sasol HTFT Synthol reactor design is based on the Kellogg HTFT design used in the Sasol 1 facility. The circulating fluidised bed (CFB) design was optimised and many of the design problems of the original Kellogg reactors were sorted out.(43) The new CFB design was larger (7500 bpd)(42) and were operated at higher pressure. Typical operating conditions of the Synthol reactors were 330-360°C and 2.5 MPa.(39) A total of 16 Synthol reactors were installed at Secunda (8 Synthol reactors on each side), giving Sasol 2 and 3 a combined design production capacity of 120 000 bpd.

The same fused iron based Fischer-Tropsch catalyst as used for the Kellogg reactors were used for the Synthol reactors. With time the catalyst formulation has been improved as the effect of various promoters were better understood, although the basic formulation remained very similar. A typical product distribution from a commercial HTFT Synthol reactor is given in Table 12.(68)(69)(70)(71)

[ff] Sasol 2 produced its first hydrocarbon product on 1 March 1980 and marketable products were produced since 25 April 1980.

[gg] Sasol 3 produced its first hydrocarbons on 10 May 1982 and first marketable products by 1 July 1982.

The distribution of water soluble oxygenates are given in Table 13.[hh,(72)(73)] It will be noted that slight variations are reported, which is expected, since it is known that the product spectrum is temperature dependent.(38) In many respects the composition of Synthol products (Tables 12-13) is similar to that of Kellogg products (Tables 7-9) as would have been expected, since the designs are very similar.

Table 12. Typical product distribution from HTFT Synthol operation.

Compound	Composition (mass %)			
	ref.(68)	ref.(69)	ref.(70)	ref.(71)
Methane	11	10	10	11
Ethylene	4	4	4	7.5
Ethane	3.4	4	3.5	
Propylene	11.4	12	12	13
Propane	1.4	2	2	
Butenes	9.3	9	9	11
Butanes	2	2	2	
C_5-C_6 olefins	12.8			
C_5-C_6 paraffins	2.6			
C_7-160°C	17.2	51	51.5	51.5
160-350°C	13			
>350°C	5.4			
Non-acid chemicals	6.5	5	6	6
Carboxylic acids		1		

[hh] This data in ref. (72) has been published before Sasol 2 was commissioned and is likely to be the pilot plant data used by Fluor for the design of Sasol 2.

Table 13. Oxygenates in the aqueous product of Synthol HTFT synthesis.

Compound	Composition (mass %)	
	ref.(72)	ref.(73)
Non-acid chemicals		
Methanol	1.2	0.9
Ethanol	46.4	49.7
1-Propanol	10.7	14.5
2-Propanol	2.5	
1-Butanol	3.5	6.3
2-Butanol	0.7	
2-Methylpropanol	3.5	
1-Pentanol	1.0	1.8
2-Pentanol	0.1	
Other alcohols	0.5	
Acetaldehyde	2.5	4.5
Propionaldehyde	0.8	
Other aldehydes	0.5	
Acetone	8.9	9.0
Butanone (MEK)	2.5	2.7
Pentanones	0.7	0.9
Other ketones	0.2	
Carboxylic acids		
Acetic acid	9.7	6.7
Propionic acid	2.2	1.5
Butyric acid	1.2	0.9
Other acids	0.7	0.5

5.2. Sasol 2 and 3 gas loops

Sasol 2 and 3 also used Lurgi gasifiers to convert coal with a high ash content into raw synthesis gas. Since the commissioning of the Sasol 1 plant, many improvements were made to the Lurgi gasifiers and by the time Sasol 2 was constructed, an improved Lurgi Mark IV test gasifier was already in operation at the Sasol 1 site.[ii] At total of 80 Lurgi Mark IV gasifiers were installed at Secunda, 40 per plant, each 3.85 m in diameter and able to processes about 1000 tons of coal per day, yielding 55 000 $m^3 \cdot h^{-1}$ (normal) raw synthesis gas.(45)(74)(75)

Since the Lurgi gasifiers are low temperature gasifiers, coal pyrolysis products are co-produced with the synthesis gas. The separation methodology followed to separate the raw synthesis gas from these pyrolysis products is very similar to that employed in the Sasol 1 design (Figure 10). It was only more involved, with additional coolers and tar separators forming part of the design (Figure 18).(76)

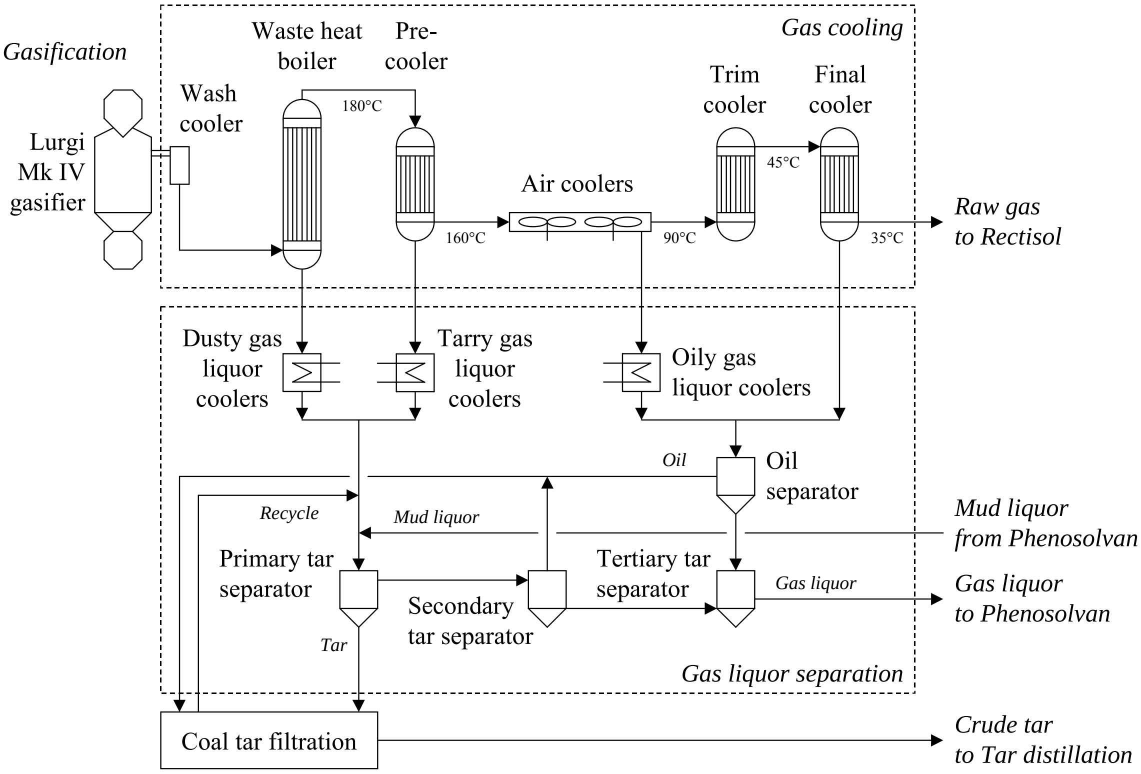

Figure 18. Sasol 2 and 3 gasification and coal pyrolysis product separation.

Purification of the raw gas to remove CO_2 and H_2S and produce pure synthesis gas, is done by a cold methanol wash in a Rectisol process.(53)(54) Due to the size of the Secunda facility, more than one Rectisol train have been built. The size of the Rectisol trains was limited by the maximum size of the vessels that could be transported by road.(74) Unlike the design of the Sasol 1 plant, in Sasol 2 and 3 the hydrogen sulphide from the Rectisol units is

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[ii] The commissioning of a Lurgi Mk IV gasifier in 1978 at Sasol 1 allowed sufficient time for optimisation and allowed the commissioning of these gasifiers at Sasol 2 to proceed without significant delay. Ref.(74)

recovered in a modified Stretford-type process, called Sulfolin.[jj] In Stretford process the hydrogen sulphide is absorbed in a sodium carbonate solution (Equation 2). In solution it is oxidised by vanadium(V) to produce elemental sulphur (Equation 3) that can be recovered. The vanadium(IV) formed during this step is converted back to vanadium(V) by reoxidation with air (Equation 4) to make the process catalytic.(77)(78)(79)

$$H_2S + Na_2CO_3\ (aq) \rightarrow NaHS\ (aq) + NaHCO_3\ (aq) \qquad \ldots (2)$$

$$2\ NaSH\ (aq) + 4\ NaVO_3\ (aq) + H_2O \rightarrow Na_2V_4O_9\ (aq) + 4\ NaOH\ (aq) + 2\ S \downarrow \qquad \ldots (3)$$

$$Na_2V_4O_9\ (aq) + 2\ NaOH\ (aq) + O_2 \rightarrow 4\ NaVO_3\ (aq) + H_2O \qquad \ldots (4)$$

The pure gas from Rectisol is mixed with internal and external recycle streams to produce a feed with a H_2:CO of 1.7-2.0 for the Synthol reactors (Figure 19). The internal recycle consists of the tail gas produced after knocking out the products that could be condensed by water cooling. These condensed products are sent to the refinery. Hydrogen from the pressure swing absorption (PSA) unit and the products from methane reforming(80) with oxygen over a nickel catalyst are combined to constitute the external recycle. To enable the recovery of hydrogen and methane, the gas loop includes a cold box where these compounds can be cryogenically separated from the heavier hydrocarbons. The inclusion of a CO_2 removal step is essential, since CO_2 solidifies at the cryogenic conditions prevailing in the cold box. The CO_2 removal is done in a Benfield unit, which uses a hot potassium carbonate wash and the reversible acid-base reaction between the basic carbonate and carbonic acid formed by dissolved CO_2 (Equation 5).(81)(82)

$$CO_2 + H_2O + K_2CO_3\ (aq) \rightleftharpoons H_2CO_3\ (aq) + K_2CO_3\ (aq) \rightleftharpoons 2\ KHCO_3\ (aq) \qquad \ldots (5)$$

The tails gas from Benfield is dried in an amine unit, which is then further dried by passing it over a mol sieve.(74) The cold box flow diagram shown in Figure 19 has been considerably simplified to avoid the complicated heat integration that is typically found in such units.(83) A large portion of the light products from HTFT synthesis is condensed in the cold box. With the exception of the C_2 and lighter products and some of the propylene, the rest of the hydrocarbons that are separated in the cold box are sent to the refinery as

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[jj] The first Stretford tower was built at Sasol 1 in 1973, but failed to work due to microbial growth in the water and the wrong type of wood used as packing material. These problems were overcome with the help of Linde and therefore the Secunda process was called Sulfolin, although it used basically the same chemistry. Ref.(75)

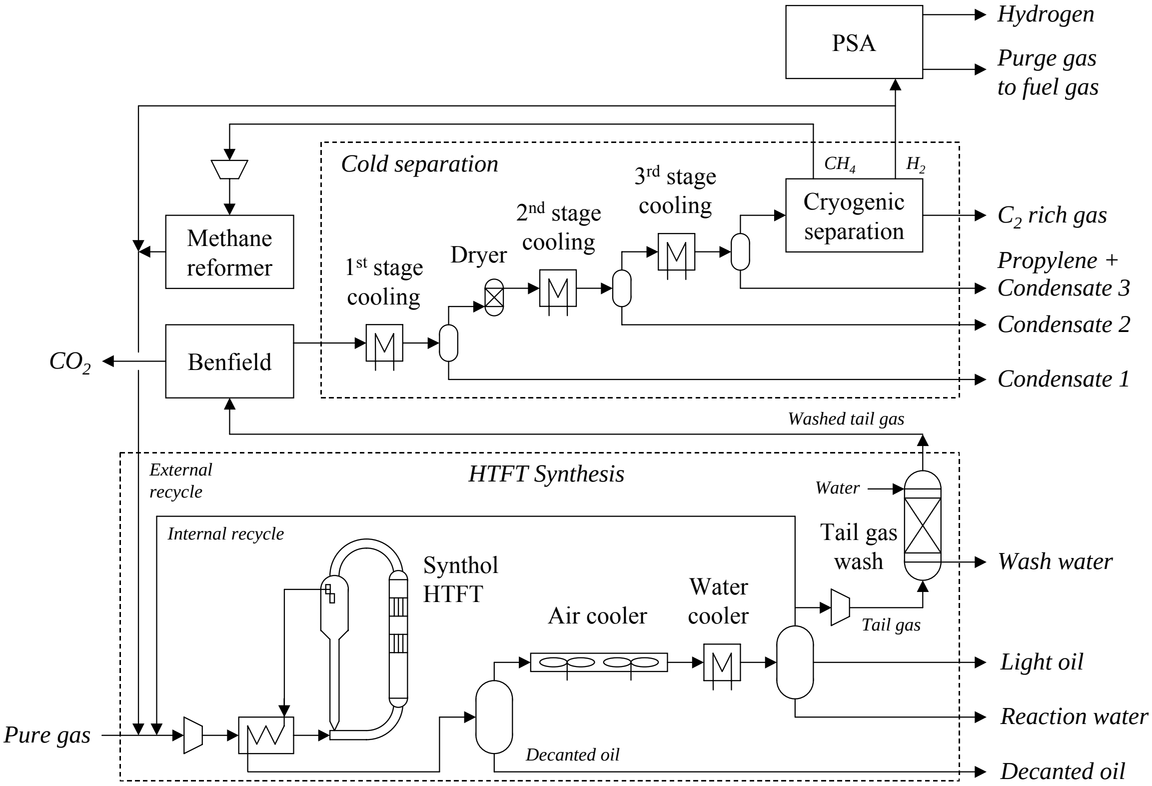

Figure 19. Sasol 2 and 3 original gas loop design (1980's).

Condensates 1, 2 and 3. Since the Condensate 1, 2 and 3 streams are produced by progressive cooling, the composition of Condensate 1 (C_3-C_7) is such that it contains heavier hydrocarbons than Condensate 2 (C_4-rich), which in turn contains heavier hydrocarbons than Condensate 3 (C_3-rich). The ethylene and some propylene are separated as pure compounds and are used as feed to produce polymers. The methane is recycled to the synthesis section where it is converted to synthesis gas in the methane reformer.

5.3. Sasol 2 and 3 refineries

The Sasol 2 and 3 refineries each consists of four different refineries (or value chains as they are called in Sasol), namely tar work-up, condensate work-up, oil work-up and chemical work-up (Figure 20). The plant organisation differs slightly from the Sasol 1 breakdown shown in Figure 13, because the Phenosolvan and Ammonia recovery units are seen as part of the gas production sections and not part of the tar refineries. A further difference is the organisational separation of condensate work-up and oil work-up, which in practise are very inter-linked, and will be discussed together.

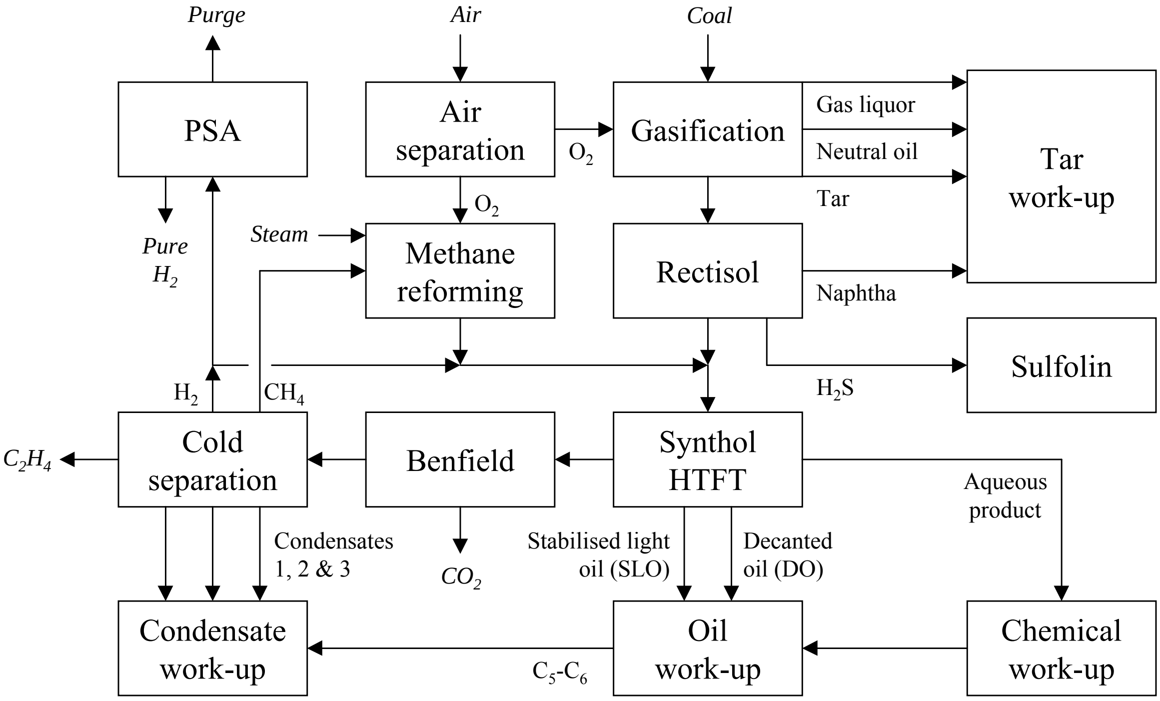

Figure 20. Block flow diagram of Sasol 2 and 3 showing the feed origin for the various work-up sections.

As noted during the discussion of the Sasol 1 refinery, the tar work-up section refines the products from low temperature coal pyrolysis that were separated from the raw synthesis gas and is strictly speaking not part of the Fischer-Tropsch refinery. A tar refinery will not be required if a high temperature coal gasification technology is used, or when natural gas is used as feed. Since the products from the tar refinery were blended with the Fischer-Tropsch derived synthetic fuels, it is an example of cross-platform integration.

Although it is not considered part of the refinery, it should be noted that both Sasol 2 and Sasol 3 included ammonia synthesis as part of their original design.(75) This makes sense, since large quantities of pure nitrogen is available from the air separation units (ASUs) as a by-product at essentially no additional cost. The manufacture of ammonia was extended to the production of nitrogen-based chemicals for the fertiliser (agricultural)[kk] and explosives (mining)[ll] industries.

[kk] Sasol entered the fertiliser industry in 1964 by adding ammonia synthesis to the Sasol 1 facility. However, things started going wrong in the 1980's when the Secunda fertiliser plant was added, since South Africa experienced its worst drought in 200 years. This was only a temporary setback.

[ll] The explosives business that was established in 1984, with a porous ammonium nitrate plant that was commissioned in Sasolburg in 1985 and a cartridge emulsion explosives plant that was commissioned in Secunda in the same year. Later an emulsion explosives plant was commissioned in the Northern Cape. The group posted a profit since 1989 and was renamed Sasol Mining Explosives (SMX).

5.3.1. Sasol 2 and 3 tar work-up

The recovery of phenolic material and ammonia by a Phenosolvan process, similar to that described for the Sasol 1 plant (section 4.4.1), also forms part of the Sasol 2 and 3 designs. The feed to the tar distillation unit consists of the phenolic pitch, after phenol extraction in the Phenosolvan unit, and crude tar from the coal tar filtration unit (Figure 21). These feeds are combined with a recycle stream from the coal tar naphtha hydrogenation unit before being distilled. A typical product distribution from tar distillation consists of six fractions, namely light naphtha (10%), heavy naphtha (8%), medium creosote (25%), heavy creosote (13%), residue oil (5%) and pitch (39%).(84)

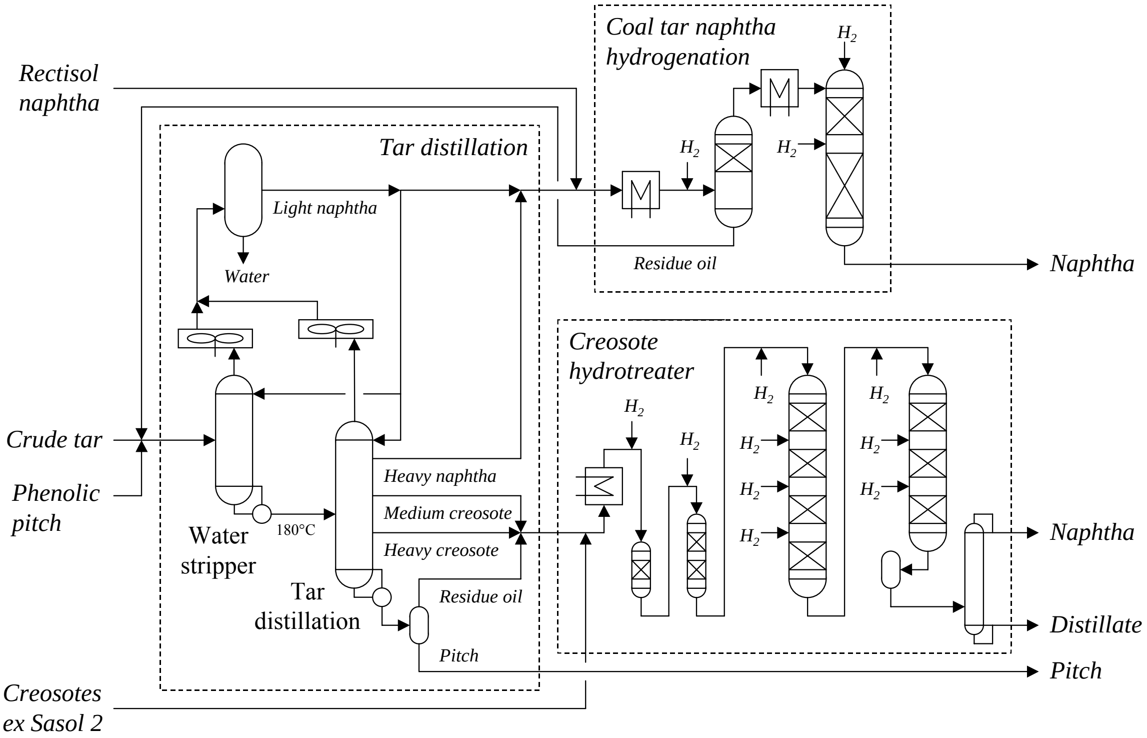

Figure 21. Sasol 3 tar work-up section. The tar work-up section of Sasol 2 is similar, but it does not contain a creosote hydrogenation unit.

The light naphtha, heavy naphtha and Rectisol naphtha from the Rectisol unit are combined to serve as feed for the Coal tar naphtha (CTN) hydrogenation unit. In this unit the feed is pre-heated and flashed to separate the naphtha range material from the heavier boiling material at around 210°C. The heavier material, called residue oil, is recycled to the tar distillation unit, while the naphtha vapour is hydrogenated at 5 MPa pressure. Separation of the heavier material takes place in the first reactor, which is operated in up-flow mode. This reactor is loaded with a mild hydrotreating catalyst and is mainly used for diene saturation.

Most of the hydrotreating is done in the second reactor that has two catalyst beds (originally a Co/Mo-Al_2O_3 catalyst) with an inter-stage hydrogen quench. The product is a hydrogenated naphtha consisting of mainly paraffins and aromatics, but with low octane number (typically around 80) and is used a fuel blending component. Most of the benzene in the fuel pool comes from this product.

The medium creosote, heavy creosote and residue oil from the tar distillation units at both Sasol 2 and Sasol 3 are combined and hydrogenated at high pressure (18 MPa) in the creosote hydrotreater at Sasol 3. The tar refinery at Sasol 2 does not have such a unit. The unit consists of four reactors with multiple catalyst beds and inter-stage hydrogen quenches. The catalysis of this unit is discussed in a recent paper.(85) The product is mixture of hydrogenated naphtha and distillate, which are used as fuel blending components. The creosote diesel is an especially important blending component, since it is the main source of diesel density in the refinery.

5.3.2. Sasol 2 and 3 condensate and oil work-up

The condensate and oil work-up sections are integrated (Figure 22). These were designed to meet the following objectives:(86) a) Convert normally gaseous C_3 and C_4 olefins to liquid

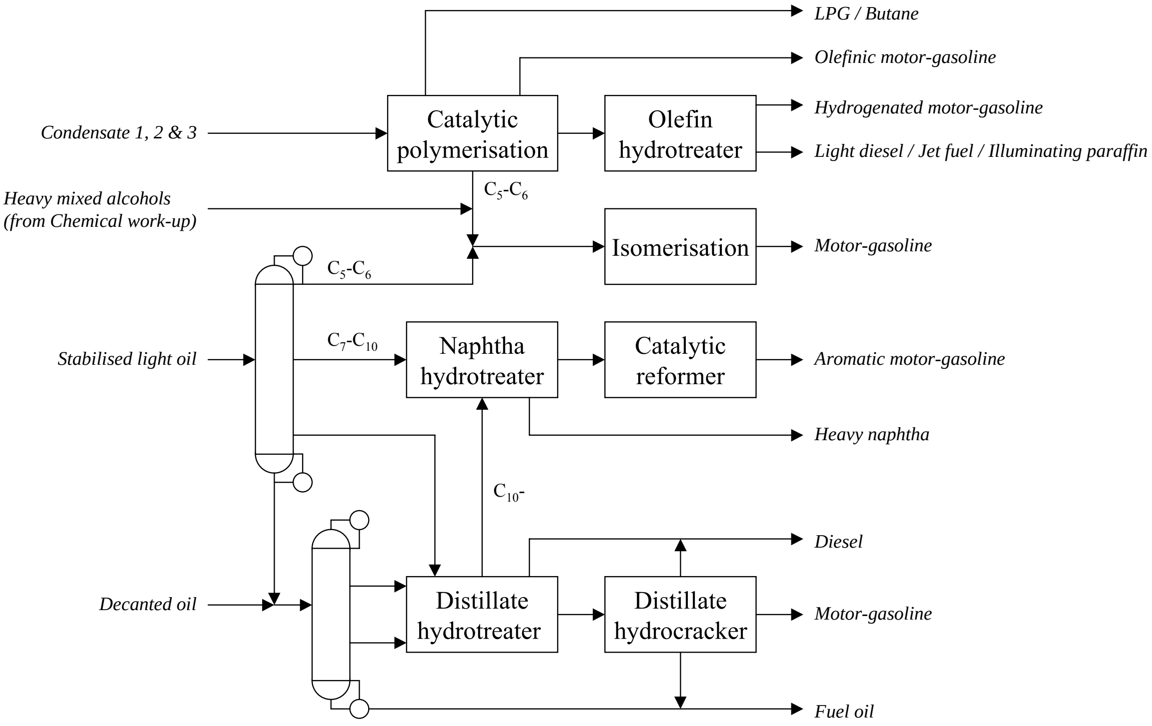

Figure 22. Block flow diagram of Sasol 2 and 3 condensate and oil work-up sections.

range products; b) Remove contaminants from Synthol oil to protect downstream catalysts and yield suitable products; c) Upgrade the quality of the motor-gasoline to meet octane specifications.

In order to meet the first of these objectives, the condensate work-up section employed solid phosphoric acid (SPA) catalysed olefin oligomerisation technology (CatPoly), which was known to work with Fischer-Tropsch products. Part of the product from this unit was hydrotreated. The second and third design objectives were met by designing the oil work-up section along similar lines as a second generation crude oil refinery, with an atmospheric distillation unit, naphtha hydrotreater (NHT), catalytic reformer (Platformer) and distillate hydrotreater (DHT). All of these units used standard crude oil technology. However, the overall refinery design was not second generation, but a third generation crude oil refinery design, with the inclusion of a vacuum distillation column and distillate selective cracker (DSC). The refinery design included only one typical Fischer-Tropsch refinery unit, namely an isomerisation unit to remove oxygenates and double bond isomerise the olefins.

It can retrospectively be argued that with more than two decades of HTFT refining experience Sasol might have known better than to adopt a crude oil refinery design. However, it should be realised that HTFT naphtha has a better octane number than crude oil(87) and that the crude oil refinery design adopted for Sasol 2 and 3 produced refined transportation fuels that met South African 1980 fuel specifications.

The UOP Catalytic Polymerisation technology was used for the olefin oligomerisation unit, which operated with solid phosphoric acid (SPA) catalyst. The olefin oligomerisation unit takes its feed from the Condensate 1, 2 and 3 streams, where it is fractionated in a feed debutaniser column, with the C_3-C_4 overheads fraction being used as feed for olefin oligomerisation and the C_5-C_6 bottoms fraction being sent to the isomerisation unit (Figure 23). The feed water content was adjusted by water injection to control the SPA catalyst hydration level.(88)(89)(90)(91) The oligomerisation unit consisted of two trains, each with four reactors having five catalyst beds with inter-bed quenches. The oligomerisation reaction is highly exothermic and part of the LPG fraction of the feed (propane and butane) is recycled to keep the temperature rise over the reactor within design parameters.

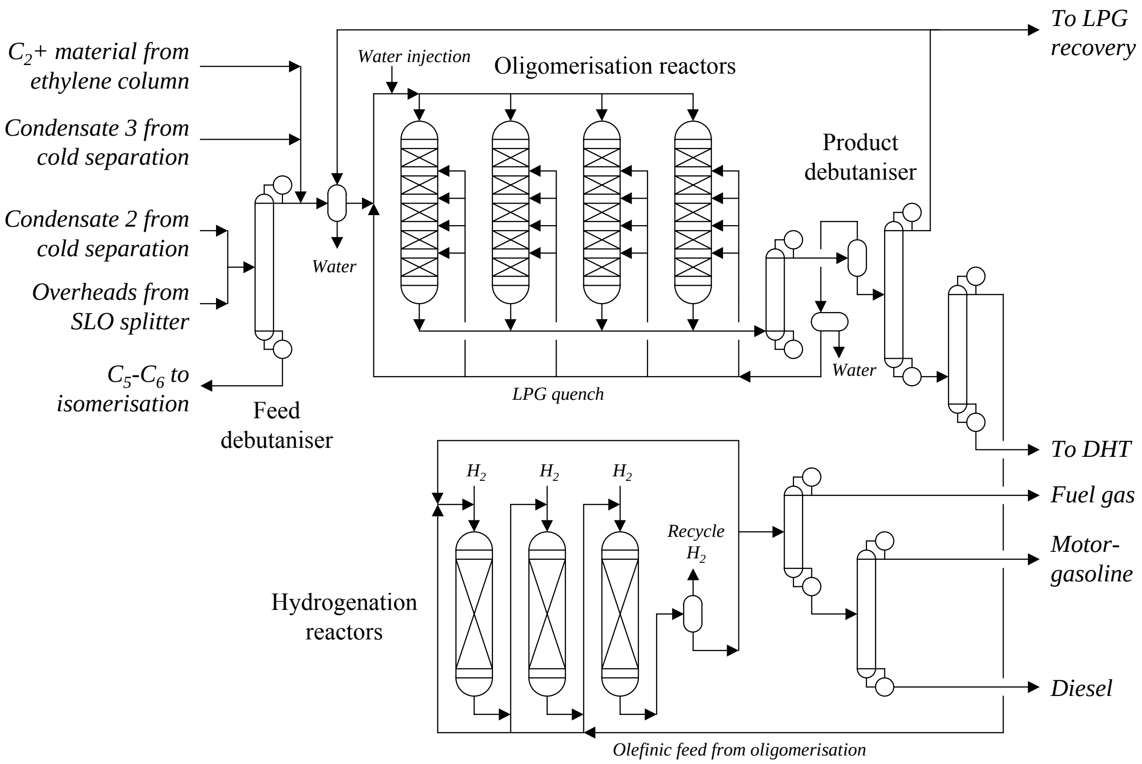

Figure 23. Catalytic polymerisation (CatPoly) process for olefin oligomerisation and the subsequent hydrogenation section (Polyhydrotreater) at Sasol 3. The CatPoly unit has two trains of four reactors each, but only train is shown.

At Sasol 2 the oligomerisation units were configured in such a way that it was possible to recycle part of the motor-gasoline fraction to boost overall distillate make. This was not done at Sasol 3 and the oligomerisation units therefore vary in design and operation. The unhydrogenated motor-gasoline has good octane (RON = 96.3 and MON = 82.3),(86) which is fairly insensitive to variations in feed composition.(92)(93)(94) The distillate range oligomers, as well as part of the motor-gasoline range olefins are hydrogenated. The octane number of the hydrogenated motor-gasoline was considerably lower(86) and varied over a wide range (RON =64-79 and MON=70-81).(95)

The olefin oligomer hydrogenation unit (Polyhydrotreater) consisted of 3 reactors, each loaded with a single bed of Co/Mo-Al_2O_3 catalyst and was operated in the range 260-350°C and 5 MPa, resulting in almost complete saturation of the olefins.

The C_5/C_6 isomerisation unit took its feed from the C_5/C_6 fraction from the Condensate streams and the SLO fractions. In addition to these feeds, some heavy alcohols (C_5+) from chemical work-up were sometimes co-processed. The isomerisation catalyst was a rare-earth exchanged Y-zeolite in a silica-alumina matrix[mm] and were used for double bond isomerisation and removal of the oxygenates in the feed. The reason for the selection of HZ-1 over more traditional alumina or bauxite catalysts is not clear. Alumina is a known dehydration catalyst and has later successfully been used in this unit with mixed Fischer-Tropsch feeds.(96) The unit consisted of two single bed reactors in parallel being operated in swing-mode at 370-410°C and close to atmospheric pressure. While the one reactor was converting C_5/C_6 material, the other reactor was being regenerated by controlled coke burn-off. A more detailed description of the reactions involved in this process is given elsewhere.(31)

The refining of the C_7+ fraction in the oil work-up section employed a conventional approach. A naphtha hydrotreater (NHT) was used to hydrogenate the feed for the catalytic reformer, mostly to remove oxygenates that would form water and cause corrosion problems. The reactor configuration was similar to that used for the hydrotreaters of the oligomerisation products shown in Figure 23. The same catalyst was initially used, but the operating conditions were more severe, with temperatures in the range of 320-420°C and an operating pressure of 6.0-6.5 MPa. The catalytic naphtha reformer was built using UOP Platforming™ technology and is of the continuous catalyst regeneration (CCR) type. This type of unit is well described in literature(97)(98) and the Sasol 2 and 3 units were designed for operation at 540°C and 1 MPa with a chlorided bimetallic Pt/Re-Al_2O_3 catalyst.[nn] Although a catalytic reformer is generally considered a source of high octane motor-gasoline, the low aromatic and naphthenic content of the Fischer-Tropsch feed resulted in a much lower conversion to aromatics than normally found (RON=87 at 84% C_5+ yield).(86)

The distillate hydrotreater (DHT) processed a mixture consisting of light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGO) from vacuum distillation, a side-cut from atmospheric distillation and the heavy product from the oligomerisation reactors. The DHT reactor contained four catalyst beds with inter-stage quenches and was operated in the range 290-380°C and 5.5-6.3 MPa. The product from the DHT was fractionated and the bottoms fraction served as feed to the distillate selective cracker (DSC).[oo] This was a much smaller unit, since HTFT technology produces little heavy material. The DSC used Mobil technology and the reactor contained a single bed of proprietary catalyst operated at 300-

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[mm] The catalyst employed was a cracking catalyst (see for example patent US 4,197,186). It is speculated that it may have been too active for this application.

[nn] Details of the catalyst composition and technology can be found in ref.(99).

[oo] The original Sasol 2 and 3 designs over-estimated the heavy-end fraction from HTFT synthesis and although two DSC reactors were built, only one was really needed.

415°C and 4.0-3.6 MPa. The product was fractionated to produce a poor quality motor-gasoline (RON<80), good diesel and small fuel oil fraction.

5.3.3. Sasol 2 and 3 chemical work-up

The sequence of primary separation at the Sasol 2 and 3 chemical work-up (Figure 24) is the same as that of Sasol 1 (Figure 17). The oxygenates in the reaction water are concentrated by the primary distillation column in the overheads fraction. The bottoms fraction consists of a dilute acidic solution and contains predominantly light carboxylic acids (1-2%). Most of the bottoms fraction is sent for biotreatment and some is used in the tail gas wash step after the Synthol reactors. The overheads fraction contains about 20% water and is further separated in the carbonyl stripper column to produce an overheads product that is rich in carbonyls (ketones and aldehydes) and a bottoms product that is rich in alcohols.

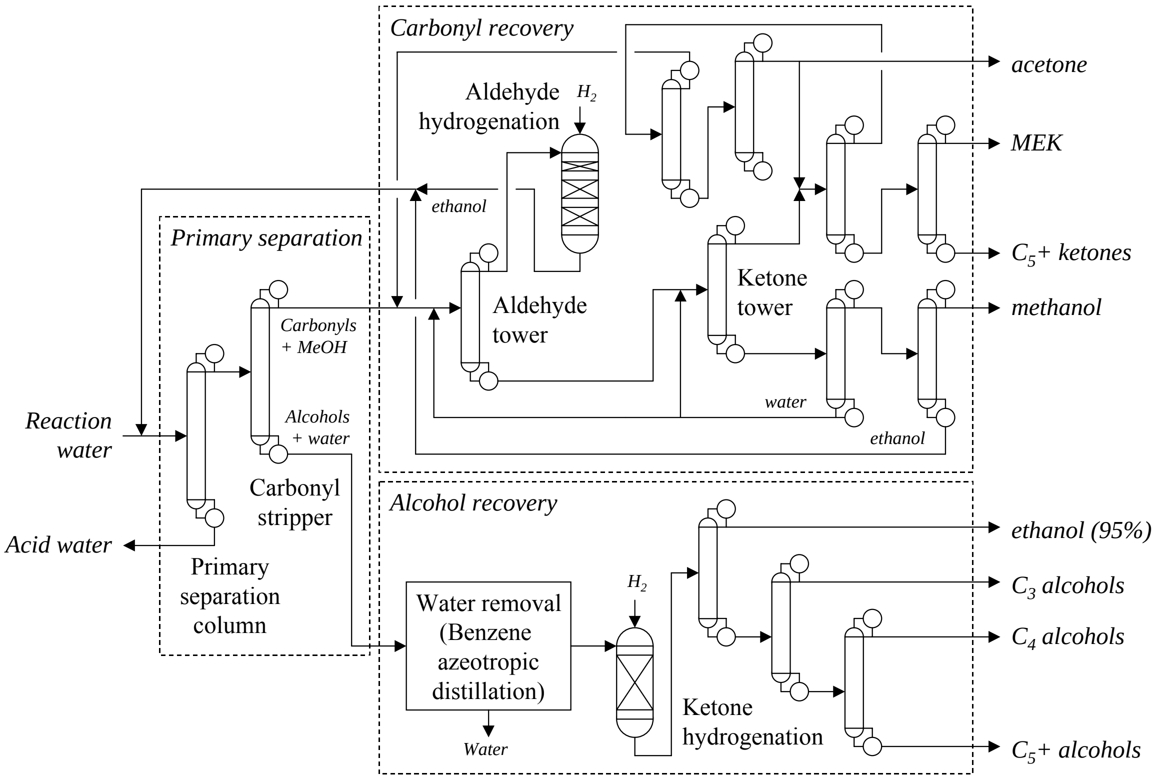

Figure 24. Chemical work-up section at Sasol 2, which is similar to that of Sasol 3.

The overhead product from the carbonyl stripper is sent to the carbonyl recovery section. The separation and processing sequence is similar to that of the Sasol 1 chemical work-up. The acetaldehyde is recovered in the aldehyde column and hydrogenated to produce more ethanol. In the ketone column the ketones are recovered overheads, while the bottoms product contained mainly water, methanol and some ethanol, which was further separated in subsequent columns. Unlike in the Sasol 1 design, the ketones were further purified to produce acetone and methyl ethyl ketone (MEK) as final products.

The bottom product of the carbonyl stripper was sent to the alcohol recovery section, which is similar to that used at Sasol 1. The water was removed by azeotropic distillation with benzene. This was followed by selective hydrogenation of the ketones in the alcohol mixture to produce alcohols. The alcohol mixture was then separated to produce ethanol, mixed propanols, mixed butanols and a heavier alcohol mixture. Not all of these steps were included in the Sasol 3 alcohol recovery section.

6. Mossgas gas-to-liquids technology (1980-1990's)

Despite the successes of Sasol 1, 2 and 3, South Africa's dependence on imported oil was still a point of concern for the South African government. In 1984 the Mossgas project was initiated to investigate the conversion of gas and associated natural gas liquids[pp] to transportation fuel.(100) The government gave the final go-ahead for the project in 1986 based on the Soekor gas find in the Bredasdorp Basin, off the coast of Mossel Bay.(101) The offshore platform landed its first gas in March 1992 and construction of the Mossgas facility was completed by the middle of 1992, achieving full production in January 1993.(100)(102)

The Mossgas facility was designed to produce 33 000 bpd products from the Fischer-Tropsch conversion of 200 000 $m^3 \cdot h^{-1}$ (normal) natural gas (22 500 bpd)[qq] and 70 $m^3 \cdot h^{-1}$ associated natural gas liquids (10 500 bpd). The project had capital cost of close to US$ 2.4 billion, but with the large unexpected drop in the oil price in the 1990's (less than US$ 20/bbl), the South African government was severely criticised for "wasting" tax payer's money. The project had a production cash cost of US$ 9-10/bbl, which nevertheless resulted in a significant operating profit.(100) The Mossgas gas-to-liquids facility is presently operated by PetroSA.

[pp] The natural gas liquids are also called gas condensates and should not be confused with HTFT Condensates.

[qq] The design figures quoted by PetroSA for the 3 Synthol reactors are 7 500 bpd, but in ref.(42) it is stated that the Mossgas Synthol reactors were designed for a production of 8 000 bpd. This increase in capacity is not due to the mechanical design, but is due to the synthesis gas composition. The synthesis gas contains less inert material resulting in higher H_2 and CO partial pressures, which causes the reactor productivity to increase.

6.1. Mossgas Fischer-Tropsch synthesis

The 1988 HTFT reactor design selected for the Mossgas project was the tried-and-tested commercial Sasol Synthol circulating fluidised bed (CFB) design, which was then in operation at Sasol 2 and 3.(20)

The Mossgas facility was operated with the same fused iron Fischer-Tropsch catalyst and Sasol Synthol operating conditions as the Sasol 2 and 3 facilities. The product distribution from HTFT synthesis was therefore similar to that reported for Sasol 2 and 3 (section 5.1), but the product slate of the feed to the refinery differed, due to the inclusion of natural gas liquids. The natural gas liquids are mainly aliphatic hydrocarbons, typical of a low sulphur paraffinic crude oil.

6.2. Mossgas gas loop

A process flow diagram of the Mossgas gas loop is shown in Figure 25.(102) The offshore production platform supplies the Mossgas facility with a mixture of natural gas (NG) and natural gas liquids (NGL). These feed materials are separated in the natural gas liquid recovery section. Part of the natural gas can also be liquefied in a liquefied natural gas (LNG) plant to provide a backup supply of gas (twenty-four hours) during upsets at the offshore production platform.(100) Typical compositions of the natural gas, natural gas liquids

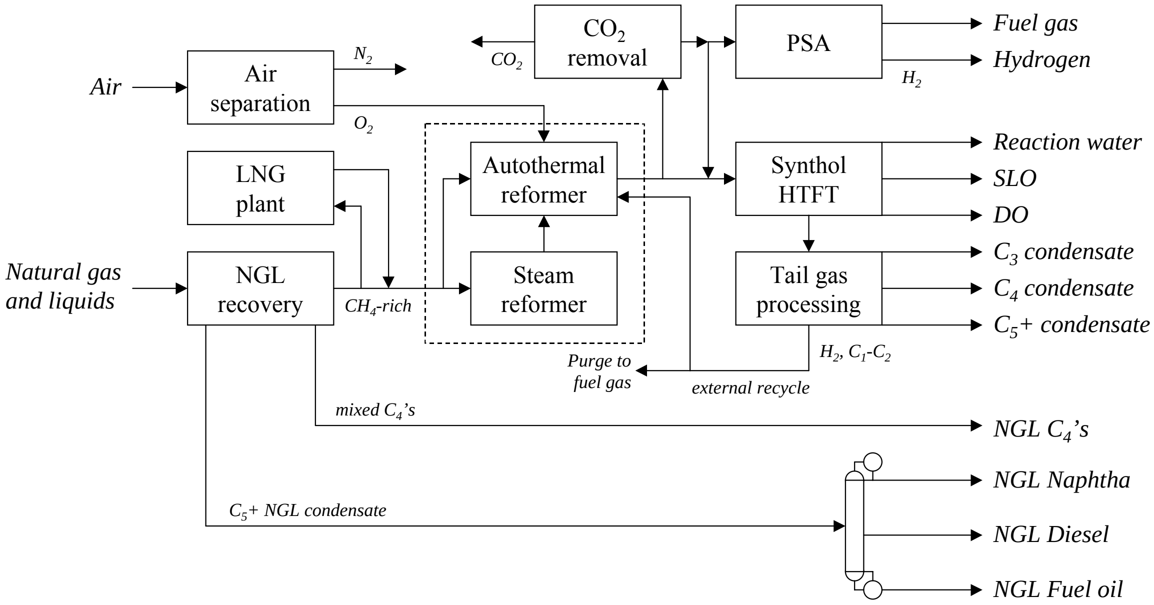

Figure 25. Mossgas gas loop.

and products from the NGL recovery section are given in Table 14. The condensate fraction from the NGL recovery section is further fractionated to produce a naphtha feed to the refinery, a straight run diesel blending component and a fuel oil fraction.

Table 14. Design composition of the natural gas (NG) and natural gas liquids (NGL) from the production platform, as well as the products from NGL recovery.

Compound	Feed material (mass %)		Products from NGL recovery (mass %)		
	NG	NGL	gas	C_4's	condensate
H_2S	8 ppm		8 ppm		
N_2	2.2	0.0	2.3		
CO_2	5.4	1.2	5.9		
H_2O	70 ppm	60 ppm	<0.1		
Methane	70.5	6.0	74.8		
Ethane	11.0	5.2	12.9		
Propane	6.4	8.7	3.9	0.5	
n-Butane	3.1	10.4	0.2	61.3	0.3
iso-Butane				37.1	0.0
Pentanes	1.4	68.5		1.1	16.8
Hexanes					7.1
C_7-120°C					21.2
120-180°C					21.1
180-400°C					29.2
>400°C					4.3

The methane-rich gas from NGL recovery is desulphurised and used as feed to gas reforming.(102) Mossgas employs the Lurgi Combined Reforming Process, which is a two step reforming approach. The primary reformer is a tubular steam reformer that is followed by a secondary autothermal reformer (ATR). Steam reforming[rr] is mainly used for hydrogen production, since it produces a H_2:CO ratio well above that required for Fischer-Tropsch synthesis. Part of the methane rich feed is bypassed and is combined with the product of the primary reformer, as well as the C_2 and lighter product from tail gas processing (external recycle) to serve as feed to the ATR. In the ATR the methane is partially combusted with

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[rr] The Mossgas steam reformer produces a H_2:CO ratio of around 7:1. Steam reforming is not considered the preferred technology for large GTL plants, since it has a poor economy of scale compared to ATR (ref.(80)).

oxygen from the air separation unit, steam reformed and subjected to the water-gas shift reaction over a nickel-based catalyst (Equations 6-8).(80) There are three identical reforming trains serving the three Synthol reactors and the synthesis gas to each Synthol reactor has a H_2:CO ratio of around 3:1.[ss],(100)

Partial combustion: $2\ CH_4 + 3\ O_2 \rightarrow 2\ CO + 4\ H_2O$ ... (6)

Steam reforming: $CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$ ... (7)

Water-gas shift: $CO + H_2O \rightleftharpoons CO_2 + H_2$ ... (8)

About 30% of the synthesis gas from the secondary reformer is sent to a Benfield unit for CO_2 removal. The remaining CO_2 in the synthesis gas is used to indirectly adjust the H_2:CO ratio in the Sasol Synthol reactor. This is possible because the fused Fe-based Fischer-Tropsch catalyst is active for the water-gas shift reaction. The synthesis gas composition is adjusted by the CO_2-free synthesis gas, which also serves as feed to the pressure swing absorption (PSA) unit for refinery hydrogen production.

The product from Sasol Synthol HTFT synthesis is cooled down in a similar way as shown in Figure 19 for Sasol 2 and 3. The products are decanted oil (DO),[tt] stabilised light oil (SLO), aqueous product (reaction water) and tail gas. Tail gas processing is much simpler than in the Sasol 2 and 3 gas loop, since the hydrogen, methane, ethane and ethylene are not recovered as separate products in a cold box, but recycled as a mixture to the ATR. Although this reduces the carbon efficiency of the Mossgas gas loop design, the capital cost associated with the gas loop is less. The heavier condensate products in the tail gas are separated by pressure distillation to yield C_3, C_4 and C_5+ condensate streams. Unlike the HTFT Condensate 1, 2 and 3 streams at Sasol 2 and 3, these condensates are proper distillation cuts, making refining more efficient.[uu]

[ss] This is a very high H_2:CO ratio, since HTFT Synthol requires a H_2:CO ratio of less than 2:1.

[tt] Decanted oil is strictly speaking the product from slurry oil after removal of the suspended catalyst particles in mixer-settlers to produce a gunk stream.

[uu] The C_3 condensate contains 87% propylene, 12% propane, 0.2% C_2 and 0.8% C_4 hydrocarbons; the C_4 condensate contains 85% butenes, 13% butanes and the remainder C_3 and C_5 hydrocarbons; the C_5+ condensate contains less than 1% C_4 material.

6.3. Mossgas refinery

The processing of natural gas liquids is integrated with the refining of the Fischer-Tropsch syncrude in the Mossgas facility. There is consequently not a separate work-up section dealing with natural gas liquids. The Fischer-Tropsch derived condensates are likewise integrated with the refining of the Fischer-Tropsch oil fraction. The refinery therefore consists of only two sections, namely an oil work-up to refine all the hydrocarbons and a chemical work-up to refine the water-soluble oxygenates in the reaction water.

6.3.1. Mossgas oil and condensate work-up

Although the Mossgas oil work-up section has been built scarcely a decade after Sasol 2 and 3, the design is clearly modelled on a fourth generation crude oil refinery (Figure 26).(102) The co-processing of natural gas liquids makes the design better suited to an oil refining approach, yet, the design also took far more cognisance of the nature of the Fischer-Tropsch products. For example, there is no vacuum distillation column and the refinery boasts an oligomerisation unit using the Conversion of Olefins to Distillates (COD) process that was specifically designed for the upgrading of Fischer-Tropsch olefins to diesel.

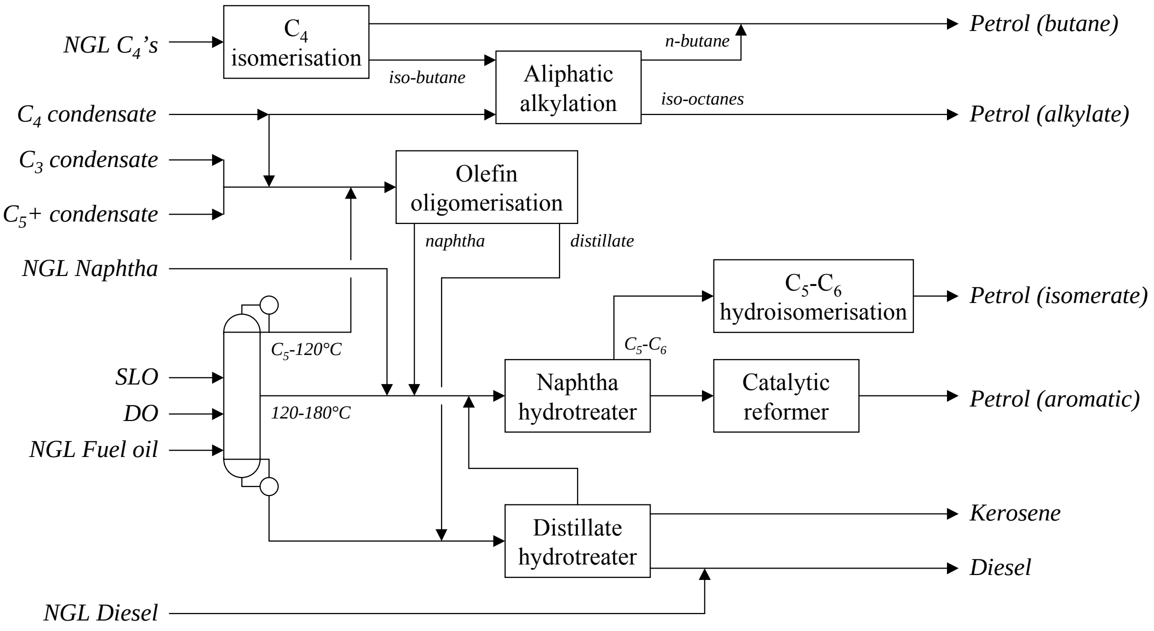

Figure 26. Mossgas oil work-up.

The abundance of butanes from the NGL recovery section and abundance of butenes from the HTFT condensate, make alkylate production a natural choice. The butanes are skeletally isomerised to produce iso-butane over a chlorided Pt-Al_2O_3 catalyst in an UOP Butamer™ process.(103) The iso-butane is then reacted with the HTFT derived butenes in a HF catalysed alkylation process from UOP to produce an alkylate rich in iso-octanes.[vv]

The HTFT C_3 condensate, HTFT C_5+ condensate and C_5-C_8 overheads fraction from SLO distillation are combined to provide an olefin rich feed to the COD process. This process has been developed in South Africa by the Central Energy Fund (CEF) and Süd-Chemie.(105) The process is in many respects similar to the Mobil Olefins to Gasoline and Distillate (MOGD) process(106) and also uses a ZSM-5 zeolite catalyst (Süd-Chemie COD-9).(107)(108) The mixture of olefins is converted in three reactors, which allows one of the reactors to be taken off-line for in situ catalyst regeneration by controlled carbon burn-off. For distillate mode operation, the operating conditions are typically 200-320°C and 5.5 MPa. The product consists of fuel gas, as well as propane, butane, COD gasoline and COD distillate.[ww] The distillate is of high quality (cetane 52-54), but of low density.(105)(109) The unhydrogenated COD gasoline is of a poor quality (RON=81-85, MON=74-75)(105) and is therefore reprocessed with the SLO naphtha. The fuel properties are inherent to the type of catalysis used.(110)

The C_9-C_{10} SLO fraction, NGL naphtha and COD naphtha form the combined feed to the naphtha hydrotreater (NHT). The NHT (UOP technology) is used as feed pretreatment for both the C_5-C_6 hydroisomerisation and catalytic reforming units to saturate the olefins and hydrodeoxygenate the oxygenates. The removal oxygenates are especially important, since both processes downstream from the NHT are sensitive to water. The hydroisomerisation unit uses UOP Penex™ technology(111) that is based on a chlorided Pt-Al_2O_3 catalyst, while the catalytic reformer unit uses UOP Platforming™ technology(98) that is also based on a chlorided catalyst. Both processes are used to produce final products.

The distillate hydrotreater (DHT) hydrogenates the COD distillate and the distillate from SLO distillation to produce diesel and kerosene. The straight run distillate from NGL recovery is combined with this product to make a final diesel fuel. The DHT is based on IFP

[vv] The selection of a HF catalysed process is somewhat surprising, since the HTFT product is rich in 1-butene, which is known to be the worst C_4 olefin feed for HF alkylation, resulting in a fairly low octane alkylate (RON=87-89). Conversely, using H_2SO_4 would have resulted in double bond isomerisation to produce a much better alkylate (RON=96-98). Ref (104), p.522.

[ww] Typical COD production figures are: fuel gas 1100 $m^3 \cdot h^{-1}$ (normal); propane 4 $m^3 \cdot h^{-1}$, butane 2 $m^3 \cdot h^{-1}$, COD gasoline 15 $m^3 \cdot h^{-1}$, and COD distillate 46 $m^3 \cdot h^{-1}$. Ref.(102)

(now Axens) technology.(100) Since the distillate is low in aromatics, it also finds a niche application as indoor heating fuel.

6.3.2. Mossgas chemical work-up

The chemical work-up section processes the reaction water of a similar composition to that of Sasol 2 and 3. Rather than separating the water soluble organic compounds, the carbonyls are partially hydrogenated to produce alcohols, thereby simplifying work-up considerably.(100) The carbonyl to alcohol hydrogenation is performed with a Süd-Chemie G-134 nickel on silica-alumina catalyst, which has proven to be very stable in this application and the refinery is still operating with part of its 1993 start-up batch of catalyst.(112) The anhydrous alcohol product produced after water removal can either be sold as solvent, or can be added to the diesel to produce a 5% oxygenated diesel.(109)

7. Shell gas-to-liquids technology (1980-1990’s)

Shell started research into Fischer-Tropsch synthesis in 1973 and the work was originally focused on coal-to-liquids conversion. In 1980 the focus shifted to natural gas as a feedstock. The development of the Shell Middle Distillate Synthesis (SMDS) process began in 1983, when a pilot plant was constructed at the Shell Research and Technology Centre in Amsterdam.(113)

The first commercial gas-to-liquids facility to be built with the SMDS technology, was the 12 500 bpd plant in Bintulu, Sarawak, Malaysia. Discussions with the Malaysian government already commenced in 1985 and the Shell MDS (Malaysia) Sdn Bhd company was founded in 1986. The Central Luconia gas fields were identified as feed source. The process design package was completed in 1988. Construction started in November 1989, with mechanical completion being achieved early in 1993, followed by successful commissioning later in the same year.(114) After a plant turnaround, it was partly destroyed by an explosion in the air separation unit in December 1997. A new air separation unit was constructed and the plant was re-commissioned in May 2000. It has been in operation since then.(113)

7.1. Shell Bintulu Fischer-Tropsch synthesis

Due to the limitation that is imposed on the carbon number distribution from Fischer-Tropsch synthesis (Anderson-Schultz-Flory distribution) it is not possible to tailor-make a Fischer-Tropsch catalyst to produce products that are limited to a specific range. The approach adopted by Shell was to use the Fischer-Tropsch reaction to produce heavier products (high α-value), which could then be selectively cracked to the desired carbon number range.(115) For this purpose Shell developed a low temperature Fischer- Tropsch (LTFT) technology.

Catalyst selection was focussed not only on activity, but also on producing a catalyst with an α-value of 0.90 or higher.(114) The development of a new Fischer-Tropsch catalyst was also intrinsically linked to the selection of reactor-type to be used. Details of the reactor selection and fundamental work that was done in this regard has been published by Sie and co-workers.(114)(115) The main factor that resulted in the selection of a multi-tubular fixed bed reactor, was timing.[xx],(114) Other beneficial properties of multi-tubular fixed bed reactors that were cited were: high volumetric utilisation of reactor space by the Fischer-Tropsch catalyst, the ability to have a catalyst gradient along the reactor, no need for a solid-liquid separator and minimal catalyst attrition. The Fischer-Tropsch catalyst that was developed was based on cobalt,(116) not only due to the high α-value that could be obtained, but also because it was believed to be more stable than an equivalent Fe-based catalyst. The inability to replace catalyst during operation in a fixed bed reactor, as opposed to slurry bed and ebullating bed reactors, was therefore not a concern. The Shell Co-based Fischer-Tropsch catalyst could be regenerated in situ and had a useful catalyst lifetime of around 5 years.(116)(117)

The Shell Fischer-Tropsch synthesis process, called heavy paraffin synthesis (HPS), seems to have an α-value of around 0.91 based on its published product distribution.(117) Synthesis gas conversion of up to 95% with a C_5+ selectivity in the range 90-95% have been reported.(113) The Bintulu-plant has four multi-tubular reactors with a rated capacity of around 3000 bpd each. The catalyst is Co-based and Shell appears to have concentrated on the development of a silica support.(44) However, according to SRI(113) the catalyst is a promoted cobalt on a alumina based refractory oxide material, although it is more likely that the Fischer-Tropsch catalyst is based on zirconia.(118)

[xx] Scale-up of multi-tubular fixed bed reactors are comparatively simple, since each tube is essentially a reactor and piloting done on a single tube can be representative of commercial operation. The Sasol experience with Arge fixed bed reactors further proved that these reactors are stable and easy to operate. It had a low risk factor.

7.2. Shell Bintulu gas loop

The natural gas feed is converted into synthesis gas by partial oxidation with oxygen from an air separation unit (Figure 27). The partial oxidation unit uses the Shell Gasification Process (SGP) that was developed in the 1950's. The gasifiers are operated at 1300-1500°C and pressures up to 7 MPa, giving a carbon efficiency of 95% with a methane slip of 1%.(117) The SGP produces a synthesis gas with a H_2:CO ratio of 1.7:1, which is lower than the 2.15:1 usage ratio required for Fischer-Tropsch synthesis with Shell's Co-based LTFT catalyst.(113) The hydrogen deficiency is made up by a methane steam reformer, which operates at around 850°C and converts the methane to a hydrogen rich gas (H_2:CO>3) over a nickel catalyst.(117) Part of the synthesis gas production from the steam reformer is used to produce hydrogen for the refinery.

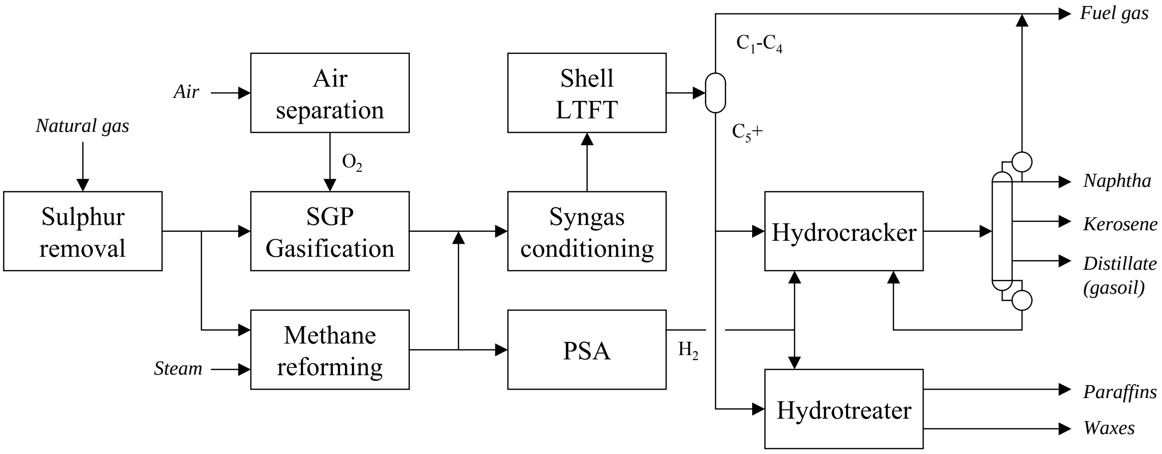

Figure 27. Process flow diagram of the Shell Bintulu facility.

After heat recovery, the cooled synthesis gas is cleaned by water scrubbing and passed over guard beds to remove potential Fischer-Tropsch catalyst poisons, such as sulphur compounds, before being used for synthesis.(116) Since high conversion is achieved during Fischer-Tropsch synthesis, the gas loop is not closed. The product from LTFT synthesis is stabilised and the C_1-C_4 fraction is used as fuel gas. The heavier hydrocarbons are used as feed material to the refinery

7.3. Shell Bintulu refinery

The refinery section employed to upgrade the products from LTFT synthesis is remarkably simple (Figure 27). It contains only two processing units, namely a hydrocracker and a hydrotreater.(119) The hydrocracker is operated in the range 300-350°C and 3-5 MPa with a proprietary hydrocracking catalyst from Shell (Pt or Pd on Al_2O_3).(113) The hydrocracker has four functions, namely, olefin hydrogenation, hydrodeoxygenation (HDO),[yy] hydrocracking and hydroisomerisation to produce preferably middle distillate.(115) The hydrotreater is employed for olefin hydrogenation and HDO to produce paraffins and wax for the chemicals market.

The product is fractionated and the unconverted wax-fraction can either be sold as a wax, or recycled to the hydrocracker. Depending on the hydrocracking severity, the product composition can be varied from 15% lights and naphtha, 25% kerosene and 60% gas oil in gas oil mode, to 25% lights and naphtha, 50% kerosene and 25% gas oil in kerosene mode. Some typical product properties are given in Table 15.(115)(116) Although the wax, paraffins and LPG can be sold as final products, the marketing of the fuels related products depend on Shell's ability to blend it with the products from their crude oil refineries to meet fuel specifications.

Table 15. Typical product properties from the Shell Bintulu LTFT refinery.

Property	Naphtha	Kerosene	Gas oil
Density @ 15°C ($kg \cdot m^{-3}$)	690	738	776
Boiling range (°C)	43-166	155-191	184-357
Aromatics (%)	0	<0.1	<0.05
Cetane index	-	58	76
Viscosity @ 40°C (cSt)	-	-	2.7
Smoke point (mm)	-	>50	-
Flash point (°C)	-	42	-
Freezing point (°C)	-	-47	-

8. Sasol gas-to-liquids technology (2000's)

In July 1997 a memorandum of understanding was signed between Sasol, Philips Petroleum and QPGC for the construction of a 20 000 bpd Fischer-Tropsch based gas-to-liquids plant in Ras Laffan, Qatar. Philips Petroleum withdrew after the collapse of oil prices in 1998. By mid-2001 a new agreement was reached, with Qatar Petroleum having a 51%

[yy] The product contains some primary alcohols, with other oxygenates being present in much lower quantities.

stake in the joint venture and Sasol a 49% stake. Natural gas from the Al Khaleej field was earmarked as feed for which the gas supply infrastructure was already developed by a joint venture between Qatar Petroleum and ExxonMobil.(120) This allowed front-end engineering and design of a 34 000 bpd facility to proceed, which was called Oryx GTL.(75)

The Oryx GTL plant achieved mechanical completion in 2006 and was officially opened in June 2006. The commissioning phase started in mid-2006 and the production of the first GTL products was announced in February 2007.(121) Commissioning problems are constraining output to 7000-10000 bpd and additional downstream equipment is required.(122)

8.1. Oryx GTL Fischer-Tropsch synthesis

The Oryx GTL plant uses LTFT technology based on the Sasol Slurry Phase Distillate™ process, using a newly developed Co-Al_2O_3 Fischer-Tropsch catalyst.(75)(123) The reactor technology has originally been developed and commercialised with an Fe-based LTFT catalyst at the Sasol 1 plant in the 1990's. A commercial 5 m diameter slurry phase reactor was commissioned in May 1993.(20) One of the main differences between the use of Co-based and Fe-based LTFT catalysts in the Sasol Slurry Phase Distillate™ process is catalyst lifetime, with the Co-based LTFT catalyst being more resistant to reoxidation by water, allowing it to be more productive under high per pass conversion operation.(48) Typical operating conditions are 230°C and 2.5 MPa.

The Oryx design uses two slurry bed reactors, each weighing 2100 ton and is about 60 m high and almost 10 m in diameter.(124)(125) The reactors were pre-fabricated and shipped due to the difficulty of on-site assembly.(75) The Co-based LTFT catalyst is manufactured by Sasol and Engelhard (now BASF) joint venture in a new catalyst preparation plant at De Meern, The Netherlands.

8.2. Oryx GTL gas loop

The gas loop design for Oryx (Figure 28) consists of autothermal reforming (ATR) of the natural gas, followed by LTFT synthesis and tail gas processing.(126) The natural gas feed is conditioned by removing sulphur over a ZnO guard bed and removing the coke precursors with a copper catalyst. The cleaned gas is preheated in the pre-reformer by heat exchange with the hot product gas from the ATR. The reformed gas is cooled to about 70°C to knock-out the water and ammonia in a water wash column, before it is used as feed to LTFT

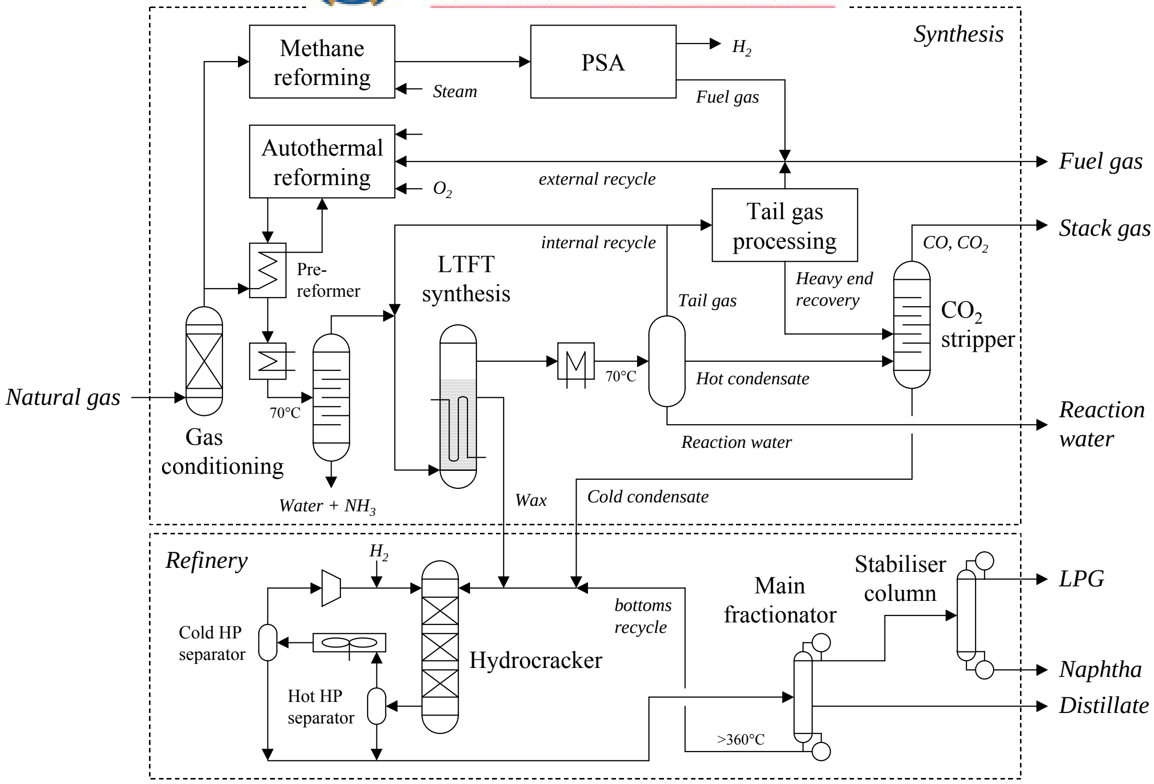

Figure 28. Process flow diagram of the Oryx GTL facility.

synthesis reactors. Part of the tail gas from LTFT synthesis is recycled to adjust the H_2:CO ratio from the ATR to the desired synthesis gas ratio for synthesis, called the internal recycle.

The product from LTFT synthesis is filtered in the reactor to separate the catalyst from the hydrocarbon product. The catalyst remains in the reactor and the hot wax goes through a secondary filtration step before being sent to the refinery. The wax-free gaseous products are cooled down to about 70°C to condense hydrocarbons and water. The hydrocarbon fraction (hot condensate) is phase separated from the aqueous product (reaction water) that contains some dissolved oxygenates, like methanol. The gaseous product is called the tail gas. The tail gas that is not used for the internal recycle, is cryogenically cooled to condense the C_3+ hydrocarbons and some water, which is called the heavy end recovery stream. The heavy end recovery stream and hot condensate are passed through a CO_2 stripper column, where the dissolved CO and CO_2 are separated, before it is sent to the refinery as a cold condensate. The uncondensed gas contains mainly C_1-C_2 hydrocarbons, H_2, CO and CO_2. Part of this product is recycled directly to the ATR as an external recycle, with the rest being purged for use as fuel gas.

A separate steam reformer is used to convert some of the natural gas into a hydrogen-rich synthesis gas. The hydrogen is recovered in a pressure swing absorption (PSA) unit for use in the refinery, while the hydrogen lean product is sent to the fuel gas system.

8.3. Oryx GTL refinery

The basic refinery design (Figure 28) is very similar to that used for the Shell Bintulu refinery that was shown in Figure 27. The refinery section receives two feed streams, namely wax and condensate that are combined to serve as feed to the hydrocracker. The hydrocracker is the only conversion unit in the refinery and uses ChevronTexaco Isocracking™ technology with a Chevron hydrocracking catalyst. The hydrocracking catalyst is a commercially available sulphided base metal catalyst on an acidic support. Typical operating conditions are a LHSV of 1.2 h^{-1}, 350°C and 7 MPa, with the temperature being adjusted to keep the per pass conversion at around 65%. The product from hydrocracking is distilled to produce LPG (3-7%), naphtha (20-30%) and distillate (65-75%), with the unconverted >360°C waxy product being recycled to the hydrocracker.(127)

The reaction water is separated by distillation into an alcohol-rich overheads product that is incinerated and a carboxylic acid containing water product that is biologically degraded to purify the water. No oxygenates are recovered from the reaction water.

Table 16. Typical properties of the products from a Co-based Sasol Slurry Phase Distillate™ process in combination with a hydrocracker as it is used in the Oryx GTL refinery.

Property	Naphtha	Distillate
Density @ 15°C (kg·m^{-3})	685-687	769-777
Boiling range (°C)	51-131	151-334
Aromatics (%)	0.3	0.5
Cetane number	39	72
Viscosity @ 40°C (cSt)	-	2.0-2.4
Flash point (°C)	-20	58
Freezing point (°C)	-	-15
Lubricity, HFRR (mm)	-	617
Net heating value (MJ/kg)	-	43.79

The products from the Oryx GTL refinery (Table 16)(127)(128)(129) are similar to those from the Shell Middle Distillate Synthesis process, since they use a similar refining methodology to process similar syncrudes. The naphtha has a low octane value (RON=50-55) with a *n*-paraffin:iso-paraffin ratio of 60:40.(127) The degree of branching is determined by the hydrocracker operation. The naphtha makes a good steam cracking feedstock(128) and the intention is to market it as such. The distillate has virtually no sulphur and has a high cetane number, but lacks the density to meet international diesel fuel specifications. The intention is to sell it as a diesel fuel blending stock. The simple refinery design used for Oryx GTL consequently suffers from one major drawback, namely that it does not produce transportation fuels or chemicals, only intermediate products and LPG. To upgrade the Oryx GTL product slate to final products, a more complex refinery is required.

9. Evolution of Sasol Fischer-Tropsch refineries

Over the past 30 years significant changes occurred in fuel specifications, which included the phasing out of leaded motor-gasoline, sulphur reduction and more stringent octane number and cetane number specifications. These changes, often motivated by environmental concerns, affected refineries by requiring changes in their product specifications and the emission standards of their refining processes. It affected refineries world-wide and necessitated modifications and changes to remain viable. There were also changes imposed by catalyst manufacturers, who developed new catalysts and phased out older catalyst types, as was the case with equipment. Unless refineries were designed with foresight, as some were, this forced refiners to continuously play catch-up. In the context of Fischer-Tropsch refining it was no different. The South African Sasol 1 refinery is more than 50 years old and sections of the original plant are still in operation. Although fuels are no longer produced at Sasol 1, it had to endure some changes with respect to fuels and chemicals production. Recently Sasol 2 and 3, which are more 20 years old, required a large capital investment in order to meet new fuel specifications.(130) The other commercial Fischer-Tropsch refineries, Mossgas, Shell Bintulu and Oryx GTL, are all comparatively new and have not yet needed changes to remain viable.[zz]

Fuel specifications and environmental legislation are not the only change drivers. There are ample opportunities to use Fischer-Tropsch synthesis as a platform for petrochemicals. Many chemicals that must otherwise be specifically synthesised, are produced in significant quantities during Fischer-Tropsch synthesis, like linear α-olefins, carboxylic acids, alcohols, ketones and waxes. The recovery of these chemicals affect fuel production and in itself caused Fischer-Tropsch refineries to evolve.

[zz] Neither the Shell Bintulu plant, nor the Oryx GTL plant is aimed at on-specification final fuels production.

9.1. Evolution of Sasol 1

The Sasol 1 plant was designed to produce fuel, yet, the main change driver had been the extraction of chemicals, rather than complying with new fuel specifications. The process to recover and produce chemicals started in 1958 with the production of ammonium sulphate (Figure 14) from the ammonia recovered in the Phenosolvan process. In the 1990's, when the LTFT slurry bed reactor was commissioned and the old Kellogg CFB reactors were decommissioned, Sasol 1 became a chemicals-only production facility.

Many of the major changes took place in the 1960's after a decision in 1962 to expand production in the direction of chemicals. The nitrogen from the air separation plant was converted into ammonia, in an ammonia synthesis plant commissioned in 1963.(35) Butadiene and styrene were produced and sold for synthetic rubber manufacturing. In 1964 Gaskor was founded to supply local industries with methane-rich gas and a pipeline to the Iscor steel works in Vanderbijlpark was completed in 1966.(35) In 1966 the first naphtha cracker was built to produce ethylene for Safripol (Suid-Afrikaanse Poli-olefiene, Engl. Transl. "South African Polyolefins") and was followed by a second cracker in 1969 to keep up with ethylene demand for the production of high density polyethylene (HDPE).(75) With all the chemicals extraction and production units, the product diversity from the Sasol 1 became impressive. It included: Motor-gasoline, diesel, kerosene, fuel oils, LPG, bitumen, sulphur, fuel gas, ethylene, propylene, butadiene, styrene, liquid nitrogen, liquid oxygen, argon, carbon dioxide, paraffin waxes, oxidised waxes, C_2-C_5 alcohols, acetone, methyl ethyl ketone (MEK), creosote, tar acids (phenols, cresols, xylenols), aromatic solvents, aliphatic solvents and ammonia derivatives.(35)

The construction of the inland oil refinery Natref next to Sasol 1 created new fuels opportunities and on 5 July 1971 a new formulation of petrol was marketed. The combination of crude oil and syncrude derived fuel proved to be remarkably beneficial.

The design requirements for refineries in the 1950's did not place the same emphasis on emissions and environmental impact as is current design practice. Early in the 1970's changes were made to address this shortcoming in the Sasol 1 design. Electrostatic precipitators were added to the power stations and these were commissioned in October 1972. The rotten egg smell caused by hydrogen sulphide emissions from Rectisol was addressed by routing the gas to a Stretford process for sulphur removal. However, the gas composition and material of construction proved incompatible and this unit was never successfully commissioned.(75) The Sasol Clean Air Technology (SCAT)(131) was developed to address this problem, but this technology was never commercialised. Inhabitants of Sasolburg had to wait until 2005 for this problem to be solved, when in 2004 Sasol 1 was converted from a coal-to-liquids facility into a gas-to-liquids facility by importing gas from Mozambique.[aaa],(132)

During the commissioning of Sasol 2 and 3, a pipeline was also constructed between Secunda and Sasolburg. With the large quantity of ethylene that became available, it was no longer economically viable to keep the two naphtha crackers at Sasolburg operational and these were decommissioned in 1983. However, demand for ethylene kept increasing and in 1988 one of the naphtha crackers was re-commissioned as an ethane cracker, to convert ethane from the Secunda plants into ethylene.(75)

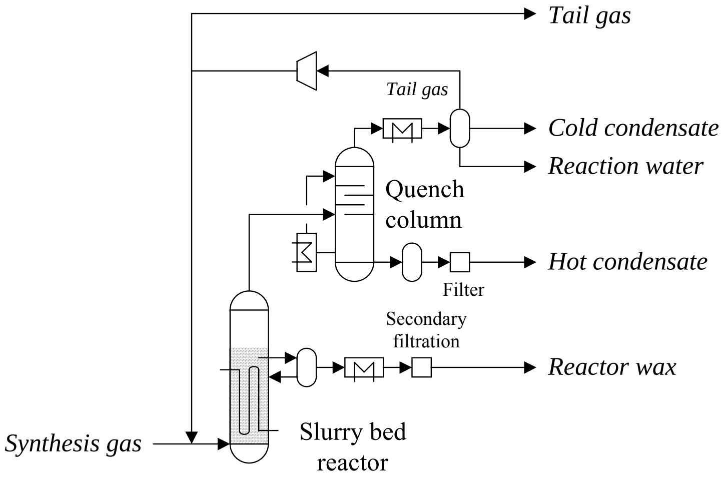

Figure 29. Sasol 1 slurry bed reactor flow diagram.

Due to its much smaller size, Sasol 1 became the test bed for new reactor technologies, with a 1 m diameter demonstration unit to test the Sasol Advanced Synthol (SAS) fixed fluidised bed in the 1980's and the Sasol Slurry Bed Process (SSBP) in 1990.(20) The success of these two projects led to significant changes at all Sasol's operations. A commercial scale diameter slurry bed reactor (Figure 29)[bbb] was commissioned at Sasol 1 in 1993,(20)(48) which paved the way for converting Sasol 1 to a chemicals-only facility. The product slate could be simplified by having only LTFT synthesis and the Sasol 1 process

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[aaa] A pipeline was constructed to import gas from Mozambique and the gasification section at Sasol 1 was modified with the addition of autothermal reformers (ATR). The Lurgi gasifiers were kept in operation along side the ATR's for some time.

[bbb] The 5 m diameter slurry bed reactor was designed for a synthesis gas capacity of 182 000 $m^3 \cdot h^{-1}$ (normal) with on-line removal and addition of catalyst. It uses a similar precipitated Fe-based Fischer-Tropsch catalyst as the Arge LTFT reactors and typical operating conditions are 245°C and 2.1 MPa.

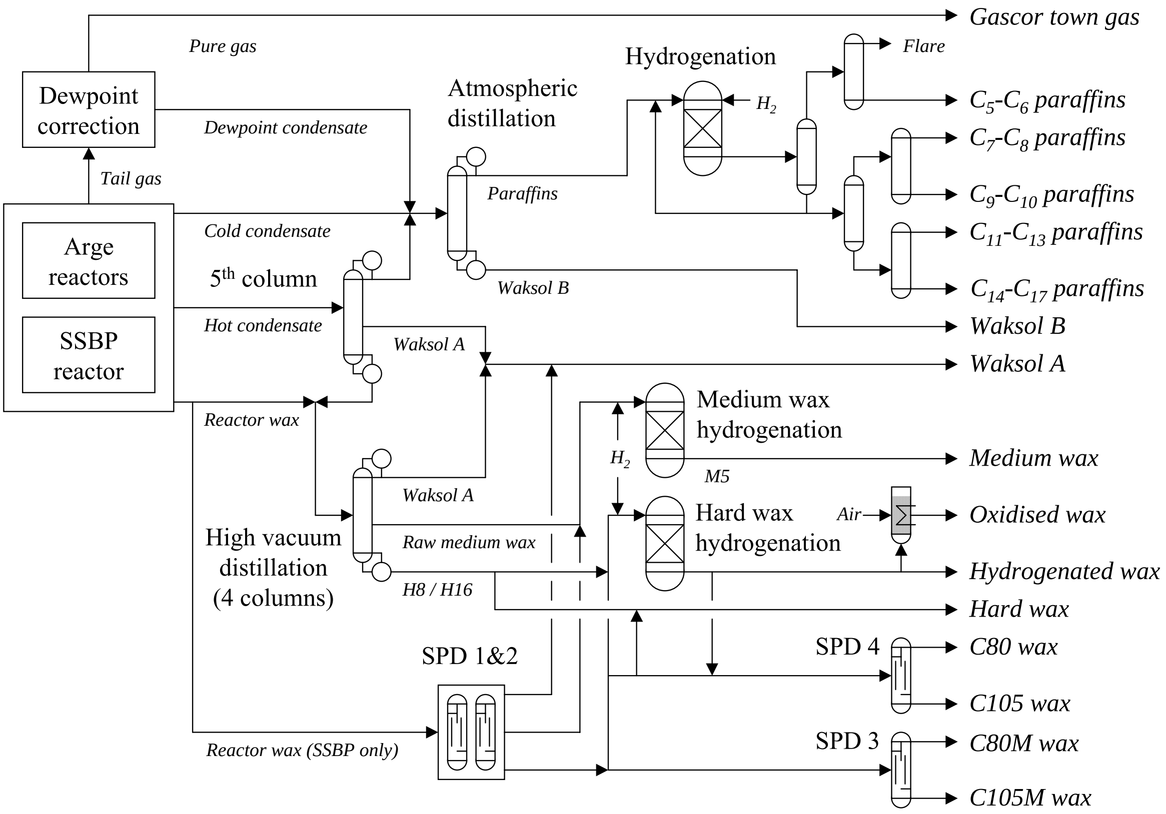

Figure 30. Sasol 1 refinery flow diagram in the mid-1990's.

configuration after the addition of the SSBP (Figure 30) is significantly different to that of the original design (discussed in Section 4).

The atmospheric distillation unit (ADU) separates the lighter fractions into paraffins and Waksol B. The feed materials to the ADU are caustic washed cold condensate (not shown in Figure 30; see Figure 16 for details), dewpoint condensate and the overheads from the 5th column. The paraffins are separated in different cuts that are sold to the solvent market, while Waksol B is sold to the fuel market. The 5th column, so called because it is the fifth column that forms part of the high vacuum distillation section, has a bottom temperature of 215°C and is operated at 14 kPa absolute pressure to avoid wax cracking. The Waksol A (or gatsch) overheads product is a waxy oil that is sold to the fuel market, while the bottoms product is combined with the reactor wax to serve as feed to the four columns in the high vacuum distillation (HVD) section (Figure 16). The medium wax that is recovered as an overheads product from the second and third columns have a congealing point of 51°C and is combined with the overheads product from the fourth column that has a congealing point of 62°C. This combined medium wax product is hydrogenated (Ni-based catalyst, 160°C and 2-3 MPa) and sold to the market, typically for use in candle manufacturing. The bottoms product is hard wax, which has a slightly brown colour. The wax is hydrogenated in two reactors in series (Ni-based catalyst, 230°C and 4.5-5.5 MPa) in flooded up-flow mode, with hydrogen being added only to the first reactor. Details of the wax hydrogenation process and the catalysis involved can be found elsewhere.(64) Part of the hydrogenated hard wax production is converted into various grades of oxidised waxes by partial air oxidation in batch reactors. The chemistry and principle of operation has been discussed elsewhere.(133)(134)

When the slurry bed reactor was installed, the wax distillation capacity became insufficient. A new section making use of short path distillation (SPD) was constructed. The method of distillation is therefore very different and allows the production of hard wax cuts with congealing points of 80°C (C80 and C80M waxes) and 105°C (C105 and C105M waxes) respectively. These columns were subsequently replaced by an even more efficient distillation configuration.

The evolutionary process is still on going, with imported material from the Secunda facility enabling the continued operation of phenolic extraction,[ccc] which was recently expanded with the commissioning of a Tar Naphtha Phenol Extraction (TPNE) plant.(135) The chemical work-up section is also kept operational with material imported from Secunda. Other chemicals production facilities that were added to the Sasol 1 portfolio included plants such as the synthesis of methyl iso-butyl ketone (MIBK) and methyl iso-butyl alcohol (MIBC) from acetone over a Pd on acidic resin catalyst (Amberlyst CH28).(136)

9.2. Evolution of Sasol 2 and 3

Sasol 2 and 3 are no longer known by these names. The two refineries became so integrated that they are now called Sasol West and Sasol East and the refinery complex is collectively known as Sasol Synfuels. Unlike Sasol 1, it remained a coal-to-liquids facility and it also remained an HTFT facility.[ddd]

In June 1995 an 8 m diameter Sasol Advanced Synthol (SAS) fixed fluidised bed reactor was commissioned at Secunda. The SAS technology proved to be more efficient than the Synthol CFB technology, although both use the same fused iron catalyst and produced a similar product slate.(42) The success of the first SAS led to the decision in March 1996 to

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[ccc] With the conversion of Sasol 1 from a CTL facility to a GTL facility, the tar products obtained by low temperature gasification in Lurgi gasifiers were no longer produced at Sasol 1. This would have implied closure of the tar processing facilities at Sasol 1, but it was decided to import material from Secunda and keep these facilities operational.

[ddd] Capacity growth on natural gas that will be imported from Mozambique is currently being planned.

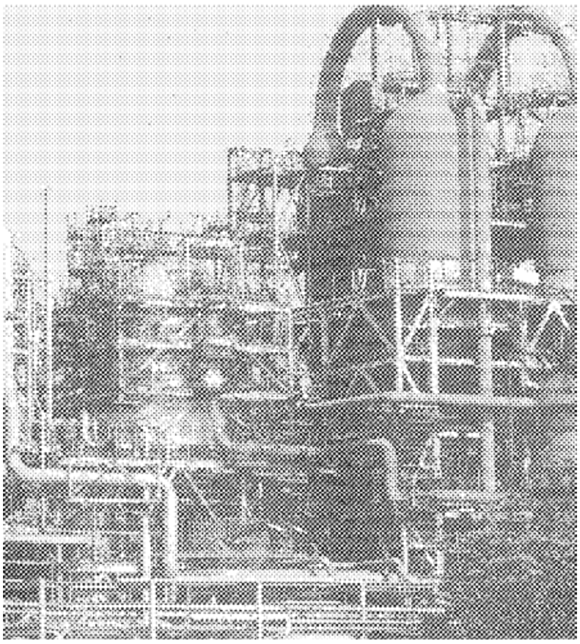

Figure 31. The construction of new SAS reactors next to the Synthol CFB reactors at Sasol Synfuels in Secunda. One SAS reactor replaces approximately two Sasol Synthol CFB reactors, yet it is much smaller in size. (This figure has been reproduced directly from Ref.(75) and is copyright protected).

change the Fischer-Tropsch synthesis section and replace all the old gooseneck Synthol CFB reactors that were so typical of Sasol, with SAS reactors (Figure 31). The synthesis sections at Sasol West and East each have two trains of 4 Synthol CFB reactors and it was decided to install one 8 m diameter and one 10.7 m diameter SAS reactor per train.[eee] The first new SAS reactor came on stream in September 1998 and the last SAS reactor in February 1999. A ninth SAS reactor (8 m diameter) was added in 2001 to serve as backup.(75)

The commissioning of the 120 000 tpa polypropylene plant at Secunda during late 1989, early 1990, heralded the start of new chemicals production era.[fff,(75)] The polypropylene plant was built using BASF technology and Secunda Synfuels refineries were affected only by the addition of a propylene-propane splitter and extraction of some propylene. There were also risk-mitigation projects associated with polymer production, like the Dimersol™ E plant(137) that converted ethylene to motor-gasoline during upset conditions.[ggg] Further extraction of propylene would follow in later years to feed chemical

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[eee] With Secunda synthesis gas and operating conditions the 8 m diameter SAS has a capacity of around 11 000 bpd and the 10.7 m SAS has a capacity of around 20 000 bpd.

[fff] The original plant had cost R 540 million and during the 1990's a further R 280 million was spent, increasing the output from the plant to 220 000 tpa. Ref.(75)

[ggg] The plant was built with IFP technology and used a homogeneous Ni-based catalyst to produce mainly C_4 and C_6 olefins from ethylene. It was expensive to keep the plant idling and alternative uses for the plant had

projects like the production of acrylic acid and 1-butanol.[hhh] The second major expansion in the polymer field came in 2006, with the addition of new polyethylene and polypropylene facilities as part of project Turbo.(130)

Probably the best-known expansion drive of Sasol in chemical production was the various α-olefins purification processes. Linear α-olefins in the C_4-C_8 range are used as co-monomers for the production of polyethylene.(138) The price is mainly determined by the cost of ethylene, which gave Sasol a significant cost advantage, since Sasol could recover these molecules by extraction from the HTFT product.(139) The extraction process to recover 1-hexene requires an etherification step to remove the close-boiling olefins and is similar to that used for the purification of 1-butene from cracker raffinate.(140) In 1992 a pilot plant was constructed for the purification of 1-pentene and 1-hexene, which was followed by a twin-train plant at Secunda to produce 100 000 tpa 1-pentene and/or 1-hexene. After debottlenecking the capacity was increased to 140 000 tpa and in 2000 a third 1-hexene train was added with a capacity of 80 000 tpa. This gave Sasol about 25% of the global market share for 1-hexene.(75) The marketing of 1-pentene was not successful despite the benefits of using it as a co-monomer,(141)(142) since Sasol would globally be the sole-supplier. The extraction of 1-octene followed in 1999, with the construction of a 50 000 tpa extraction plant. The purification of 1-octene required a different process configuration and it is significantly different to that employed for 1-hexene purification. It uses extractive distillation to remove the oxygenates and super-fractionation to purify the final product. In the first 1-octene train the carboxylic acids were neutralised with potassium carbonate before oxygenate extraction with NMP, but in the second 1-octene train the neutralisation step could be eliminated by applying azeotropic distillation for acid removal.(143) Due to the increasing demand for 1-octene, a third train has been approved, which has to use a synthetic route for the production of 1-octene from 1-heptene, since the first two trains have recovered all the 1-octene in the syncrude.[iii],(144)

The technology to purify linear α-olefins for the co-monomer market was also applied to the C_{12}-C_{13} range material. These detergent range olefins were purified and then hydroformylated with CO and H_2 over a classic Rh-based catalyst(145) in an OXO-process

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been actively sought in the late 1990's. It was eventually decommissioned and the capital written off, although some of the equipment are still in theory available for re-use.

[hhh] Although the acrylic acid and 1-butanol plants are using propylene from the Secunda facility, these plants were constructed at the Midlands site in Sasolburg (across the road from Sasol 1).

[iii] The capital cost of this 100 ktpa facility is estimated at R 2.1b and should be ready for operation in 2008.

licensed from Davy Process Technology.[jjj] The aldehydes thus produced are hydrogenated to alcohols for the detergent alcohol market.(146) The Safol detergent alcohols (DA) plant was commissioned in 2002.

The Secunda facility was also expanded to produce chemicals in support of Sasol Solvents business unit. In June 1996 the *n*-propanol purification plant was commissioned, with a capacity of 45 000 tpa, which is 30% of the world production. In September 1999 a high purity (99.99%) ethanol plant was commissioned.(75) Both plants separated and purified molecules present in the HTFT syncrude. Kvaerner technology was used for a process to convert ethanol into ethyl acetate(147) and this plant was commissioned in May 2001.

A delayed coker plant was added to the tar value chain in the late 1990's, mostly with the aim of producing anode coke. The design is very flexible and allowed the production of various types and grades of coke, although it is not suited for the production of anode coke, due to thermal expansion coefficient of the coke. This unit affected the tar refinery (Figure 21) by producing typical by-product streams like coker naphtha that had to be processed in the CTN hydrogenation units and coker gas oil that had to be processed in the creosote hydrotreater.

Other chemical production facilities were also constructed, but these have since been decommissioned. Acetaldehyde was used to produce crotonaldehyde by successive aldol condensation and dehydration steps. The crotonaldehyde could then be hydrogenated to produce 1-butanol. The aldol condensation step was difficult to control, causing a lot of off-specification product to be produced. This plant was eventually shut down and a 1-butanol plant based on propylene hydroformylation was built. Presently the acetaldehyde is hydrogenated to produce ethanol, using the same approach as in the original Sasol 1 design (Figure 17). An acid recovery pilot plant was built in the chemical work-up section to recover acetic acid and propionic acid from the bottoms product of the primary separation column (Figure 24). This stream contains about 1-2% carboxylic acids and is quite corrosive. It was found that the carboxylic acids could be selectively extracted with methyl tertiary butyl ether (MTBE). However, corrosion problems and equipment failures, resulting in poor on-stream time, plagued the pilot plant at Secunda. Furthermore, to scale-up this process to commercial scale would have required a large MTBE inventory, as well as the largest diameter extractor in the world, which made it a very energy intensive process.(75) Acid recovery was therefore never taken beyond the pilot plant stage.

[jjj] Originally Kvaerner, then became Davy Process Technology that was recently bought by Johnson Matthey.

Irrespective of all the chemical production projects, Sasol Synfuels at Secunda is still mainly a fuels refinery, with some chemicals co-production.[kkk] It benefited from the pre-2000 South African fuel specifications, which allowed a motor-gasoline rich in olefins and short on octane before lead addition. The olefin content in the final fuel was limited to 30% only by an internal Sasol specification. Furthermore, the oil work-up section had been designed along similar lines as a second generation crude oil refinery with only some third generation units included in the design (section 5.3.2). The refinery was therefore poorly designed to cope with the changes in international fuel specifications that were being debated in the 1990's, for example Euro-3 and Euro-4, especially with respect to the olefin content of motor-gasoline. Yet, the only refinery unit for octane production that was added before 2000 was a catalytic distillation column for the production of tertiary amyl methyl ester (TAME)(148) and since then only a pentene skeletal isomerisation unit (IFP technology)(149) was added to increase TAME production (Figure 32).

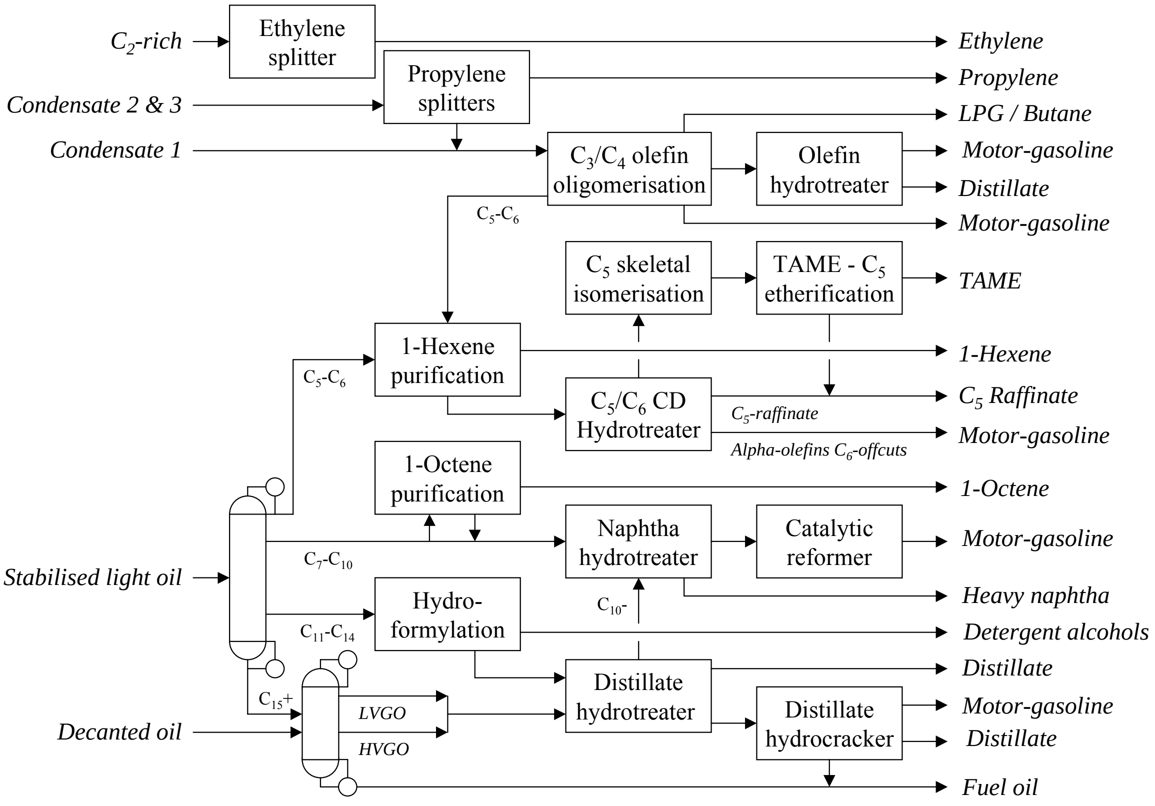

Figure 32. Sasol Synfuels oil and condensate refinery in 2004, before the refinery changes that were implemented with the construction of additional units for project Turbo.

[kkk] Fuels production at the Sasol Synfuels refineries year on year contribute more than 50% to the overall profit of the Sasol group of companies, making it the single most important asset and cash cow for growth. The operating profit of Synfuels for the second half of 2006 was R 8 360m, 69% of the operating profit of Sasol.

The first major change in South African fuel specifications came with the phase-out of leaded motor-gasoline. The impact of this on Sasol Synfuels was limited, since it coincided with the introduction of "Dual fuel™" that used methylcyclopentadienyl manganese tricarbonyl (MMT) as lead replacement. This was only an interim measure, since the South African fuel specifications that were legislated in June 2006 required no intentional metal addition to motor-gasoline, although provision was made for lead replacement petrol (LRP).[lll] The phasing out of LRP is expected.

The trend was nevertheless clear and the intention of lowering the benzene content to 3% in 2008 and 1% in 2012 has been announced.[mmm] A limitation on the olefin content of motor-gasoline may possibly be on the cards, as well as various other changes to bring South African specifications in line with European specifications. This threat has been identified by Sasol and resulted in project Turbo (Figure 33), a proactive attempt to ready Sasol Synfuels for the anticipated changes in fuel specifications.(130) Project Turbo is a R 13 billion project,

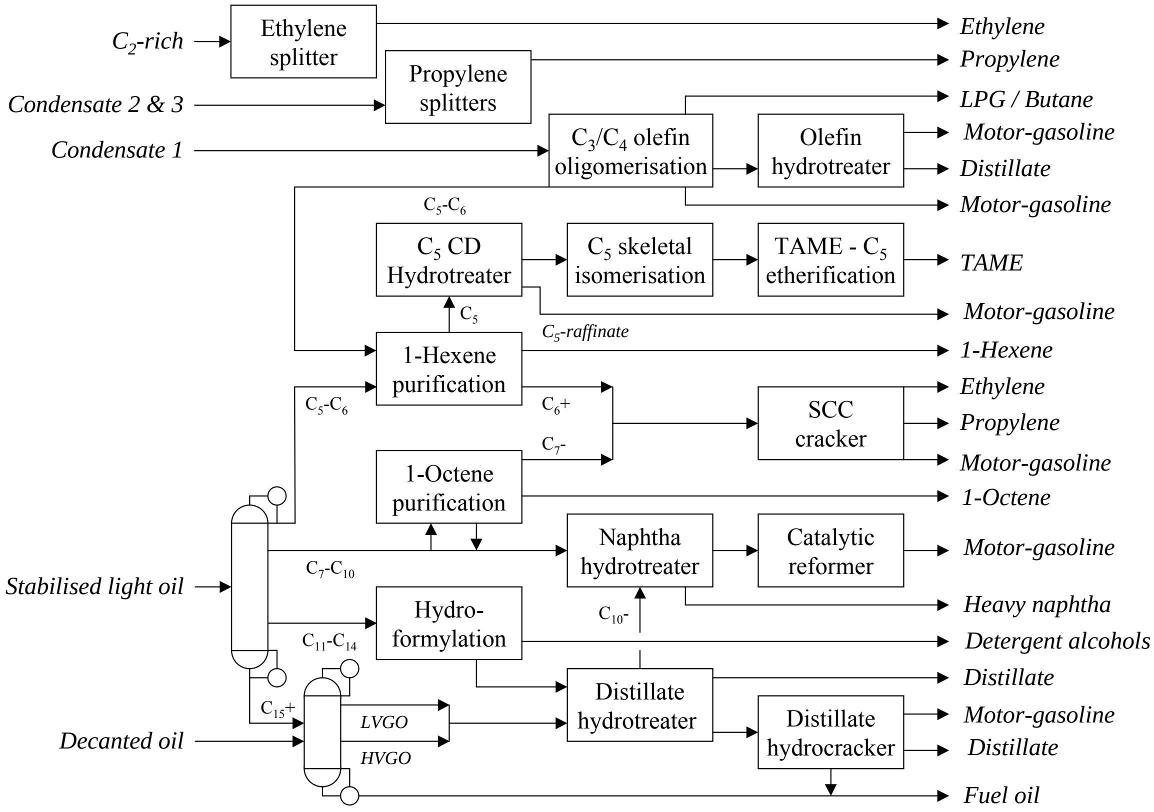

Figure 33. Sasol Synfuels oil and condensate refinery in 2006, after construction of project Turbo to meet the anticipated future South African fuel specifications.

[lll] Legislation published by the Department of Mineral and Energy affairs (DME) in the government gazette Vol.492 no.28958 on 23 June 2006.

[mmm] This timetable has since been moved out, with 3% benzene in fuel being required much later.

of which 40% of the cost is associated with upgrading the refinery, while the rest of the cost is associated with an expansion of the polymer business linked to the Synfuels refinery.[nnn] As interim measure, other less costly changes were implemented to increase the fuel quality.(150)

The construction of a high temperature fluid catalytic cracker as main refinery intervention to meet future fuel specification, was more aimed at chemicals production rather than fuels. The KBR Superflex™ Selective Cracking (SCC) technology,(151)(152) has been selected for this purpose. The refining philosophy underlying this decision is to convert the lowest quality fuel components into chemicals, namely ethylene and propylene, rather than upgrading the quality of the fuel per se. According to the SCC design, a high-octane aromatic motor-gasoline will be co-produced.[ooo]

Other changes are also being implemented, such as the separation of the olefinic feed to the oligomerisation units into a butene-rich feed to Sasol East and a propylene-rich feed to Sasol West. This would increase the octane number of the hydrogenated motor-gasoline at Sasol East(33) and increase the distillate production at Sasol West.(154)

10. Future Fischer-Tropsch refineries

10.1. Change drivers in Fischer-Tropsch refining

When considering Fischer-Tropsch refineries of the future, the tacit assumption is made that there will be future Fischer-Tropsch refineries. The energy security, refining cost and environmental advantages to justify such an assumption have been discussed previously. Once the decision to use Fischer-Tropsch technology has been made, the same change drivers as listed for crude oil refineries apply, although they affect Fischer-Tropsch refineries differently.

a) *Feedstock availability and cost.* Presently all Fischer-Tropsch based facilities use either natural gas or coal as feedstock. Hence, the classification as gas-to-liquids (GTL) or coal-to-liquids (CTL). In principle other feed materials can also be used to produce synthesis gas and in theory biomass-to-liquids (BTL), residue-to-liquids (RTL) and waste-to-liquids

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[nnn] The actual project cost reported in Sasol's interim financial results at the end of 2006 was R 14 750m.

[ooo] The KBR technology claims are interesting from a fundamental point of view. It claims to produce 16% ethylene, 25% propylene, 10% butenes, 2% C_5+ olefins and 24% aromatics (the rest being paraffins, CO, CO_2, water and coke) from a feed that contains about 75% olefins, 5% aromatics, 10% oxygenates and 10% paraffins. Ref. (153) FCC is a carbon rejection technology, yet it results in a product that requires hydrogen rejection.

(WTL) may be considered as options in future.(155) The selection of feedstock determines the operating profitability of the plant, as well as the capital cost. The type of feed material will also influence the gasifier type, which in turn may require the construction of an associated tar refinery. Coal might be seen as one of the options to supplement crude oil for transportation fuel, but tar refineries are not-in-my-backyard (NIMBY) facilities due to their potential environmental impact. At this stage it is not clear which of these materials will be the preferred feedstock for the future, despite the current spate of GTL facilities being planned and constructed.(156) Some of the integration opportunities with crude oil, natural gas, coal pyrolysis products and other feed materials have been discussed elsewhere.(127)

b) *Market demands*. When considering Fischer-Tropsch, the market can potentially be much more than just transportation fuels. The one extreme to consider is a fuels-only refinery and the other extreme is to consider a chemicals-only refinery, like the present Sasol 1 refinery. Combination refinery designs for fuels-and-chemicals can also be considered, like Sasol Synfuels, since Fischer-Tropsch syncrude has significant chemicals potential.(123)(157) Eventually it is market forces and plant location that will favour one design over another, rather than just technical differences.

c) *Refinery and refining cost*. Usually there is trade-off between capital cost and operating cost. In the context of Fischer-Tropsch technology, there are five key decisions that will significantly influence the refinery design and cost: feed stock (GTL or CTL), gasifier type (tar producing or not in the case of CTL), Fisher-Tropsch synthesis (HTFT or LTFT), product slate (fuels, chemicals or both) and market (intermediate or final products). For example, when a refinery produces fuels, the refinery cost can be significantly reduced if only intermediate blending components are produced, like Shell Bintulu and Sasol Oryx. Producing fuels that meet international fuel specifications require a more complex and costly refinery. However, there is always more risk involved in producing intermediate products. There are other cost-benefit parameters to consider in the refinery design too, like future environmental legislation, refinery flexibility, future fuel specifications, availability of capital, market foresight, corporate flexibility (like product exchange with other facilities) and risk aversion. These factors will be discussed in more detail in Chapter VIII.

It should be clear that the factors influencing Fischer-Tropsch refineries are similar to that affecting crude oil refineries, but that the potential diversity that can be introduced by the selection of feed, synthesis gas production, Fischer-Tropsch synthesis and product market, makes it more complex.

10.2. Design of future Fischer-Tropsch refineries

Fischer-Tropsch refining in future and the technology selection for such future refineries is the topic of the second part of this thesis. A detailed analysis of different refining technologies and their compatibility with Fischer-Tropsch syncrude will be made, taking cognisance not only of the technology fit, but also of future fuel specifications and the environmental footprint of the technology. Based on this analysis, specific Fischer-Tropsch refinery designs for the future will be proposed and discussed.

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CHAPTER VII

Refining technologies evaluated in Fischer-Tropsch context

Refining technologies for olefin conversion, hydrogen addition, carbon rejection and hydrogen rejection are discussed. The objective of each technology, as well as the chemistry and catalysis involved, is described to allow an analysis of its compatibility with Fischer-Tropsch syncrude. This has shown that key crude refining technologies such as fluid catalytic cracking and Pt/Al_2O_3 *catalytic reforming have poor compatibility with Fischer-Tropsch feed and refining needs, emphasising the difference between Fischer-Tropsch syncrude and crude oil refining. The technologies are also discussed in terms of their environmental friendliness, since this is considered an important aspect for future selection.*

1. Introduction

In the past there has been little incentive to develop Fischer-Tropsch specific refining technologies, due to the small number of Fischer-Tropsch refineries. This situation has not changed much and commercial Fischer-Tropsch operators had to adapt crude oil refining technology to make it compatible with Fischer-Tropsch feed materials. This often took the form of hydrogenating the olefins and oxygenates to hydrocarbons, so that the Fischer-Tropsch feed becomes similar to a paraffinic crude oil feed.

Some exceptions are noted, such as the development of a technology and catalyst for the hydrocracking of Fischer-Tropsch wax by Shell(1) and the development of the conversion of olefins to distillate (COD) process by the Central Energy Fund of South Africa.(2) The former process is employed in the Shell Bintulu refinery, while the latter process is employed in the PetroSA (Mossgas) refinery. In addition to these two technologies, there is also the development of the especially dry C84/3 solid phosphoric acid catalyst by Süd-Chemie Sasol Catalysts for use in the Synfuels olefin oligomerisation units.(3) Other Fischer-Tropsch specific technology developments were mostly done for chemicals production, such as those applied in the Sasol linear α-olefin purification processes.(4)

Technology selection for use with Fischer-Tropsch streams is not a trivial exercise and the commercial implementation of technologies in Fischer-Tropsch refineries does not imply a good technology fit. The devil is in the details. A thorough understanding of the composition of the Fischer-Tropsch feed, including its trace components, the chemistry of the process and the catalysis involved, are all required to make a proper technology selection. This type of analysis is available from neither literature, nor technology licensors.

The refining technologies that are evaluated in this chapter, will be discussed in terms of the: a) Objective of the technology; b) chemistry involved; c) catalysts; d) feed requirements; e) environmental issues; f) compatibility to Fischer-Tropsch products and g) its prospects for future application in Fischer-Tropsch refineries.

2. Olefin conversion

2.1. Double bond isomerisation

The octane numbers of olefins are dependent on the position of the double bond. In general the octane numbers of linear α-olefins are much worse than that of linear internal olefins (Table 1).(5) When a feed material has a high linear α-olefin content, double bond isomerisation can be used to improve the octane number significantly. The same is not true of branched olefins, where there is much less gain in doing so.

Table 1. Octane numbers of some linear olefins.

Compound	RON	MON	½(RON+MON)	Δ Relative to α-olefin
1-hexene	76.4	63.4	69.9	-
trans-2-hexene	92.7	80.8	86.8	16.9
trans-3-hexene	94.0	80.1	87.1	17.2
1-heptene	54.5	50.7	52.6	-
trans-2-heptene	73.4	68.8	71.1	18.5
trans-3-heptene	89.8	79.3	84.6	32.0
1-octene	28.7	34.7	31.7	-
trans-2-octene	56.3	56.5	56.4	24.7
trans-3-octene	72.5	68.1	70.3	38.6
trans-4-octane	73.3	74.3	73.8	42.1

Double bond isomerisation is a facile reaction that favours the formation of internal olefins from α-olefins at low temperatures, for example, the 1-butene to 2-butenes ratio at

200°C is 0.13:1 and at 450°C it is 0.38:1.(6) It is an almost thermoneutral conversion, with a heat of reaction (ΔH_r) in the order of 5-10 kJ·mol^{-1}. The reaction is acid catalysed and takes place via a carbocation intermediate, but it can also take place via a carbanion intermediate or a radical intermediate(7) (Figure 1) in different reaction environments.

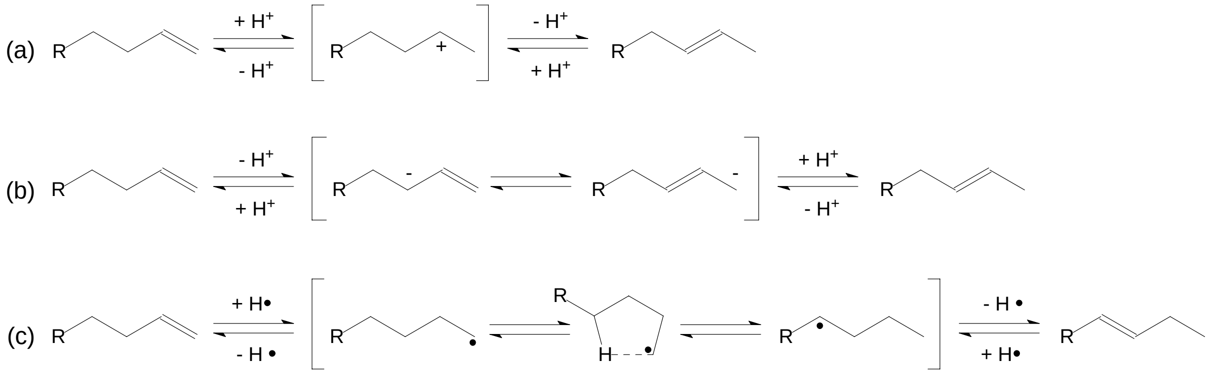

Figure 1. Double bond isomerisation mechanisms by (a) carbocation, (b) carbanion, and (c) radical intermediates.

Industrially, double bond isomerisation is generally catalysed by solid acid catalysts with sufficient Brønsted acidity for olefin protonation. Numerous examples of such catalysts have been recorded in the extensive review by Dunning,(8) with more recent literature reporting studies on catalysts such as sulphonic acid resins,(9) various zeolites(10) and mixed oxides.(11) Isomerisation by other mechanisms are less common, although double bond isomerisation over basic zeolites(12) and in alkaline media,(13) as well as during hydrogenation with palladium(14)(15)(16) and nickel(17)(18)(19)(20) catalyst have been noted.

Double bond isomerisation as octane enhancing side-reaction during hydrogenation is only relevant when the olefinic feed is being partially hydrogenated. Unless the olefinic feed is highly branched, there is a precipitous drop in octane number when an olefinic feed is hydrogenated. Yet, when the olefinic feed is highly branched, there is little gain in octane number during double bond isomerisation. This form of double bond isomerisation is therefore not especially valuable in refining context.[a]

Acid catalysed double bond isomerisation has previously been used in refineries to upgrade products with a high linear α-olefin content.(21)(22) These applications used bauxite or silica-alumina materials and were not environmentally friendly on account of their high operating temperatures (>340°C)(23) and high frequency of regeneration. Such a high

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[a] It could have been beneficial for mixed olefin feeds containing both linear and branched olefins if the hydrogenation catalyst had a higher rate of branched olefin hydrogenation than linear olefin hydrogenation. This is not the case in practice though, with sterically hindered olefins being more difficult to hydrogenate.

operating temperature is not a prerequisite for double bond isomerisation, but were used since these processes also doubled as heteroatom conversion technologies. It is possible to conduct double bond isomerisation at milder operating conditions. By using a catalyst with stronger acidity, such as acidic resins, or even silica-alumina materials, double bond isomerisation can be performed at <100°C.(24)(25) However, with more acidic catalysts olefin oligomerisation can become a significant side-reaction.(26) Furthermore, unless the catalyst is only weakly acidic, the process can only be considered for C_4-C_6 olefin feeds, since C_7 and heavier olefins are prone to catalytic cracking.(27)

Since naphtha range Fischer-Tropsch primary products are rich in linear α-olefins, there is a good technology fit with double bond isomerisation. Catalyst selection is crucial though, since Fischer-Tropsch derived naphtha feeds contain oxygenates. The oxygenates are not necessarily detrimental and when silica-alumina based catalysts are employed, catalyst activity may be improved by the water that is being produced during oxygenate conversion.(28)

Although double bond isomerisation technology has been proven with Fischer-Tropsch derived feed, its prospect for future application is slim. From Table 1 it is clear that even with the significant gain in octane that can be achieved, linear internal olefins still have moderate to poor octane numbers. The octane deficit cannot be corrected by the addition of tetraethyl lead, as was the case when this technology was developed. Its usefulness is further restricted by the fuel specifications that limit the olefin content of motor-gasoline. It will consequently not be practical to employ a process relying only on double bond isomerisation to upgrade Fischer-Tropsch syncrude.

2.2. Oligomerisation

The solubility of short chain hydrocarbons in naphtha is quite high and on account of their high octane number, it is desirable to include these compounds in motor-gasoline (Table 2).(5) The amount of short chain hydrocarbons that can be accommodated in motor-gasoline is, however, limited by their vapour pressure and the vapour pressure specification of the fuel. Olefin oligomerisation[b] provides a way to convert the normally gaseous short chain olefins into liquid products.

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[b] Oligomerisation is preferred as term over dimerisation, since it refers to the addition of 2-10 olefin monomers.

Table 2. Octane numbers and Reid vapour pressure (at 37.8°C) of short chain aliphatic hydrocarbons.

Compound	RON	MON	RVP (kPa)
Paraffins			
ethane	111.4	100.7	-
propane	112.1	97.1	1301
n-butane	93.8	89.6	357
isobutane	101.3	97.6	500
Olefins			
ethylene	100.4	75.6	-
propene	102.5	84.9	1569
1-butene	97.4	80.8	436
cis-2-butene	100.0	83.5	315

The oligomerisation of olefins is a highly exothermic reaction, with a heat of reaction of each dimerisation step typically being in the order of 85-105 $kJ \cdot mol^{-1}$. Low temperatures and high pressures therefore thermodynamically favour oligomerisation. The mechanism by which olefin oligomerisation takes place is dependent on the type of catalysis. If only the main commercial oligomerisation processes are considered,(29) three different mechanisms are represented (Figure 2).

Acidic resin and zeolite-based processes follow a classic Whitmore-type carbocation mechanism (Figure 2.a), solid phosphoric acid (SPA) based processes follows an ester based mechanism (Figure 2.b) and homogeneously catalysed organometallic based processes catalyses olefin oligomerisation by a 1,2-insertion and β-hydride elimination mechanism (Figure 2.c). It should be noted that this is a simplified mechanistic description. Other mechanistic variations have been suggested to account for specific types of oligomerisation catalysis.(30)

It is necessary to consider the different olefin oligomerisation technologies separately, since they have different processing aims, different feed requirements and yield different products.

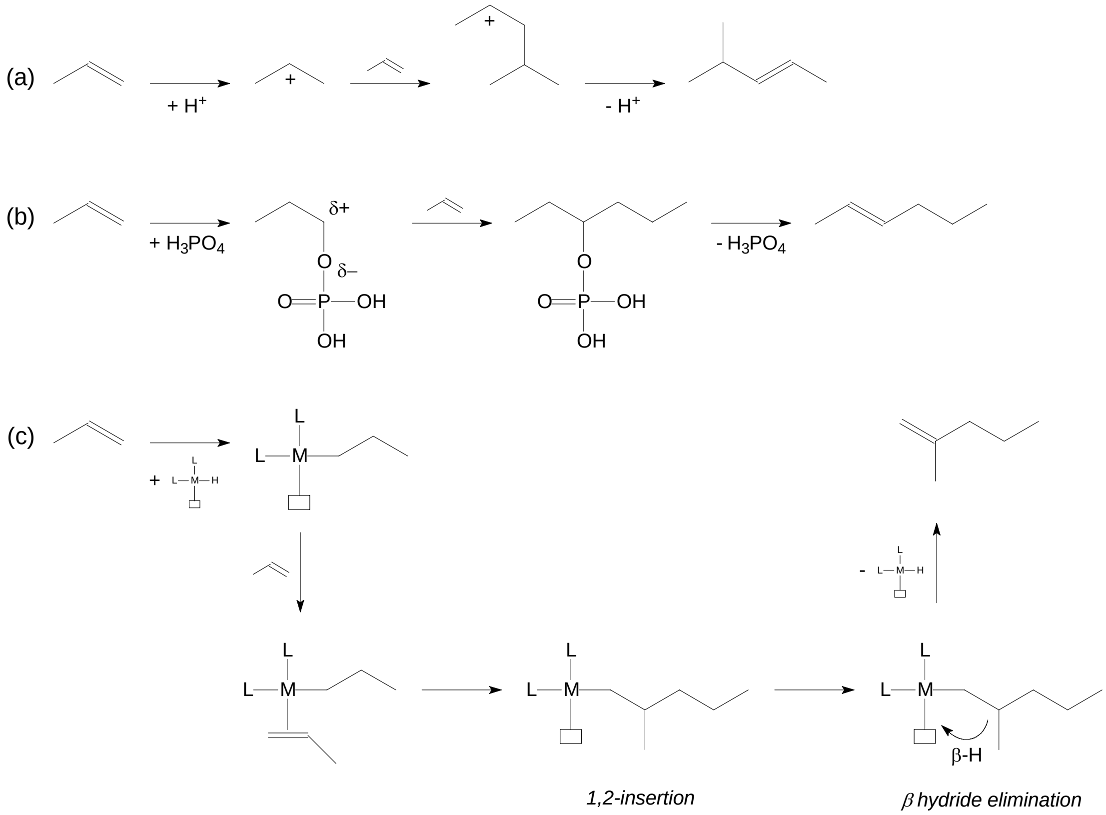

Figure 2. Olefin oligomerisation by the (a) classic Whitmore-type carbocation mechanism, (b) ester-based mechanism, and (c) organometallic catalysis by a 1,2-insertion and β-hydride elimination.

Acidic resin. The use of sulphonated styrene-divinylbenzene based resins for olefin oligomerisation, such as Amberlyst 15 (Rohm and Haas), is a fairly recent development. Resin based oligomerisation technology development received a boost with the phase out of MTBE.(31) Processes like NExOCTANE™ (Fortum Oy)(32) was developed to convert MTBE units to dimerisation units that operated at similar conditions (<100°C, liquid phase) and used the same catalyst. Other technology suppliers include Snamprogetti/CDTech, UOP and Lyondell.(33) Instead of etherifying the iso-butene, it is dimerised to trimethylpentenes that can be hydrogenated to give high-octane trimethylpentanes. This makes the technology an environmentally friendly alternative to aliphatic alkylation for the production of alkylate-quality high-octane paraffins. To maximise dimerisation selectivity and limit heavy oligomer formation, the reaction is moderated by the addition of polar compounds, typically *tert*-butanol.(34)(35) Only branched olefins are targeted for conversion, with iso-butene and iso-amylene being the main feed materials. The feed needs to be free of typical acid catalyst poisons, but oxygenates in general does not seem to be a problem, with limited side-reactions being noted during conversion over Amberlyst 15 at 70°C and 0.4 MPa.(36) The application of acidic resin catalysed oligomerisation of Fischer-Tropsch feed benefits from the oxygenate tolerance of this system, but it is only of limited use in a Fischer-Tropsch refinery, since Fischer-Tropsch olefins are mostly linear (not branched).[c]

Zeolite. The Mobil Olefins to Gasoline and Distillate (MOGD)(37) and Conversion of Olefins to Distillate (COD)(2) processes make use of a ZSM-5 based catalyst. The chemistry and catalysis of olefin oligomerisation over ZSM-5 has been studied extensively, with the pioneering work of Garwood(38) clearly showing its equilibration properties at high temperature. At low temperature, H-ZSM-5 catalyses oligomerisation with limited cracking, resulting in the formation of oligomers that are multiples of the monomer, but above temperatures of around 230°C[d] it equilibrates the carbon number distribution of the product.(39)(40) In the temperature region where the feed is "equilibrated", the process is insensitive to the carbon number distribution of the olefins in the feed and the operating conditions (temperature and pressure), as well as product recycle can be used to determine the product distribution.(41) Oxygenates are known to reduce catalyst activity,(42) but this does not preclude the use of ZSM-5 with Fischer-Tropsch feed material. The COD process operates commercially with an oxygenate containing HTFT feed. Both the MOGD and COD processes employ conditions around 200-320°C and 5 MPa. The distillate produced by oligomerisation is hydrogenated to a high quality diesel, with >51 cetane number and good cold flow properties.(2)(37)(43) The motor-gasoline is of a lower quality (RON = 81-85, MON = 74-75).(2) The linearity of the oligomers, which is responsible for the good cetane number of the diesel fuel and poor octane number of the olefinic motor-gasoline, is due to the pore constraining geometry of the ZSM-5 catalyst.(44) Despite the low coking propensity of ZSM-5, the catalyst has to be regenerated every 3 months by controlled coke burn-off. The catalyst lifetime extends over multiple cycles and overall the process is environmentally friendly. Another zeolite based process that has recently been introduced is the ExxonMobil Olefins to Gasoline (EMOGAS™) technology. In the absence of nitrogen bases, it is claimed to have a catalyst lifetime of 1 year and has been designed for retrofitting SPA-units.(45) The zeolite-type (not H-ZSM-5) has not been stated explicitly, although ExxonMobil patents[e] suggest that it is a zeolite of the MFS-type (H-ZSM-57) or TON-type (Theta-1 / ZSM-22). The carbon number distribution of the product is similar to that of SPA, with little material boiling

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[c] Linear olefins can be oligomerised, but the product will have a lower degree of branching and consequently a lower hydrogenated octane number.

[d] The exact temperature is dependent on the catalyst acid strength and other operating conditions.

[e] Patent applications WO 2001083407, WO 2003035583 and WO 2003035584.

above 250°C.(46) Other zeolites have also been investigated for oligomerisation, but generally deactivates too fast to be of commercial value in this type of service.(47)

Amorphous silica-alumina (ASA). The IFP Polynaphtha™ process was originally designed to use an amorphous silica-alumina catalyst.[f] The difference between ASA and its zeolitic counterparts, relates mainly to its lower acid strength and the less pore constraining geometry of ASA, since it is not crystalline. However, there are other differentiating features too, such as its hydrogen transfer propensity(48) and reaction by a different mechanism to the classic Whitmore-type carbocation mechanism. The latter is evidenced by its *cis*-selective nature for double bond isomerisation and the differences in products obtained from the oligomerisation of linear α-olefins and linear internal olefins.(49) It has been found that ASA catalysts work well with Fischer-Tropsch feeds, including oxygenate containing feed materials, yielding a distillate with higher density (810 $\text{kg}\cdot\text{m}^{-3}$; much needed in Fischer-Tropsch refining) than any of the other oligomerisation catalysts. However, the hydrogenated distillate has good cold flow properties, but with a cetane number of only 28-30.(50)(51) The naphtha properties are feed dependent and short chain olefins yield a better quality motor-gasoline (RON = 92-94, MON = 71-72) than ZSM-5, although the distillate cetane is of poorer quality. Similar cycle lengths and regenerability as ZSM-5 has been demonstrated in service as olefin oligomerisation catalyst, making ASA based oligomerisation technology as environmentally friendly as ZSM-5 based technology. There is also a fair amount of interest in the more structured ASA derivatives, like MCM-41, for olefin oligomerisation, but these catalysts have not yet been applied commercially.(52)(53)(54) One variation on ASA catalysts that deserve special mention is the Hüls Octol process, which uses a nickel promoted silica-alumina molecular sieve (montmorillonite)[g] catalyst.(55) For fuels applications the Octol A catalyst, which gives a more branched product, is preferred.(56) The addition of nickel to the catalyst introduces a different reaction mechanism, namely 1,2-insertion and β-hydride elimination, which implies that more than one mechanism is operative in parallel.

Solid phosphoric acid (SPA). The Catalytic Polymerisation (CatPoly) technology of UOP was the first of many solid acid catalysed olefin oligomerisation technologies to be commercialised.(57)(58) The catalyst is manufactured by impregnating a natural silica source such as kieselguhr (diatomaceous earth) with phosphoric acid. The active phase is a viscous layer of phosphoric acid on the support, with the support itself being inactive.(59) Olefin

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[f] The Axens IP 501 catalyst that is now being licensed for the Polynaphtha™ technology is different from the ASA based catalyst on which the technology has originally been developed.

[g] Personal communication with Dr. Karl-Heinz Stadler (Süd-Chemie).

oligomerisation takes place via an ester mechanism, whereby a phosphoric acid ester stabilises the polarised hydrocarbon intermediate.(60)(61) The operating temperature and amount of water in the feed determine the ratio of different phosphoric acid species on the catalyst, which in turn determines its activity and selectivity behaviour.(62) The technology was nevertheless reported to be insensitive to the feed composition (C_2-C_5 olefins)[h] and the olefinic motor-gasoline thus produced invariably has a RON in the range of 95-97 and MON in the range of 81-82.(63)(64)(65)(66) However, this does not imply that the olefin oligomers produced by different type of feed are isostructural. It was found that the quality of the hydrogenated motor-gasoline is very dependent on feed and operating conditions.(67) This is relevant to Fischer-Tropsch refining, since it is likely that at least some of the olefinic motor-gasoline will have to by hydrogenated to meet the olefin specification of motor-gasoline. Surprisingly it was found that a low temperature isomerisation pathway is operative during 1-butene oligomerisation that results in the formation of a significant fraction of trimethylpentenes.(68) It is consequently possible to produce a hydrogenated motor-gasoline with 86-88 octane from a 1-butene rich Fischer-Tropsch feed. SPA oligomerisation is not a distillate producing technology,(69) although distillate yield can be improved by manipulating the water content and operating conditions.(70) The distillate has a low cetane number (25-30), but excellent cold flow properties, making it a good jet fuel, but poor diesel fuel. Since the catalyst is influenced by water, only a limited amount of oxygenates can be tolerated in the feed and catalyst activity is inhibited at high oxygenate concentration. This limits application of SPA in a Fischer-Tropsch refinery to the conversion of the condensate streams. Attempts to use SPA catalysed oligomerisation with stabilised light oil (SLO) gave poor results(71) and some oxygenate classes were found to be especially detrimental to the catalyst.(72) SPA is a cheap catalyst and spent SPA catalyst is therefore not regenerated. The process is nevertheless environmentally friendly, because the catalyst is produced from natural silica and the spent catalyst can be neutralised with ammonia to produce ammonium phosphate plant fertiliser, rather than a solid waste.

Homogeneous catalysts. Olefin oligomerisation by the IFP Dimersol™ process,(29) is the only refinery technology where homogeneous organometallic catalysis is applied industrially.[i] The Dimersol™ process makes use of a nickel-based Ziegler-type catalyst system and oligomerisation takes place by a β-hydride elimination mechanism.(73) There are

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[h] This statement holds true only for feed materials that are not very rich in iso-butene, which gives a somewhat higher octane value.

[i] Aliphatic alkylation also employs homogeneous catalysis, but not organometallic catalysis.

a number of variants of the Dimersol™ process:(74) a) Dimersol™ E for the oligomerisation of ethylene and FCC off-gas (C_2/C_3 olefin mixture) to motor-gasoline;[j] b) Dimersol™ G for the oligomerisation of propylene and C_3/C_4 olefin mixtures to motor-gasoline;(75)(76) and c) Dimersol™ X for butene oligomerisation to linear octenes for plasticiser alcohol manufacturing.(77)(78) Because the technology makes use of a homogeneous organometallic catalyst system, it is sensitive to any impurities that will complex with the nickel. Amongst other, it is sensitive to dienes, alkynes, water and sulphur, that should not exceed 5-10 $\mu g \cdot g^{-1}$ in the feed.(76) Conversely, the advantage of a process based homogeneous catalyst system, is that the catalyst dosing can be increased to offset deactivation by feed impurities. The catalyst has to be removed from the reaction product by a caustic wash, which makes this a less environmentally friendly technology. In a more recent incarnation of this technology, called Difasol™, the catalyst is contained in an ionic liquid phase,(73) which makes catalyst separation easier. The Difasol™ process does not generate the same amount of caustic effluent as the Dimersol™ process. In a lifetime test conducted over a period of 5500 hours, it was found that the nickel catalyst consumption in the Difasol™ process was only 10% of that found with the Dimersol™ process, while that co-catalyst consumption was half.(79) There may be a competitive advantage to use the Dimersol™ X and Difasol™ technologies for the oligomerisation of Fischer-Tropsch butenes on account of their low iso-butene content, but such an application is for chemicals production, not fuels refining.

Thermal. The thermal oligomerisation of cracker gas streams to motor-gasoline had been practised widely in the past,(80)(81) but has since been completely replaced by catalytic oligomerisation. This happened not only due to the higher efficiency of the catalytic processes, but also due to the lower octane number (MON = 77)(81) obtained by thermal oligomerisation. The reaction takes place by a radical mechanism,(82) which results in the formation of products that have a low degree of branching. This explains the low octane number of motor-gasoline produced by thermal oligomerisation. Branching is not introduced by isomerisation of radicals and there is consequently similarities to Lewis acid catalysed oligomerisation, such as with BF_3.(84) Thermal oligomerisation of linear α-olefins, as is prevalent in HTFT products, results in lubricating oils with good viscosity properties.(85) Mechanistically thermal oligomerisation is better suited to the production of distillates and lubricating oils from Fischer-Tropsch products, as was indeed shown.(86) The technology

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[j] This type of technology was in commercial operation at the Sasol Synfuels site to convert excess ethylene to motor-gasoline. It was originally installed as a risk-mitigation option to avoid flaring of ethylene. The plant became redundant in the 1990's and was officially written off early in the 2000's.

unfortunately requires high temperatures. A method to overcome this shortcoming by heat-integrating thermal oligomerisation with high temperature Fischer-Tropsch synthesis has been suggested,(86) which makes the overall process more energy efficient. Attempts to further reduce the energy requirements by making use of radical initiators, such at di-tertiary butyl peroxide (DTBP), failed due to low initiator productivity.(87)

2.3. Olefin skeletal isomerisation

In a refinery the skeletal isomerisation of olefins is mainly used to convert linear olefins to branched olefins for etherification with alcohols to produce fuel ethers such as methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). There was consequently a lot of activity in the early 1990's in this field when oxygenated motor-gasoline was introduced. Industrial skeletal isomerisation processes have been developed with mostly *n*-butenes and *n*-pentenes in mind.(88)(89)(90)(91) Studies on the skeletal isomerisation of *n*-hexenes are more limited,(92)(93) since these compounds are not generally used as fuel ethers.

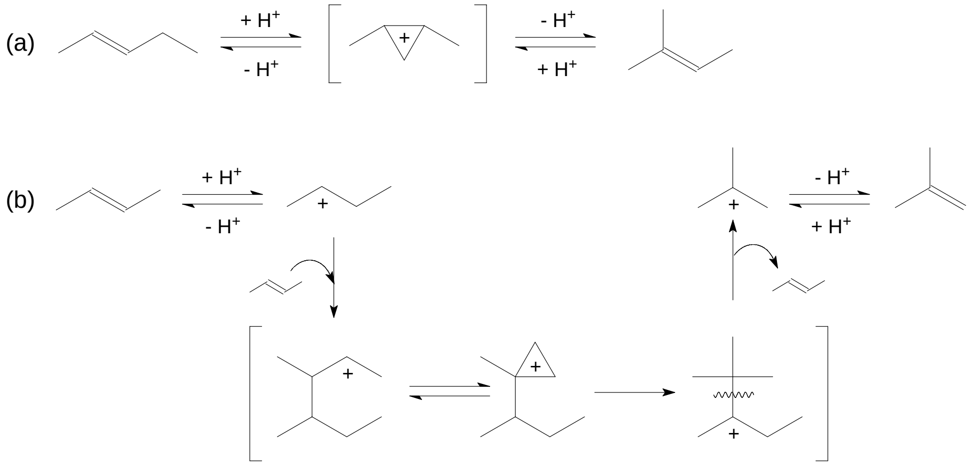

Figure 3. Skeletal isomerisation by (a) monomolecular rearrangement through a protonated cyclopropane intermediate, and (b) bimolecular mechanism involving dimerisation, isomerisation and cracking.

There are two mechanistic routes by which the skeletal isomerisation takes place (Figure 3), namely monomolecular isomerisation via a protonated cyclopropane intermediate and a bimolecular process involving dimerisation, followed by skeletal isomerisation and cracking.(88)(90)(91) The relative contribution of these two mechanisms depend on the feed material. Skeletal rearrangement via a monomolecular mechanism requires a carbon chain length of at least 5 carbon atoms to avoid the formation of a primary carbocation intermediate and is the dominant mechanism whereby pentene and heavier feeds are isomerised. The bimolecular mechanism is expected to be the dominant mechanism for butene isomerisation, but despite this seemingly simplistic explanation, the butene skeletal isomerisation mechanism is still actively being debated.(94)(95)(96)(97)

Butene skeletal isomerisation. Various catalysts have been investigated for the skeletal isomerisation of *n*-butene,(98) and it has been shown that ferrierite is by far the most selective for high temperature isomerisation, but requires operating temperatures of 350°C and higher.(90) With ferrierite it is possible to come close to the equilibrium conversion, which is a maximum at around 50% *n*-butene conversion at 350°C. At typical operating temperatures there is a gradual loss of catalyst activity due to coking.(99) For commercial processes cycle lengths in the order of 500 hours have been reported.(89) Catalyst activity is generally restored by controlled carbon burn-off. Although butene skeletal isomerisation is a fairly clean process in terms of solid waste, the high operating temperature and frequent catalyst regeneration makes it energy intensive, which increases its environmental footprint. There is no advantage in processing Fischer-Tropsch butenes over cracker-derived raffinate-II butenes and with the decline in MTBE use globally, it is not seen as an important Fischer-Tropsch refining process.[k] Nevertheless, it may be considered as feed pretreatment step for indirect alkylation,(31)(32)(34)(100) if the refinery is very octane constrained.

Pentene skeletal isomerisation. The skeletal isomerisation of *n*-pentene is more facile and a wider selection of commercial technologies is available, using different catalysts, such as acidic molecular sieves (UOP),(88) ferrierite (Lyondell)(89) and alumina (IFP).(91) From a thermodynamic, as well as an environmental point of view, it is better to operate at lower temperatures. At lower temperatures the process is less energy intensive, the equilibrium concentration of branched olefins is higher and catalyst coking is reduced. The UOP Pentesom™ process, which uses an acidic molecular sieve catalyst, makes use of this advantage and has a start-of-run temperature of less than 300°C. However, it was found that oxygenates typically present in feed materials derived from Fischer-Tropsch synthesis, adsorbs on the catalyst and requires a temperature of at least 320°C to desorb.(101) This reduces the cycle length from 1 year, that is obtainable with cracker-derived feed, to only 1-2 months with Fischer-Tropsch derived feed. Ferrierite is also negatively affected by oxygenates, but conversely, oxygenates were actually found to be beneficial during alumina

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[k] Sasol considered building a butene skeletal isomerisation plant to improve the octane number from their olefin oligomerisation process. However, after it was shown that little benefit over butene-only SPA oligomerisation could be obtained, the project was shelved. Ref.(67)

catalysed skeletal isomerisation.(102) This was indeed found in practice and after initial teething trouble,(103) the alumina based ISO-5™ process that was implemented at Sasol Synfuels was found to work well with Fischer-Tropsch pentenes. The ISO-5™ process has an operating temperature around 410°C and makes use of continuous catalyst regeneration (CCR) to burn off coke formed on the catalyst. On account of the high temperature and significant side-product formation (10-15%) of this alumina based process, it is not considered environmentally friendly. Despite its commercial implementation in a Fischer-Tropsch refinery, it is not seen as important refining technology for the future, unless future motor-gasoline specifications mandate the inclusion of fuel ethers.

2.4. Etherification

With the mandatory inclusion of oxygenates in reformulate fuels, as promulgated in legislation such as the Clean Air Act Amendment of 1990 in the USA, refiners mainly had a choice between alcohols and ethers (Table 3).(104) Ethers were preferred over alcohols for a number of reasons:

a) Ethers have a lower vapour pressure than the alcohols;

b) Ethers have a lower phase separation tendency in the presence of small amounts of water that gives it better storage and transport stability; and

c) The production of fuels ethers was a convenient way to reduce the volatile short chain olefin content in motor-gasoline.

Table 3. Blending vapour pressure (VP) at 37.8°C, boiling point (T_b) and blending octane numbers of fuel alcohols and ethers.

Compound	VP (kPa)	T_b (°C)	RON	MON
Fuel alcohols				
methanol	524	64.7	>120	95
ethanol	154	78.3	120	99
2-propanol	95	82.4	117	95
2-methyl-2-propanol	103	82.2	105	95
Fuel ethers				
2-methoxy-2-methylpropane (MTBE)	55	55.3	118	101
2-ethoxy-2-methylpropane (ETBE)	40	72.8	118	101
2-methoxy-2-methylbutane (TAME)	25	86.3	115	100

Etherification as practised industrially, is an equilibrium limited reaction between an alcohol and an olefin containing a C=C bond on a tertiary carbon (Figure 4). The reaction is catalysed by an acid and is generally performed at low temperature to favour the etherification equilibrium. The catalyst most often used for etherification is Amberlyst 15, a sulphonic acid exchanged divinylbenzene-styrene copolymer resin catalyst from Rohm and Haas, although other acidic resin catalysts(104) and zeolites(105) can also be used. The process has to be operated with an excess of alcohol to reduce olefin oligomerisation as side reaction. When an excess of alcohol is used, the catalyst protonates the alcohol and the alcohol becomes the protonating agent,(106) thereby preventing the formation of oligomers. The alcohol also acts as solvating agent, breaking the hydrogen bonds between sulphonic acid groups and thereby reducing the acid strength of the catalyst.(107) This helps to reduce oligomerisation as side-reaction.

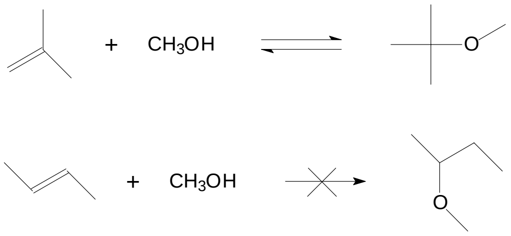

Figure 4. Etherification reaction between an olefin and an alcohol.

From a technical point of view, methanol is the preferred alcohol for etherification, since it does not form an azeotrope with water[1] and it results in a higher equilibrium ether concentration. For example, the equilibrium constant for MTBE is 32 at 70°C, but for ETBE it is only 18 at 70°C.(108) The olefin feed is refinery dependent, but isobutene that is derived from naphtha steam cracking and/or fluid catalytic cracking (FCC), is most often used on account of its high volatility. The second choice is the reactive isoamylenes, which is less volatile and therefore more easily assimilated in motor-gasoline. Rather than preparing a carbon number cut by distillation, the etherification of all reactive olefins in FCC naphtha to ethers has been investigated.(109)(110) This simplifies feed preparation, but it complicates product separation. Furthermore, it has been shown that most hexyl ethers have a low octane number.(111)

When a cracker-derived feed material is used, diene removal is a prerequisite. The dienes are very reactive and can form heavy polymers under etherification conditions. This is

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[1] Water is produced as side-product by alcohol etherification: 2 $CH_3OH \rightarrow CH_3OCH_3 + H_2O$.

not a problem when using Fischer-Tropsch derived feed, but the presence of oxygenates other than alcohols are potentially problematic. The oxygenates inhibit the etherification reaction and participate in side-reactions,(36) often forming water, which is known to inhibit the reaction.(112)

Etherification is an environmentally friendly technology. It is not energy intensive and is quite selective. However, it became a victim of politics, which resulted in a ban on MTBE in fuel in many States of the USA.(113) It is therefore doubtful that much new etherification capacity will be installed in future.

2.5. Aliphatic alkylation

Aliphatic alkylation is one of the most important technologies for the production of high octane paraffins. With fuel specifications putting increasingly tighter limits on non-paraffinic compound classes in motor-gasoline, the viability of motor-gasoline production in a refinery becomes more and more reliant on the paraffin quality of the base stock.

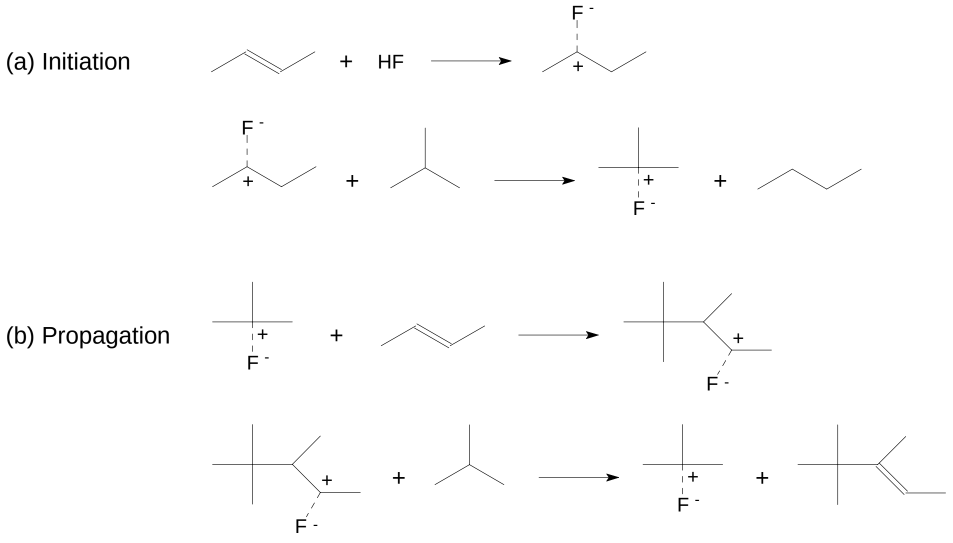

Figure 5. Aliphatic alkylation mechanism illustrated by the initiation and propagation steps involved during hydrofluoric acid catalysed alkylation of isobutane with 2-butene.

Aliphatic alkylation entails the alkylation of isobutane with an olefin (usually butene) to produce a highly branched paraffin (Figure 5). There are mainly two technology types to accomplish this, both making use of liquid acids, namely HF and H_2SO_4 alkylation.(114)(115) The field of aliphatic alkylation has seen incremental advances since its development, but a comparison of reviews shows that the same technologies that were commercially available in the 1950's,(116) are still the commercial technologies available today.(117) The projected development of solid acid catalysts for this process "[t]he trend is definitely toward solid catalysts operating at temperature that do not require refrigeration" (1958),(116) has not yet come to pass.(118)(119) The main reasons that solid acid catalysed aliphatic alkylation processes have not yet found commercial use can be traced to the rapid deactivation of solid acid catalysts that runs contrary to the high on-stream availability that is required from alkylation units.

Aliphatic alkylation units based on HF is more feed sensitive and the feed has to be dried (<20 $\mu g \cdot g^{-1}$) to limit corrosion. Other olefinic feed impurities, such as ethylene and dienes, increase the acid consumption, but can generally not justify the cost of a selective hydrogenation feed pretreatment step. The type of olefin that is used for alkylation has a significant influence on the octane number of the product (Table 4),(117) as well as acid consumption.(120) A high isobutene content in the feed is detrimental, because it rapidly oligomerises to form heavy products. The effect of oxygenates as feed impurities are still inadequately understood.(114)

Table 4. Influence of the olefin feed on the research octane number (RON) of the product obtained by isobutane alkylation with HF and H_2SO_4 alkylation processes.

Olefinic feed	Research Octane Number (RON)	
	HF-process	H_2SO_4-process
propene	90-91	88-90
1-butene	94	92-94
2-butene	>97	92-94
pentenes	-	91
mixed olefins	93	91-93

It is interesting to note that at 99% H_2SO_4 concentration, the quality of the alkylate being produced from 1-butene is better than that from 2-butene.(121) Sulphuric acid, like phosphoric acid, is capable of forming esters with olefins. It is speculated that a similar low temperature skeletal isomerisation pathway may be operative as was previously noted for solid phosphoric acid.(68) Since HTFT derived butenes are rich in 1-butene, contain little isobutene and have a low concentration of dienes, there may be some competitive advantage to use Fischer-Tropsch butenes with an H_2SO_4 alkylation process. Conversely, since HF is not isomerising and very sensitive to water, Fischer-Tropsch butenes will have a disadvantage compared to cracker-derived feedstocks.

Aliphatic alkylation not only requires olefins, but also requires isobutane and there is little isobutane in Fischer-Tropsch syncrude. This is quite the opposite of crude oil refining, where olefin availability is constraining. Even if all the n-butane in syncrude is isomerised, only part of the total butene product could be used for alkylation.[m]

The biggest drawback of current aliphatic alkylation technologies is their significant environmental footprint. Liquid acid processes are not considered environmentally friendly, especially not HF processes. Due to the current lack of alternative technologies for alkylate production in crude oil refining context, these liquid acid processes are tolerated. This may well change in future. There is luckily a more environmentally friendly Fischer-Tropsch specific alternative to liquid acid aliphatic alkylation, namely SPA catalysed oligomerisation combined with olefin hydrogenation.(122)(123)

2.6. Aromatic alkylation

Aromatic alkylation is not normally associated with refining, but rather with petrochemical production. However, with the reduction in the amount of benzene that may be included in motor-gasoline, various options for benzene reduction have been presented, amongst other benzene alkylation.(124) One of the advantages of benzene alkylation over alternatives such as benzene extraction and benzene hydrogenation, is that it retains the octane value of benzene.

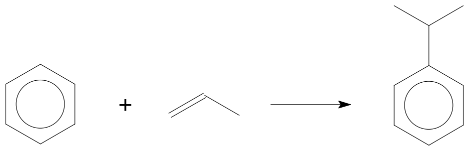

Figure 6. Aromatic alkylation with an olefin.

The alkylation of benzene with an olefin is an acid catalysed reaction (Figure 6). Various commercial processes exist for the alkylation of benzene with either ethylene or propene and the catalysts most often used are solid phosphoric acid and zeolite-type materials such as ZSM-5 (Mobil-Badger 1980's), MCM-22 (Mobil-Ratheon / Mobil-Badger 1990's), Y-zeolite (CDTech) and modified-Beta (Enichem).(125)(126) The main difference between

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[m] The PetroSA HTFT refinery is an exception, since it has an HF alkylation unit. Additional butane is available from the associated gas condensate that is landed with the natural gas. Ref.(122)

SPA and zeolite catalysed processes is that SPA has a low multiple alkylation tendency, while zeolite-based processes require a transalkylation reactor after the alkylation reactor to increase the yield of mono-alkylated products.(127) In a refining context multiple alkylation is not necessarily a problem and the choice of alkylating olefin and degree of alkylation is more a function of the desired product properties (Table 5)(5)(128) for the target fuel, namely motor-gasoline, jet fuel or diesel. The degree of alkylation can also be controlled by the aromatic to olefin ratio in the process. Aromatic alkylation processes are generally operated at an aromatic to olefin ratio of around 1:5 to 1:8 to limit multiple alkylation. This results in a benzene conversion of less than 20% per pass and necessitates recycling of the benzene. It also implies that the benzene should be purified sufficiently to enable such recycling. The other feed requirements are catalyst specific, with zeolites being more sensitive to heteroatom compounds in the feed than SPA.

Table 5. Fuel properties of some alkylbenzenes that can be prepared by benzene alkylation with olefins.

Compound	Density ($kg{\cdot}m^{-3}$)	RON	MON	Cetane
ethylbenzene	874.4	107.4	97.9	8
cumene	868.5	113	99.3	15
sec-butylbenzene	866.2	106.8	95.7	6
tert-butylbenzene	870.7	>115	107.4	-1
m-diethylbenzene	868.3	>115	97	9

It has been shown that aromatic alkylation can play an integral part in Fischer-Tropsch refinery design.(129) This allows the synthesis of specific high octane motor-gasoline components, while creating a platform for chemical growth. Since the purpose of benzene alkylation in refining context is to reduce benzene in motor-gasoline, the objective of the technology is "environmentally friendly". SPA-based alkylation is more environmentally friendly than zeolite-based processes, since the SPA is operated at a lower temperature, requires no transalkylation reaction and can be operated at a lower aromatic to olefin ratio,(130) making it less energy intensive. This is contrary to the trend for chemicals production by benzene alkylation that is moving more towards zeolite based processes.(125) SPA alkylation has also been shown to have specific benefits for application in a Fischer-Tropsch refinery, since it enables the production of on-specification fully synthetic jet fuel.(131)

2.7. Metathesis

A review of metathesis technologies shows that metathesis has not been developed with fuels refining in mind. It is used mainly in the olefins business to produce propene from ethylene and 2-butene, and vice versa (Olefins Convertion Technology - OCT, ABB Lummus and Meta-4™, IFP), as well as for the production of linear α-olefins (Shell Higher Olefins Process - SHOP, Shell).(132) Application of the OCT-process for the production of 3-hexene that is isomerised to 1-hexene has also been commercialised.(133)

The ability to change the carbon number distribution of an olefin pool may be of interest to Fischer-Tropsch refining, due to the high olefin content of the syncrude. Unlike oligomerisation that only produces heavier olefins from lighter olefins, or cracking that only produces lighter olefins from heavier hydrocarbons, metathesis produces heavier and lighter olefins, while retaining the same average molecular mass in the product as in the feed.[n]

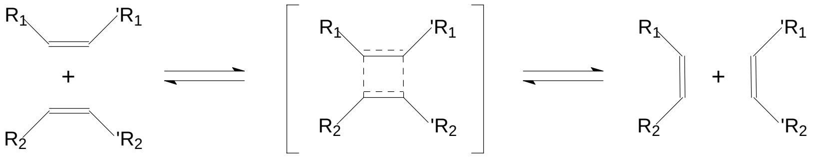

Figure 7. Olefin disproportionation (metathesis) reaction.

The metathesis reaction, which is a form of olefin disproportionation, requires an unsymmetric olefin or a mixture of olefins to result in productive disproportionation (Figure 7).(134) The most commonly used heterogeneous catalysts are based on WO_3 (OCT), MoO_3 (SHOP) and Re_2O_7 (Meta-4™). The need for frequent catalyst regeneration(135) increases the energy consumption of the process and makes it less environmentally friendly. It has also been noted that oxygenates change the catalytic behaviour of metathesis catalysts,(136) which detracts from its use in a Fischer-Tropsch environment.

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[n] Metathesis does not change the number of moles in the feed, it is a pure disproportionation reaction. When the average molecular mass of the product is different to that of the feed, it is indicative of side reactions such as oligomerisation and/or cracking.

3. Hydrogen addition

3.1. Hydrotreating

Hydrotreating is the mainstay of refining. It is the primary method to convert heteroatom containing compounds into hydrocarbons. Hydrotreating fulfils two functions in the refinery, both related to the removal of specific functional groups. Firstly it is useful as a feed pretreatment step for refinery operations that are sensitive to impurities. For example, hydrogenation of dienes to mono-olefins as feed pretreatment before aliphatic alkylation reduces gum formation during alkylation. Secondly it is used to meet final product specifications in terms of composition. For example, the hydrogenation of sulphur containing compounds to meet the sulphur specification of transportation fuel.(137) Hydrotreating is therefore often classified in terms of its function, namely hydrodesulphurisation (HDS),(138) hydrodenitrogenation (HDN),(139)(140) hydrodeoxygenation (HDO),(141) hydrodearomatisation (HDA),(142) hydrodemetalisation (HDM) and hydrogenation of olefins (HYD).(143)

Hydrotreating is invariably exothermic and the specific heat release is related to the compound type being hydrogenated (see Chapter V, Tables 5 and 6). When Fischer-Tropsch naphtha and distillate cuts are hydrotreated, the heat release can be very high.(144) This not only requires a reactor design that is capable of proper heat management, but also necessitates careful catalyst selection ensure that the reaction rate is not too high. In this respect the hydrotreating of Fischer-Tropsch materials tend to require less active catalysts in order to avoid hot spot formation and hydrogen starvation at the catalyst surface. This presents a problem, since catalyst manufacturer are discontinuing lower activity catalysts in favour of very high activity catalysts.

During hydrotreating hydrogen addition occurs. In the case of HDS, HDO and HDN, hydrogen sulphide (H_2S), water (H_2O) and ammonia (NH_3) are co-produced, which have to be removed downstream of the hydrogenation reactor. The rate of heteroatom removal for isostructural compounds is generally in the order HDS > HDO > HDN.(141) This order may change when the compounds are not isostructural.

Most commercial refinery hydrotreating catalysts are bi- or trimetallic, with Ni/Mo, Ni/W, Co/Mo, Ni/Co/Mo on alumina being the main type encountered in practice.(145) On account of the sulphur content of crude oil, these catalysts are all designed to be operated as sulphided metal catalysts and are called sulphided catalysts for short.(146) A smaller group of hydrotreating catalysts are used for selective hydrogenation and are used in the absence of sulphur. These unsulphided catalysts are generally based on Ni, Pd or Pt on alumina.[o]

The selection of hydrotreating catalysts is very application specific.(147) In practice hydrotreaters are not loaded with a single type of catalyst, but with different layers, each performing a specific function. However, it is not only the catalyst activity that is important, but also its deactivation behaviour with the intended feed.(148) Special catalyst types are often loaded on top of the main catalyst beds to help with feed distribution and to remove feed impurities that can lead to deposit formation. Catalyst grading with an HDM catalyst on top to trap metals and avoid pressure drop problems is therefore common practice.

In a Fischer-Tropsch refinery, HDO and HYD are the main hydrotreating duties required. However, the absence of sulphur in the feed creates a problem for most hydrotreating catalysts, since they have been designed as sulphided catalysts. Standard crude oil refinery hydrotreating technology is consequently ill-suited to Fischer-Tropsch feeds. This can be overcome in two ways, by either using only unsulphided catalysts, or by adding sulphur compounds to the feed to keep the sulphided catalysts in a sulphided state. It is clear that from an environmental point of view the latter is undesirable. Ironically, it is the latter approach that is followed. This is mainly due to the action of the carboxylic acids in Fischer-Tropsch syncrude that necessitates special catalyst properties, but oxygenates in general may cause problems with unsulphided catalysts not designed for HDO.(149)(150) Since the market for Fischer-Tropsch specific hydrotreating catalysts is still small, such catalysts have not yet become commercially available.

Another aspect relevant to the hydroprocessing of Fischer-Tropsch syncrude is demetallisation. In syncrude the metals are present mainly as metal carboxylates that are produced during corrosion and catalyst leaching. These metal carboxylate species can be stable under hydrotreating conditions and are not removed by standard HDM catalysts. The stability of the metal carboxylates depend on both the metal, as well as the chain length of the carboxylate. Removal of the metal carboxylates does not require hydrogenation, since it follows a thermal decomposition pathway.(151)(152) At temperatures below their decomposition temperature the metal carboxylates can cause scaling in preheaters and result in catalyst bed plugging. When the metal carboxylates decompose the metal oxide that is formed will deposit on the catalyst and may be reactive under hydrotreating conditions. When a

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[o] There are many more hydrotreating catalyst types if selective hydrogenation of specific functional groups is also considered. Such transformations are mostly found in the petrochemical industry and not in refineries, although it should be noted that many compounds present in Fischer-Tropsch syncrude are seen as chemicals.

sulphiding agent is added to keep the catalyst in a sulphided state, stable sulphides can be formed and the decomposition of iron carboxylates to yield stable iron sulphides is especially troublesome in Fischer-Tropsch refineries.(150)

3.2. Hydroisomerisation

The process of hydroisomerisation can increase the degree of branching of paraffins. This is achieved by rearrangement of the carbon chain in an analogous way to olefin skeletal isomerisation. Hydroisomerisation is divided into four categories based on the type of feed material being processed, namely isobutane production (for use in aliphatic alkylation), C_5/C_6 hydroisomerisation (for octane improvement of light straight run naphtha), C_7 isomerisation (for octane improvement, but not yet commercially available) and hydroisomerisation of waxy paraffins (for lubricating oil production). This classification may initially seem arbitrary, but it is actually based on fundamental catalytic considerations.

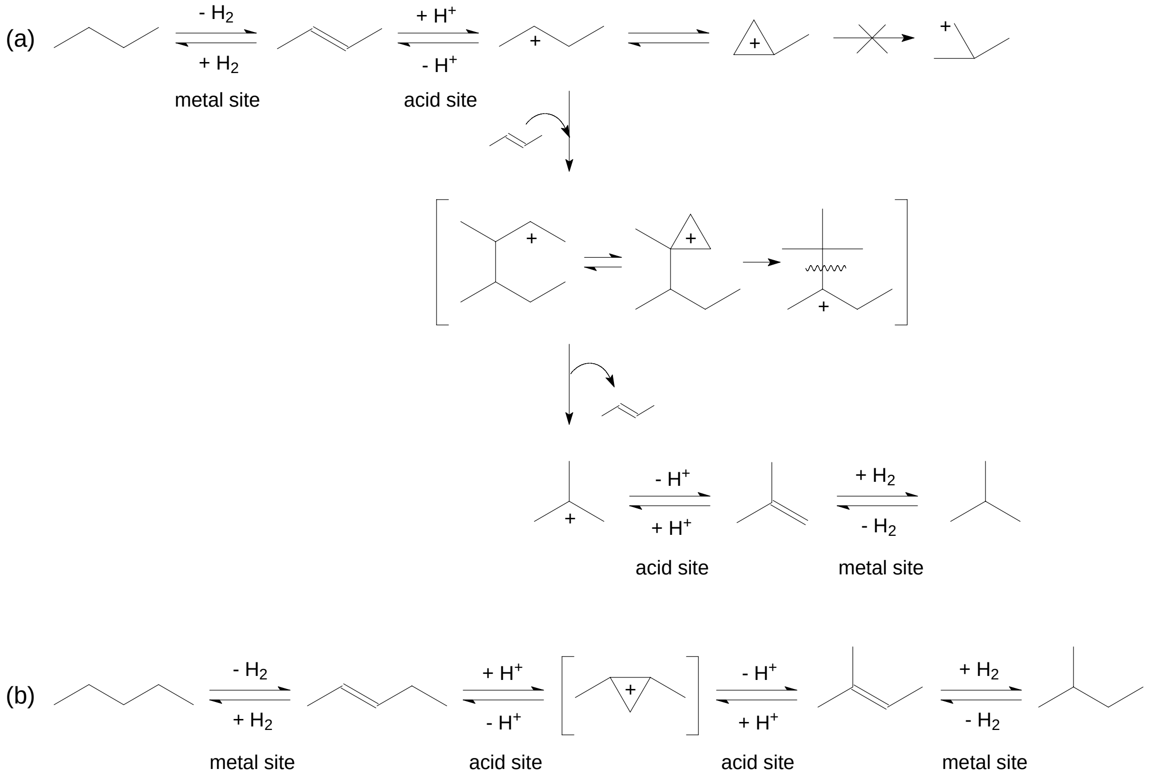

Figure 8. Hydroisomerisation of (a) butane that proceeds through a bimolecular mechanism to avoid the formation of a primary carbocation, and (b) C_5 and heavier paraffins that can proceed through a monomolecular mechanism.

Hydroisomerisation catalysts are bifunctional, since both metal sites and acid sites are necessary for the reaction to proceed (Figure 8). The metal sites are responsible for dehydrogenation of the paraffin to produce an olefin. The olefin can then be skeletally isomerised on the acid site, which is the rate determining step. The metal sites are then again responsible for the hydrogenation of the olefin.(153) The balance between metal and acid sites are important for catalyst performance, since it determines partial pressure of olefins on the catalyst surface and thereby the probability that acid catalysed side-reactions can take place, such as olefin oligomerisation and cracking.(154) The optimum metal to acid ratio, as well as acid site strength is different for the different classes of hydroisomerisation catalysts and other isomerisation mechanisms may even be operative, like in the case of butane isomerisation.(155)(156) The cracking propensity of C_6 and lighter aliphatics is low. The C_6 and lighter aliphatics cannot crack to produce a tertiary carbocation intermediate and the probability of cracking to produce less stable secondary or primary carbocation intermediates is correspondingly lower. However, a C_4 aliphatic cannot rearrange without passing through a primary carbocation intermediate, which is very unstable. The same mechanistic limitations as discussed for olefin skeletal isomerisation applies (see section 2.3). Once the carbon chain length is C_7 or longer, cracking can readily proceed, which is why there are no commercially available C_7 hydroisomerisation processes. Hydroisomerisation of waxy paraffins is always accompanied by some losses due to cracking, but this is not necessarily negative, since it is a residue upgrading technology and cracking results in the production of mainly naphtha and distillate range material. It can therefore be seen as a form of mild hydrocracking, which it indeed is.

C_4 isomerisation.(157) The principal technology for *n*-butane isomerisation to isobutane is the chlorinated Pt/Al_2O_3 catalysed Butamer™ process of UOP. It operates at 180-220°C,[p] 1.5-2.0 MPa, space velocity of 2 h^{-1} and with hydrogen to hydrocarbon ratio of 0.5-2.0. The conversion is thermodynamically limited and side-product formation is less than 2%. To maintain the acidity of the catalyst, constant chlorination is required. It is consequently important to ensure that the feed is water-free and free of oxygenates that can potentially form water at reaction conditions. The need for constant chlorination also increases the environmental footprint of this technology.

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[p] There are generally two reactors, the first reactor operating at a higher temperature to increase reaction rate and the second reactor at a lower temperature, which is thermodynamically more favourable for isobutane formation. (Equilibrium concentration of isobutane at 180°C is 60%, but at 300°C it is only 40%).

C_5/C_6 isomerisation.(157)(158)(159)(160) There are mainly three catalyst types currently being used for C_5/C_6 paraffin isomerisation, namely chlorinated Pt/Al_2O_3 (for example UOP I-8/I-80, Procatalyse IS 612, Albemarle AT-20), Pt/mordenite (for example Süd-Chemie Hysopar, Procatalyse IS 632, UOP HS-10) and sulphated zirconia (UOP LPI-100). The chlorinated Pt/Al_2O_3 catalysts have similar requirements, advantages and drawbacks as those already listed for C_4 isomerisation. The main advantage is the low operating temperature (120-180°C), which favours the isomerisation equilibrium. The main drawback, apart from the environmental concern related to the use of a chlorinated system, is the sulphur and water sensitivity of the catalyst.(161) This led to the development of Pt/mordenite zeolite catalysts, which are resistant to sulphur and water.[q] The drawback of a Pt/mordenite catalyst is that it requires a higher operating temperature (250-270°C), which is less favourable in terms of the isomerisation equilibrium. Although sulphur is not a problem in a Fischer-Tropsch environment, oxygenates and water are ever-present, giving Pt/mordenite a competitive feed advantage. This catalyst type is also more environmentally friendly, since it requires no chlorination and exceptionally long catalyst lifetimes (>8 years)[r] have been reported. Sulphated zirconia catalysts have some tolerance to water ($<35\ \mu g\cdot g^{-1}$)(163) and operate at lower temperature (180-240°C) than the zeolitic system. A catalyst cycle length of 18 months before regeneration has been reported.(159) The isomerisation equilibrium advantage gained by a catalyst operating at low temperature, can be offset by the recycling of unconverted *n*-paraffins. Various process options are possible.(164)(165)(166) In most refineries the C_5/C_6 paraffins are present as a light straight run (LSR) naphtha mixture and in all C_5/C_6 isomerisation processes there is a feed specification to limit inclusion of C_7 paraffins to less than 2%.[s] In practise the conversion of the *n*-pentane is equilibrium limited, but the isomerisation of the C_6 paraffins are slower and kinetically controlled. Of all the C_5/C_6 compounds in LSR, *n*-hexane has by far the worst octane number (Table 6) and most process configurations aim at maximising the conversion of *n*-hexane.

C_7 isomerisation.(167)(168) The C_7 content of feed to C_5/C_6 isomerisation processes is limited, due to the high cracking propensity of C_7 and heavier material. Yet, *n*-heptane has an octane number of 0 (by definition) and skeletal isomerisation would clearly be beneficial. Although progress has been made in the search for catalysts that reduce cracking and have sufficient pore diameter to allow multi-branched C_7 paraffins to diffuse, a catalyst and

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[q] New developments in this field are noted. Ref.(162)

[r] Personal communication with Dr. Karl-Heinz Stadler of Süd-Chemie (Germany).

[s] For recycle processes the inclusion of benzene and cyclohexane in the feed is also limited.

process for this purpose at this stage remains on the wish-list of refiners. The field is nevertheless actively being researched.

Table 6. Octane numbers of C_5/C_6 paraffins.(5)

Compound	RON	MON	½RON + ½MON	Relative to *n*-paraffin
C_5 paraffins				
n-pentane	61.7	62.6	62.2	-
2-methylbutane	92.3	90.3	91.3	29.2
2,2-dimethylpropane	85.5	80.2	82.9	20.7
C_6 paraffins				
n-hexane	24.8	26	25.4	-
2-methylpentane	73.4	73.5	73.5	48.1
3-methylpentane	74.5	74.3	74.4	49.0
2,2-dimethylbutane	91.8	93.4	92.6	67.2
2,3-dimethylbutane	103.5	94.3	98.9	73.5

Waxy paraffin isomerisation.(169)(170)(171)(172) Hydroisomerisation and hydrocracking of long chain paraffins always occur in parallel. The co-production of lighter products during waxy paraffin hydroisomerisation is therefore inevitable. The reaction conditions and catalyst selection can be optimised to maximise lubricating oil production. The sulphur-free nature of LTFT waxes makes them ideal feed materials for unsulphided noble metal catalysed hydroisomerisation, which is similar to that used for hydrocracking.

3.3. Hydrocracking

The shrinking market for residues (boiling point >360°C) as heavy fuels, necessitated refiners to convert residues into products in the distillate and naphtha boiling ranges. One way of accomplishing this is by hydrocracking. The aim of hydrocracking is threefold, it removes heteroatoms by hydrotreating, it cracks the heavy material to lighter material and it reduces the aromatic content, especially polynuclear aromatics content, to meet final product specifications.

The conversion of residue material into lighter boiling fractions requires C-C bond scission, which in turn requires high temperatures, even in the presence of a catalyst. In order to convert the residue at lower temperatures than required for acid catalysed paraffin cracking, hydrocracking employs bifunctional catalysts. These bifunctional catalysts have both metal and acid sites, similar to that used for hydroisomerisation. As mentioned previously, the performance of the bifunctional catalyst is determined by the balance between the metal and the acid sites.(154) The mechanism of hydrocracking follows the same basic steps as hydroisomerisation, but rather than hydrogenating the branched olefin directly, the branched olefin is cracked by β-scission before being hydrogenated (Figure 9).(173)(174)(175) Cracking by β-scission of the olefin is not the only mechanism that is operative, but it is the dominant mechanism during hydrocracking.[t] It can nevertheless be expected that the metal to acid site ratio of hydrocracking catalysts will be less than that of hydroisomerisation catalysts.

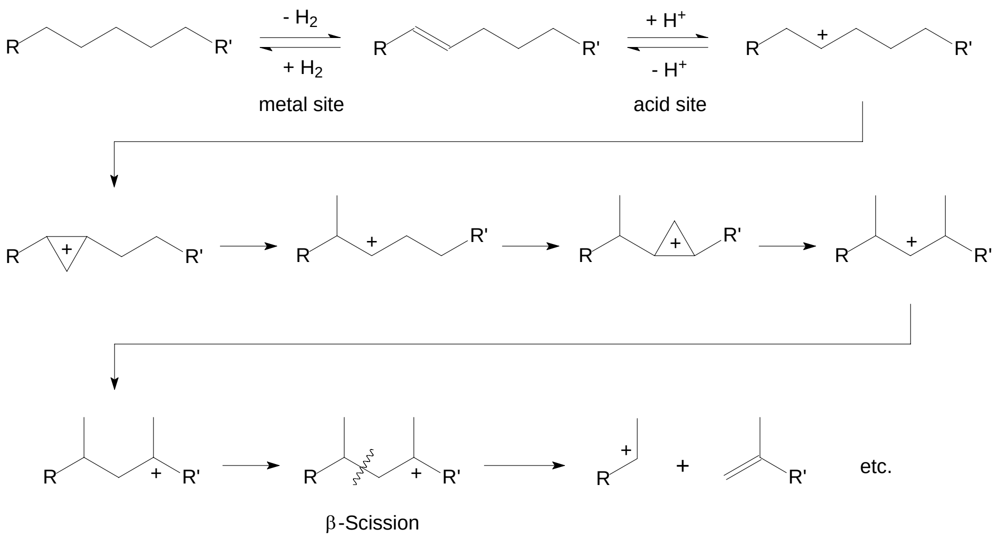

Figure 9. Hydrocracking mechanism.

The metal sites on hydrocracking catalysts are also responsible for heteroatom removal by HDS, HDO and HDN. The metal sites are similarly responsible for the hydrogenation of coke precursors, by hydrogenating aromatics that are thermodynamically favoured at high temperatures.

The conditions necessary for hydrocracking is determined by the feed quality and catalyst type, but in general hydrocrackers are operated at 360-440°C, 7-15 MPa and a space velocity of around 0.3-2.0 h^{-1}.(176) Hydrogen is co-fed in a ratio of 800-1800 normal $m^3 \cdot h^{-1}$ per 1 $m^3 \cdot h^{-1}$ of liquid feed.

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[t] During high temperature catalytic cracking of paraffins, cracking via a pentacoordinated carbocation is an important mechanistic route too. However, cracking of a carbocation that is formed by olefin protonation is much faster and therefore dominant during hydrocracking.

Hydrocracking catalysts can be divided into sulphided base-metal catalysts and unsulphided noble metal catalysts. Typical sulphided hydrocracking catalysts employ Ni/Mo or Ni/W (Co/Mo less often used) on an amorphous silica-alumina (ASA) or zeolitic support. Sulphur acts as a poison for noble metal catalysts, but with proper feed pretreatment, unsulphided noble metal hydrocracking catalysts using Pd or Pt on ASA or zeolitic supports can also used.

Hydrocracking of LTFT waxes is unique in that the feed is sulphur-free and consists of mainly linear paraffins, with small amounts of olefins and oxygenates. Unsulphided base metal hydrocracking catalysts seem to be ideal for this application, but both Ni-based and Co-based hydrocracking catalysts display high methane selectivity.(177)(178) In contrast, unsulphided noble metal catalysts seem to work very well, not only on small scale,(179) but also on commercial scale, as used in the Shell Middle Distillate Synthesis (SMDS) process in Bintulu, Malaysia.(180) The hydrocracking of LTFT waxes is much more facile that crude derived residues and lower temperatures (300-370°C) and lower pressures (3-7 MPa) can be used.(179)(180)(181)(182) The oxygenates that are present in Fischer-Tropsch products adsorb strongly on hydrocracking catalysts to cause some inhibition, but this can be beneficially used as selectivity modifier.(183)(184) In general it can therefore be said that hydrocracking has a good fit with Fischer-Tropsch product refining and although it is a fairly energy intensive processing step, unsulphided hydrocracking is otherwise an environmentally friendly technology.[u]

4. Carbon rejection

4.1. Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) is used for the conversion of heavy residues to lighter material that is more hydrogen rich in comparison to the feed. It is often the main source of short chain olefins in a crude oil refinery and its operation is generally focussed on motor-gasoline production. In larger refineries that it is close to petrochemical producers, additional revenue can be generated by selling the propylene as chemical feedstock. Refinery propylene, mainly

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[u] It is somewhat surprising that the Oryx GTL facility uses Chevron's Isocracking™ technology, which employs a sulphided base metal hydrocracking catalyst operating at medium pressure. Since the wax is sulphur free, the process requires sulphur addition to the LTFT feed.

derived from FCC, presently supplies 25% of the European propylene market, 50% of the North American market and 20% of the Asian market.(185)

Catalytic cracking is a high temperature acid catalysed process. Most FCC catalysts are based on Y zeolite (10-50%) mixed with a diluent, such as kaolin, to reduce the catalyst cost. The zeolite and diluent are contained in a matrix or binder made from silica, alumina or silica-alumina. The catalyst may additionally contain additives such as pseudoboehmite to increase cracking activity and various other promoters. During FCC operation various other catalysts (catalyst additives) may be added to the catalyst mixture to customise it for the specific feed.(186) The additives are not necessarily incorporated into the catalyst, but are co-fed with the catalyst. Some of these additives are combustion promotors (Pt or Pd salts), SO_x transfer agents (basic metallic oxides), metal traps and octane improvers (H-ZSM-5 zeolite).

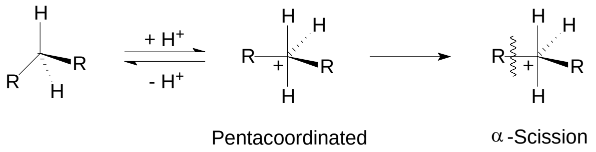

Figure 10. Cracking by protolysis involving the direct protonation of a paraffin to form a pentacoordinated carbocation that cracks by α-scission.

Catalytic cracking is similar to hydrocracking in that it uses acid catalysed cracking by β-scission to break C-C bonds and reduce the molecular weight of the product. The ease of cracking increases with the degree of branching,(27) which is introduced by skeletal isomerisation of the carbocation (Figure 9). In addition to the β-scission mechanism, cracking can also take place by protolysis, or α-scission (Figure 10). Protonation of a paraffin will yield a pentacoordinated carbon that can crack by α-scission to yield products different from β-scission, including products that would otherwise require a primary carbocation intermediate to form via β-scission. The contribution of protolysis is determined by the availability of other carbocation creating pathways and is especially important during initial conversion, before a carbocation covered catalyst surface is created.(187) Another important process during catalytic cracking is hydrogen transfer. During hydrogen transfer one molecule is dehydrogenated, while the other molecule is hydrogenated. (Acid catalysts in general have poor hydrogen desorbing capability and in instances when molecular hydrogen is detected in FCC products, thermal cracking cannot be ruled out(187)). Hydrogen transfer does not involve C-C bond scission, but affects the product selectivity to paraffins, olefins and aromatics. This process drives the carbon rejection during catalytic cracking, since heavy aromatics (coke) are formed on the catalyst surface, while the lighter cracked products are hydrogen enriched. This is also the primary catalyst deactivation mechanism(188) and the reason why FCC includes continuous catalyst regeneration (CCR).

FCC is performed at high temperature (480-550°C), low pressure (0.1-0.3 MPa) and short contact time (<10 s). Since this is not a typical fixed bed process, a short process description is necessary. Hot regenerated catalyst (680-750°C) is brought into contact with the preheated feed (200-375°C) to the bottom of a riser. This causes thermal shock and induces some thermal (radical mechanism) cracking in the feed while heat is transferred from the catalyst to the feed. As the catalyst-feed mixture travels up the riser (2-10s), catalytic cracking occurs. At the top of the riser the temperature is typically 500-530°C. The catalyst and product are then separated in a disengager to prevent further reaction. This is quite important, because it is the intermediate cracking products that are of interest. The coked (deactivated) catalyst is then returned to the regenerator where the coke is burned off with air. This provides the energy that drives the process, which is quite energy intensive.

FCC operation is generally optimised for maximum motor-gasoline production, but light gases are invariably co-produced. The light naphtha (C_5-160°C) is olefinic (60%) and contains about 20% aromatics, giving it reasonable octane properties (RON=90-95, MON=75-82). The kerosene or heavy naphtha (160-220°C) typically has 20% olefins and 70% aromatics, with similar octane properties. The distillate cut (220-350°C) is called light cycle oil (LCO) and contains in the region of 80% aromatics. All products still contain sulphur.(186) The yield structure is influenced by the feed. The gasoline yield at constant severity gives some indication of the reactivity of the different hydrocarbon classes during FCC conversion:(186) polynaphthenes ≈ mononuclear aromatics (60%) > mononaphthenes (45) > branched paraffins (28) > *n*-paraffins (17) > dinuclear aromatics (10).

The small amount of residue from HTFT is too little to justify FCC and the hydrogen rich waxes from LTFT are not typical FCC feedstocks. Catalytic cracking of Fischer-Tropsch waxes has nevertheless been studied.(189)(190)(191)(192)(193)(194) The paraffinic nature of the feed results in very high motor-gasoline yields being obtained (almost double that with normal crude oil derived feed) and in the presence of ZSM-5, high gas production is obtained too. Although these studies showed that waxes are good feed materials for FCC, the rationale of using FCC for wax upgrading has to be different to that in a crude oil refinery. No carbon rejection is required to enrich the hydrogen content of Fischer-Tropsch residue material, since it is already quite hydrogen rich. FCC is consequently not a technology that will naturally be considered for Fischer-Tropsch refining, unless motor-gasoline production is the main aim.

When wax hydrocracking was compared to FCC of wax for the production of transportation fuels, FCC was more economical.(195) However, the naphtha fraction from Fischer-Tropsch synthesis is already very olefinic and the good octane claimed for the motor-gasoline from FCC of wax(193)(194) cannot be realised by direct blending in a Fischer-Tropsch refinery, due to the limitation on the olefin content of motor-gasoline.

FCC technology can in principle also be used in petrochemical applications for the conversion of more oxygenate rich HTFT feed to produce light olefins. Such a unit has recently been commissioned at Sasol Synfuels and is based on the KBR Superflex™ Catalytic Cracking (SCC) technology. The SCC converts oxygenate rich C_6-C_7 HTFT naphtha into ethylene, propene and high octane motor-gasoline. The SCC technology differs from standard FCC technology mainly in terms of operating temperature, which is 50-80°C higher. This implies that there is a significant contribution from thermal cracking.(196) The SCC technology has been designed to operate at even higher end-of-riser temperatures (>600°C) than deep catalytic cracking (DCC) processes that are typically operated in the temperature range 525-595°C.(197)

Despite this commercial development, in fuels refining context, FCC has a poor fit with Fischer-Tropsch feed compared to alternative residue upgrading technologies such as hydrocracking. Furthermore, a shorter catalyst lifetime is predicted due to hydrothermal dealumination of the catalyst by oxygenates in the riser and water produced by the more hydrogen-rich “coke” entering the regenerator.

4.2. Coking

Coking is used to convert heavy residues to coke and lighter fuel products. The coke has a high carbon to hydrogen ratio, making it suitable for metallurgical applications, but it may also be used for heating. It can therefore be seen as an extreme carbon rejection technology, because about 30% of the feed mass is rejected as coke(198) (in FCC it is only about 4%). Since the coke is effectively the rejected carbon and contains most of the sulphur and metals, the lighter products are comparatively hydrogen enriched and partially desulphurised, making them more amenable to conventional refining to transportation fuels. Contrary to what the name suggests, the aim of coking in a refinery is not to produce coke, but to produce hydrogen enriched distillates. The lighter products are rich in olefins, which makes coking also a source of olefins for motor-gasoline production.

Table 7. Homolytic bond dissociation energy of some C-H and C-C bonds at 298 K.

Homolytic bond dissociation reaction	Bond type	Dissociation energy	
		(kcal·mol^{-1})	(kJ·mol^{-1})
Paraffinic C-H bonds			
$CH_4 \rightarrow CH_3\bullet + H\bullet$	C-H	104.9	439
$C_2H_6 \rightarrow CH_3CH_2\bullet + H\bullet$	C-H	101.1	423
$C_3H_8 \rightarrow (CH_3)_2CH\bullet + H\bullet$	C-H	98.6	413
$C_4H_{10} \rightarrow (CH_3)_3C\bullet + H\bullet$	C-H	96.5	404
Paraffinic C-C bonds			
$C_2H_6 \rightarrow CH_3\bullet + CH_3\bullet$	C-C	90.1	377
$C_3H_8 \rightarrow CH_3CH_2\bullet + CH_3\bullet$	C-C	89	372
$C_4H_{10} \rightarrow (CH_3)_2CH\bullet + CH_3\bullet$	C-C	88.6	371
$C_4H_{10} \rightarrow CH_3CH_2\bullet + CH_3CH_2\bullet$	C-C	87.9	368
Olefinic C-H bonds			
$CH_2{=}CH_2 \rightarrow CH_2{=}CH\bullet + H\bullet$	C-H	110.7	463
$CH_2{=}CHCH_3 \rightarrow CH_2{=}CHCH_2\bullet + H\bullet$	C-H	88.8	372
Olefinic C-C bonds			
$CH_2{=}CHCH_3 \rightarrow CH_2{=}CH\bullet + CH_3\bullet$	C-C	101.4	424
$CH_2{=}CHC_2H_5 \rightarrow CH_2{=}CH\bullet + CH_3CH_2\bullet$	C-C	100	418
$CH_2{=}CHC_3H_7 \rightarrow CH_2{=}CH\bullet + (CH_3)_2CH\bullet$	C-C	99.2	415
$CH_2{=}CHC_2H_5 \rightarrow CH_2{=}CHCH_2\bullet + CH_3\bullet$	C-C	76.5	320
Aromatic C-H bonds			
$C_6H_6 \rightarrow C_6H_5\bullet + H\bullet$	C-H	112.9	472
$C_6H_5CH_3 \rightarrow C_6H_5CH_2\bullet + H\bullet$	C-H	89.7	375
Aromatic C-C bonds			
$C_6H_5CH_3 \rightarrow C_6H_5\bullet + CH_3\bullet$	C-C	103.5	433
$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2\bullet + CH_3\bullet$	C-C	77.6	325

Coking is a non-catalytic thermal process that relies on homolytic bond scission to form radicals for the reaction to proceed. The likelihood of bond rupture at a given temperature is determined by the bond dissociation energy (Table 7).(199) The temperature must therefore be high enough to promote bond scission and temperatures of 485-505°C are typically used in cokers. The feed composition determines the coke yield and feed materials with a high Conradson carbon residue produces more coke. The Conradson carbon, as determined by the ASTM D189 method,(200) is not numerically the same as the Ramsbottom carbon (ASTM D542),(201) but these values as highly correlated. Both are measures of the carbon residue forming potential of a material when subjected to high temperature.

There are mainly two types of coking, namely delayed coking and flexicoking. In delayed coking the process is operated batchwise, with coke being produced as by-product. The feed is heated to cracking temperatures in a furnace and then allowed to soak in drums to complete the thermal conversion of the feed. In flexicoking the process is continuous, with almost complete conversion of the feed into gaseous and liquid products. The coking is done in a fluidised bed, with the coke being fed to a gasifier to produce a low heating value gas, similar in composition to blast furnace gas.(198) Both processes are energy intensive, which is their main drawback from an environmental point of view. Fischer-Tropsch products can be thermally cracked,(202)(203)(204) but are not suited for coking, because of their low Conradson carbon content.[v]

5. Hydrogen rejection

5.1. Thermal cracking

Historically thermal cracking processes were classified as gas-phase or mixed-phase. Gas-phase processes typically operated at temperatures around 620°C and at low pressure, while mixed-phase processes operated in the temperature range 450-540°C.(7) Steam cracking (gas-phase) is generally associated with the petrochemical industry for the production of ethylene, as well as for the production of products such as propylene and butadiene.(205) In fuels refineries a less severe form of thermal cracking is found, namely visbreaking (mixed-phase). The term “visbreaking” is derived from “viscosity breaking”, since this form of thermal cracking had previously been used to reduce the viscosity of fuel oils.(206)(207)

Thermal cracking has also been used in some of the German Fischer-Tropsch plants and has since then found its way into other Fischer-Tropsch refinery strategies. In this respect it is presently considered as upgrading pathway for LTFT naphtha from GTL plants such as Oryx GTL, with specific feed benefits being claimed.(208) Cracking of LTFT waxes has been investigated as way to produce fuels, candle wax and lubricating oils.(202)(203)(204)(209)(210)

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[v] The delayed coker plant at Sasol Synfuels makes use of coal pyrolysis material.

The process is non-catalytic and follows a radical mechanism (Figure 11), with propagation steps that may involve reactions such as intermolecular radical transfer, intramolecular decomposition and thermal dimerisation.[w] Hydrogen is rejected as molecular hydrogen during thermal cracking.(212) The mechanism is the same as for coking, but with the difference that aromatics formation (coke precursors) is generally limited. Aromatic compounds can in principle be formed, but thermal cracking processes are operated in such a way that the residence time is limited to avoid excessive formation of aromatics.

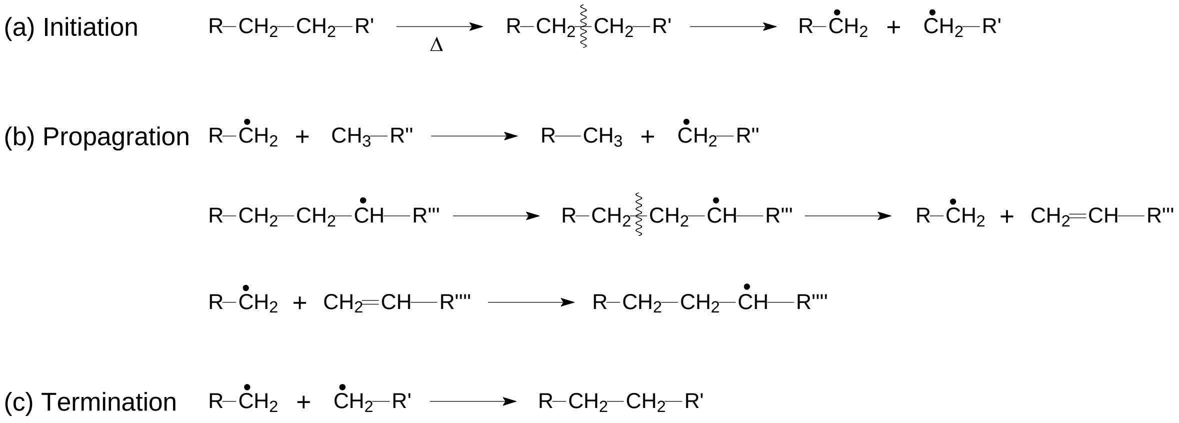

Figure 11. Thermal cracking by a radical mechanism, showing that propagation may take place by hydrogen atom abstraction (radical transfer), intramolecular cracking to produce an α-olefin and radical addition to an olefin (thermal oligomerisation).

At cracking temperatures in the range 420-500°C it was found that the product distribution from the cracking of Fischer-Tropsch waxes can be described by the Rice-Kossiakoff mechanism.(204) Oxygenates can also be thermally cracked and may either be initiated by hydrocarbon decomposition, or direct homolytic bond dissociation of the oxygenate. It should be noted that there are significant differences between the bond dissociation energies of oxygenates and oxygenate radicals. For example, it requires 349 $kJ \cdot mol^{-1}$ to convert butanone (MEK) into an acetyl and ethyl radical,(199) but only 40 $kJ \cdot mol^{-1}$ to liberate CO from the acetyl radical.(213)

Apart from the energy intensive nature of thermal cracking, it is a very clean technology. In comparison to hydrocracking it is less efficient for fuels refining, but has been shown to have some advantages over hydrocracking when it come to chemicals refining. It has been demonstrated that the <370°C boiling fraction has a high linear α-olefin content (about 40%) and that the medium wax fraction could find application as candle wax. (204)

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[w] Intramolecular isomerisation is also possible, although this type of isomerisation is limited to isomerisation of the radical position by 1-4 and 1-5 hydrogen transfer, which does not affect the skeletal structure. Ref.(211)

5.2. Catalytic reforming

Initially catalytic reforming was developed to upgrade low octane naphtha to a high octane product that is rich in aromatic compounds.(214) The hydrogen that is co-produced during this process has since become equally important,(215) due to the increasing pressure on refineries to increase their hydroconversion severity.(216)

The main reaction classes found during catalytic reforming are dehydrogenation-hydrogenation, aromatisation, cyclisation, isomerisation and hydrogenolysis. The reaction network is quite complex and is discussed in detail in literature.(217) The rate limiting step is alkane activation,(218) which is an endothermic process and one of the reasons why catalytic reforming is done at high temperature. By increasing the temperature (severity of operation) the octane number of the final product can be increased and catalytic reformers are typically operated in such a way that the product (reformate) is of sufficiently high octane to meet octane demand in the refinery. Two types of catalytic reforming are distinguished which have markedly different response to the nature of the feed.

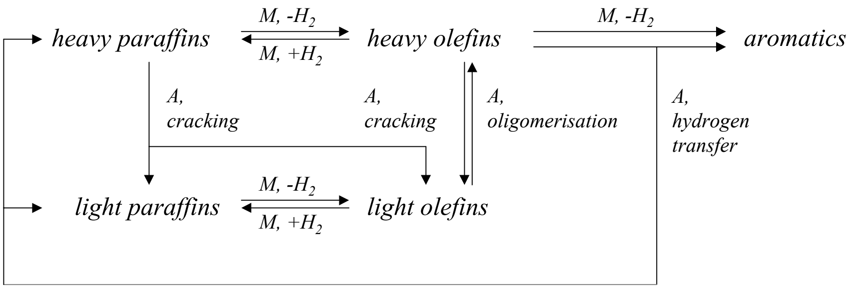
Pt/Al_2O_3 reforming. Almost all catalytic reformers found in crude oil refineries uses Pt/Al_2O_3 based bifunctional catalysts. The first platinum based reforming process to be used for refining is the UOP Platforming™ process that came on stream in 1949.(219) The platinum is often stabilised by the addition of a second metal, which in most cases is rhenium, tin or iridium. The support material is acidified by the addition of chloro-alkanes (such as CCl_4 or C_2Cl_4), which also helps to retard platinum agglomeration and aids platinum re-dispersion during regeneration.(215) The acidity of the support is necessary to catalyse skeletal isomerisation reactions such as the conversion of alkylcyclopentanes to cyclohexane species, which is a prerequisite for aromatisation. The feed plays an important role in determining the severity of operation necessary to achieve the desired reformate octane. Cyclo-paraffins (naphthenes) react much faster than acyclic paraffins and feed materials containing a high concentration of naphthenes are called rich naphthas. Rich naphthas require less severe conditions than lean naphthas to obtain the same reformate octane number. The richness of naphtha is often expressed by the number N+2A, where N refers to the percentage naphthenes in the feed and A refers to the percentage aromatics in the feed. Synthetic naphtha, like that from Fischer-Tropsch synthesis, is especially poor feed, since it contains very little naphthenes and aromatics. The conversion of synthetic naphtha therefore results in much higher gas-make and lower aromatics yield compared to crude derived feed at similar

conversion.(214) The carbon chain length of the paraffins in the feed also has an impact, with paraffin reactivity for catalytic reforming by Pt/Al_2O_3 catalysts increasing in the order $C_6 < C_7 << C_8 \approx C_9$ and heavier. The aromatics yield is consequently determined by $N+2A$ number and the nature of the paraffins in the feed. This can only partially be compensated for by the severity of reforming, since coke formation increases rapidly with an increase in temperature. Typical operating ranges are 490-525°C and 1.4-3.5 MPa for semi-regenerative (SR) reforming and 525-540°C and 0.3-1.0 MPa for reformers with continuous catalyst regeneration (CCR).(214)(215)(220) Although Pt/Al_2O_3 based reforming is a key refining technology that is very important for clean fuels production,(221) it is not an environmentally friendly technology. It is energy intensive and requires continuous addition of chloro-alkanes to keep the catalyst active. It has also been shown that Fischer-Tropsch feeds can be classified as extremely lean naphthas, making them poor feed materials for Pt/Al_2O_3 reforming. Furthermore, Pt/Al_2O_3 reforming catalysts are chlorided, which requires the feed to be dry. This further detracts from the use of Pt/Al_2O_3 reforming with Fischer-Tropsch derived feed, since it requires deep hydrodeoxygenation to remove the oxygenates present in Fischer-Tropsch derived feed.

Pt/L-zeolite reforming. The Aromax™ (Chevron Phillips Chemical company)(222) and RZ-Platforming™ (UOP)(223) technologies use monofunctional Pt/L-zeolite reforming catalysts. These catalysts have no acidity and any residual acidity in the L-zeolite structure is generally removed by ion exchange with potassium and barium. These catalysts have demonstrated very high selectivities for the aromatisation of especially C_6-C_7 paraffins and are in general considerably more active and selective for the aromatisation of *n*-paraffins.(224) The main drawback of these catalysts are their extreme sensitivity to sulphur poisoning.(225) This requires additional precautions to remove sulphur in the feed to levels below $0.05\ \mu g \cdot g^{-1}$. Sulphur removal presents no difficulty when this technology is employed with Fischer-Tropsch derived feed, since it is already sulphur-free. The effect of oxygenates on a Pt/KL-zeolite has been studied and it was found that oxygenates and CO suppressed conversion, while water had no effect.(226) This indicated that Fischer-Tropsch feeds, even containing some oxygenates, are good feed materials for Pt/L-zeolite reforming. The suitability of this technology to refine Fischer-Tropsch products has been voiced for quite some time by Mark E. Dry, one of the key figures in the development of Fischer-Tropsch technology.(227)(228) Selectivity to aromatics from *n*-paraffins are high and hydrotreated HTFT feed material from Sasol Synfuels has been successfully piloted with the Aromax™ catalyst, yielding better than predicted hydrogen and aromatics yields.(229) Environmentally speaking, Pt/L-zeolite reforming is a much cleaner reforming technology than Pt/Al_2O_3 reforming. Although it also requires high operating temperatures, it does not require constant chloro-alkane addition and a catalyst lifetime of around a year has been reported, despite its low operating pressure (0.3-1.0 MPa).

5.3. Aromatisation

The aromatisation of C_3-C_5 hydrocarbons is related to reforming, but such units are generally not associated with refineries. The aim of LPG aromatisation is to convert normally gaseous paraffins to aromatic-rich liquid hydrocarbons. Like reforming, an added advantage is the co-production of hydrogen.



M = metal function on catalyst (e.g. Zn, Ga, Pt, Pd, Ag)
A = Bronsted acid function on catalyst

light = C_5 and lighter
heavy = C_6 and heavier

Figure 12. Reaction network during aromatisation on a bifunctional metal promoted zeolite (ZSM-5 type) catalyst.

It has been shown that light paraffins can be activated and aromatised on H-ZSM-5, without the rapid catalyst deactivation being seen on many other acidic zeolites.[x] Hydrogen rejection occurs by hydrogen transfer to olefins,(231) which limits the aromatics yield that can be obtained. H-ZSM-5 nevertheless formed the basis of the M2 Forming process (Mobil).(232) However, when a metal is added to produce a bifunctional catalyst, the hydrogen can be desorbed as molecular hydrogen and the aromatics yield is substantially increased.(233) The reaction network shown in Figure 12 illustrates the role of both acidic and metallic sites on the catalyst. Commercial LPG aromatisation processes use bifunctional catalysts and are either based on Zn/ZSM-5 (for example the Alpha process of Asahi) or Ga/ZSM-5 (for example the Cyclar process of BP). Operating conditions are in the range 450-520°C and less

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[x] Although ZSM-5 has a lower coking tendency than β-zeolite and Y-zeolite, it also has a much larger coke capacity than less coking zeolites such as faujasite. More coke lay down is therefore required before complete deactivation occurs. Ref.(230)

than 1 MPa pressure. These processes are characterised by periodic operation. Each production cycle (in the order of 2 days) is followed by a regeneration cycle during which the coke on the catalyst is removed by controlled coke burn-off. During coke burn-off, some water is generated that cause hydrothermal dealumination of the zeolite and result in eventual catalyst deactivation.(234) Numerous reaction-regeneration cycles are nevertheless possible, albeit being dependent on the water partial pressure and exposure time to water vapour during regeneration.(235) Water vapour that is produced during coke-combustion is unavoidable, but the water partial pressure is actually controlled by the water content in the nitrogen recycle gas. Nitrogen is recycled to dilute the air that is used for combustion and it is impractical to remove all the water vapour from this high temperature gas stream. In this respect the application of LPG aromatisation within a Fischer-Tropsch refinery has an advantage. The air separation units associated with synthesis gas production, also produces nitrogen as by-product. It is consequently not necessary to recycle nitrogen, since nitrogen is available as fatal by-product from air separation and can be employed on a once-through basis to reduce the water partial pressure during regeneration.

From the reaction network (Figure 12) it is clear that any hydrocarbon feed material can in principle be used. However, it may not be economical to use a C_5 and heavier liquid hydrocarbon feed. Metal promoted ZSM-5 aromatisation processes have a liquid yield of around 60-70%, which implies a significant loss of liquid volume when the feed material is a liquid hydrocarbon stream.

The use of LPG aromatisation for the upgrading of light Fischer-Tropsch fractions has been suggested(122) and the upgrading of HTFT naphtha has also been investigated. In the latter application it was found that the oxygenates present in HTFT naphtha is detrimental to the catalyst lifetime, causing not only hydrothermal dealumination, but also selective loss of the metal.(236)

The environmental footprint of LPG aromatisation is determined mainly by the high operating temperature and frequent catalyst regeneration. It is not worse that FCC, although it approaches refining from the other end, namely converting light gases into liquid products.

5.4. Alcohol dehydration

Aliphatic alcohols are primary Fischer-Tropsch products and alcohol dehydration technology is therefore a form of conversion that can be considered. It is not a technology that is associated with crude oil refining, which is hardly surprising considering that alcohols are not found in crude oil.

During alcohol dehydration hydrogen is rejected in the form of water, thereby converting the alcohols into olefins. This can be especially beneficial in reducing the complexity of Fischer-Tropsch aqueous product refining.(237) By converting the alcohols into olefins, the separation of alcohol-water azeotropes can be avoided. The olefins are easily separated from the water and the olefins can then be co-processed with the rest of the Fischer-Tropsch olefins. Another application of alcohol dehydration that is becoming important is the partial dehydration of alcohols to ethers, which are employed as high cetane additives for diesel fuel.(33)(238) Since ether formation is accompanied by an increase in molecular mass, it is also a convenient way to shift naphtha range alcohols into distillate.

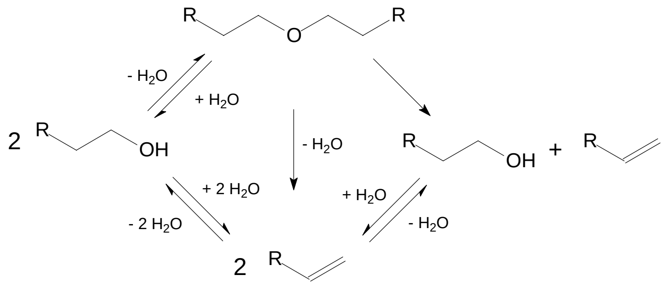

Figure 13. Alcohol dehydration by indirect bimolecular dehydration to an ether and direct monomolecular dehydration to an olefin.

Dehydration is an acid catalysed endothermic reaction. There are two mechanistic pathways (Figure 13), namely direct monomolecular dehydration of the alcohol to an olefin and the bimolecular dehydration to the ether, which can be followed by monomolecular dehydration to produce an olefin.(239) Methanol, because it contains only a single carbon atom, can only dehydrate to the ether and not directly to an olefin. Strictly speaking the dehydration reaction is reversible, but the equilibrium favours dehydration. For example, ethanol dehydration to diethyl ether and ethylene are the least favourable of the dehydration reactions, but at 300°C equilibrium constants are 3.9 and 320 respectively.(240)(241)

During commercial operation water is typically co-fed with the alcohols to reduce the adiabatic temperature decrease. The water co-feed also reduces side-reactions, since the water dilutes the surface concentration of the alcohol.(242)

The range of catalysts that can be used for alcohol dehydration is limited to those that are water-tolerant.(243) Industrially the catalyst that is most often employed for alcohol dehydration is alumina.(244) Alumina is stable in the presence of large amounts of water at the operating conditions required for dehydration, namely 300-400°C and near atmospheric pressure.[y] It is a clean conversion, albeit being energy intensive.

Dehydration to ethers is performed at lower temperatures (<250°C) and higher pressures, with acidic resins being the preferred catalysts to use. This is also a clean conversion, also from an energy usage perspective.

Dehydration of Fischer-Tropsch aqueous product alcohol mixtures to olefins has been practised commercially. The dehydration of alcohols on η-alumina is not affected by the presence of carbonyls and carboxylic acids. These oxygenates are also converted, but it was found that the alumina catalyst deactivated in a matter of days for such conversions, albeit without affecting the catalyst's activity for the alcohol dehydration reaction.(245)

It should be noted that the reverse reaction, namely olefin hydration, may also be relevant in a Fischer-Tropsch context. Ethylene hydration to ethanol is a useful way to convert ethylene into a transportable product when the Fischer-Tropsch refinery is not close to a petrochemical market. The ethanol itself can even be added to the fuel. Ethylene hydration is a commercial phosphoric acid catalysed process.(246) Propylene can also be hydrated to produce isopropanol,(247) but is less important in a refining context, since propylene has numerous other refining pathways. Like dehydration, hydration catalysts also need to be water-tolerant and only a limited number of catalysts have been investigated for this purpose.(248)

6. Discussion

Refining technologies have been evaluated in terms of their compatibility with Fischer-Tropsch syncrude as feed and their environmental friendliness. The selection of technologies for use with Fischer-Tropsch syncrude cannot be done purely on a theoretical basis, but will always to some extent be dictated by the refinery design. Nevertheless, the guiding principle should be to select the most environmentally friendly refining technologies for the task.

Since the term "environmentally friendly" has become charged with emotion and filled with political undertones, its meaning in the present context will be made clear. It is used as a term to describe the collective impact of aspects that would make a technology less efficient or cause it to generate more waste products than necessary for the conversion of

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[y] The dehydration temperature required depends on the feed. The conversion of ethanol to ethylene requires a higher temperature than any of the other alcohol dehydration reactions. It is also far easier to dehydrate

interest. The following specific aspects have been considered for the different refining technologies previously discussed (Table 8):

a) *Fischer-Tropsch fit*. If a technology is compatible with Fischer-Tropsch syncrude, it implies that the least effort will have to be expended in feed pretreatment and that the conversion itself will be suited to deal with type of molecules present in the feed. Although this does not render the technology environmentally friendly, it is likely to be less wasteful than other technologies having the same aim, but a poorer Fischer-Tropsch fit.

b) *Waste generation*. All irreversible processes or activities generate waste (second law of thermodynamics), whether it be wasted energy or "low energy" by-products. It is therefore not helpful to consider waste generation per se, but to rather focus on the generation of waste in excess of the norm. For example, the solid waste resulting from unloading a spent catalyst from a refinery process is the norm and deviations from this norm would be the generation of excessive amounts of spent catalyst waste, or very hazardous catalyst waste.

c) *Chemicals addition*. The nature of refining is such that it deals with chemicals, some of which are quite hazardous. The type of chemicals that will be highlighted as increasing the environmental footprint of the technology, are those that are either present in very large volumes, or those that are destructively added (non-catalytic) to make the process work. It should be noted that in some instances this is done to gain energy efficiency and a trade-off is involved.

d) *Energy requirements*. Processes that are energy intensive, or operate at high temperature, are considered less environmentally friendly, since they indirectly generate waste. High temperature processes are usually, but not necessarily more energy intensive than low temperature processes.[z]

The summary presented in Table 8 makes it clear that a Fischer-Tropsch refinery will look very different to a crude oil refinery. Technologies such as FCC, coking and Pt/Al_2O_3 catalytic reforming, that are the mainstay of crude oil refineries, have poor compatibility with Fischer-Tropsch syncrude. The design of Fischer-Tropsch refineries, taking cognisance of the technology selection, will be explored in the next chapter.

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branched alcohols than linear alcohols. The operating temperature can be lowered by using a more acidic catalyst, but side-reactions such as olefin oligomerisation may become a problem.

[z] A proper evaluation of the energy use of processes has to take waste heat recovery into account. It is recognised that proper quantitative analysis is necessary to correctly rank technologies with respect to their energy requirements, but such a detailed analysis has not been attempted.

Table 8. Compatibility of refining technologies with Fischer-Tropsch syncrude and their overall environmental friendliness.

Refining technology	Catalyst	FT-fit	Waste	Chemicals	Energy use
Double bond isomerisation	Alumina	Good	Low	None	High
Oligomerisation	Acidic resin	Average	Low	None	Low
	ZSM-5	Good	Low	None	Moderate
	ASA	Good	Low	None	Low
	SPA	Good	Low	None	Low
	Homogeneous	Average	Moderate	Ni-complex	Low
Olefin skeletal isomerisation	Ferrierite	Average	Low	None	High
	Alumina	Good	Low	None	High
	Acidic molsieve	Poor	Low	None	Moderate
Etherification	Acidic resin	Average	Low	None	Low
Aliphatic alkylation	HF	Poor	Low	HF	Low
	H_2SO_4	Average	Moderate	H_2SO_4	Low
Aromatic alkylation	SPA	Good	Low	None	Low
	Zeolite	Average	Low	None	Moderate
Metathesis	Metal oxide	Average	Low	None	Moderate
Hydrotreating	Sulphided	Average	Low	DMDS	Moderate
	Unsulphided	Average	Low	None	Low
Hydroisomerisation	Pt-alumina	Poor	Low	Chloroalkane	Low
	Pt-zeolite	Good	Low	None	Low
	Pt-metal oxide	Good	Low	None	Low
Hydrocracking	Sulphided	Average	Low	DMDS	High
	Unsulphided	Good	Low	None	High
Fluid Catalytic Cracking	Zeolite	Poor	Low	None	High
Coking	Thermal	Poor	Low	None	High
Thermal cracking	Thermal	Good	Low	None	High
Catalytic reforming	Pt/Al_2O_3	Poor	Low	Chloroalkane	High
	Pt/L-zeolite	Good	Low	None	High
LPG aromatisation	Metal/ZSM-5	Average	Low	None	High
Alcohol dehydration	Alumina	Good	Low	None	Moderate
	Acidic resin	Good	Low	None	Low

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CHAPTER VIII

Refinery design

Refineries are complex systems and the relevance of "chaos" theory to the description of refineries has been pointed out. This served as a warning that a purely mathematical approach to refinery design may yield optimal theoretical designs, but not necessarily operable practical designs. A distinction has been made between conceptual and real-world refinery design. Whereas the development of conceptual refinery designs require only the feed description, product requirements and knowledge of the conversion processes, real-world refinery designs are also influenced by other aspects, such as the refinery location and secondary design objectives.

1. Introduction

It is quite possible to deal with refinery design in similar terms as any other discipline dealing with inputs and outputs, such as business planning, manufacturing design or even authoring. For example, most of the goals of software engineering(1) are equally applicable to refineries: low cost of production, high performance, portability (or flexibility in refining parlance), low cost of maintenance, high reliability and delivery on time. Although the analogy to refinery design is appreciated, no attempt will be made to repeat the reasoning that has already been properly documented in textbooks. In essence it is believed that refinery design is a creative process, that can be aided by a systems approach, but cannot be efficiently replaced by it.

In the Prologue (Chapter I) the importance of issues such as energy security and environmental impact have already been mentioned. Considering an investment in a refinery as a business decision with the sole objective of making money, is therefore patently wrong. To quote from a discussion on the nature of organisations:(2) "It often seems that organizations exist simply to make money, but in reality this is rarely the case, though, of course, money plays an important part". Not all refinery design decisions are subject to the engineering favourites, optimisation(3) and economic evaluation.(4) These two disciplines tend to reduce refinery flexibility, something that should not be done during the conceptual refinery design phase. It may lead to a wonderful refinery design on paper, but an untenable design in practice. The lessons that can be learnt from the wonderful book on Systemantics by John Gall(5) should not be lost on refinery designers – refineries are complex systems and subject to all the peculiarities associated with complex systems. The behaviour of complex systems is also closely linked to "chaos" theory, as illustrated by the well-known novels on chaos theory by Michael Crichton(6)(7): "Jurassic Park" and "The Lost World". This field is considered so relevant that the introduction to refinery design is intentionally interrupted to emphasise this point. A simple mathematical example illustrates the potential impact of underestimating be behaviour of complex systems.

The Mandelbrot-set (Figure 1) is generated by plotting the number of iterations that is required for a simple equation (Equation 1) to reach a threshold criterion (Equation 2). The three-dimensional picture is represented in two-dimensions as a contour-plot of *j* for various values of *c*. The value of *c*, which is a complex number, is represented as x,y-coordinates with the real-value plotted on the x-axis and the imaginary-value plotted on the y-axis.

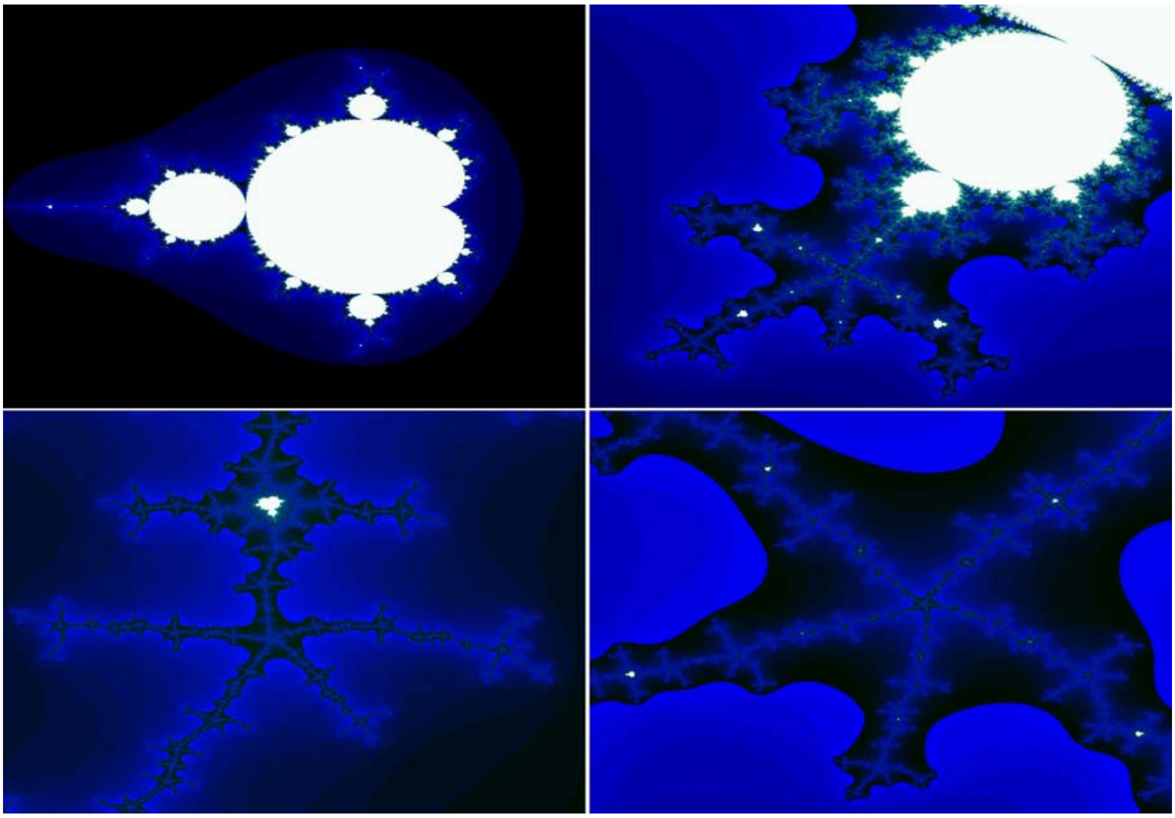

Figure 1. Mandelbrot-set showing the significant amount of variation, even when the zoom level is increased. Clockwise from the top left, the values of c being plotted are (-2+1.5i to 1-1.5i), (-0.65-0.51i to -0.45-0.71i), (-0.625-0.668i to -0.605-0.688i), and (-0.615-0.683i to -0.6137-0.6843i).

$$z_{j+1} = z_j^2 + c \qquad \text{... (1)}$$

$|z_j| > 2$ ... (2)

Despite the simplicity of the mathematical description, it is impossible to a priori predict the answer. Furthermore, even a small change in the value of *c*, can significantly change the answer, making even interpolation dangerous. There is beauty in Figure 1, but also a warning. Unless a refinery design is clearly in a stable region, small changes in feed composition or refinery operation may render the refinery inoperable. It is therefore recommended that refinery designs should have as little as possible complexity, with as much flexibility as it would allow.

The basic treatment of refinery design that is presented in this chapter focuses mainly on practical aspects and may not satisfy our more mathematically inclined brethren. The aim of this chapter is to specifically highlight the importance of design objectives and how these influence refinery designs. This does not imply that a more theoretical / mathematical based approach to refinery design is wrong. However, as already cautioned, a mathematically optimum refinery design runs the risk of being brilliant only on paper. A distinction is therefore made between conceptual refinery design and real-world refinery design.

2. Conceptual refinery design

Irrespective of the complexity inherent in refinery design, some basic steps can be identified that are common to all design approaches. In the development of any process configuration, three inputs are implicitly required, namely:(8)(9)

a) Feed description. This defines the nature of the feed material that will be refined.

b) Product description. Fuel specifications and the product slate required.

c) Processes. Conversion, separation and utility processes to be considered.

This effectively determines the scope of work for the project and contains sufficient information for the conceptual development of a refinery configuration. With this level of detail, only conceptual studies are possible. It is nevertheless useful, since it allows refinery design to be studied divorced from the factors influencing real-world refineries. In this way the limitations and sensitivities of different refinery designs can be probed, without getting bogged down in the additional complexity introduced by issues such as refinery location. This conceptual approach will be used in the next chapter to study Fischer-Tropsch refinery configurations.

It has already been noted that refinery design is essentially a creative process and that there are different tools and methodologies to guide this process. It is nevertheless instructive to look at some of the approaches that have more recently been followed for refinery designs:

a) *Linear programming.*(10) Design constraints such as fuel specifications and objective functions like minimum capital cost or highest distillate yield, can be incorporated in a linear programming model. This enables the solution of a complex optimising problem. However, it presupposes the development of multiple refinery configurations. Accurate modelling of the various refinery units is imperative to the success of linear programming.

b) *Hierarchical design.*(11) A design hierarchy (Figure 2) has been proposed for refinery debottlenecking, which can also be used to guide design. It is akin to the Michael Jackson programming approach,(1) were the data flow, “in” transformed to “out”, determine the structure of the design. In the hierarchical design approach, the feed flow is used to determine design bottlenecks and it can also be used for analysing sub-systems of the refinery. For example, hydrogen availability can be used to drive refinery design.(12)

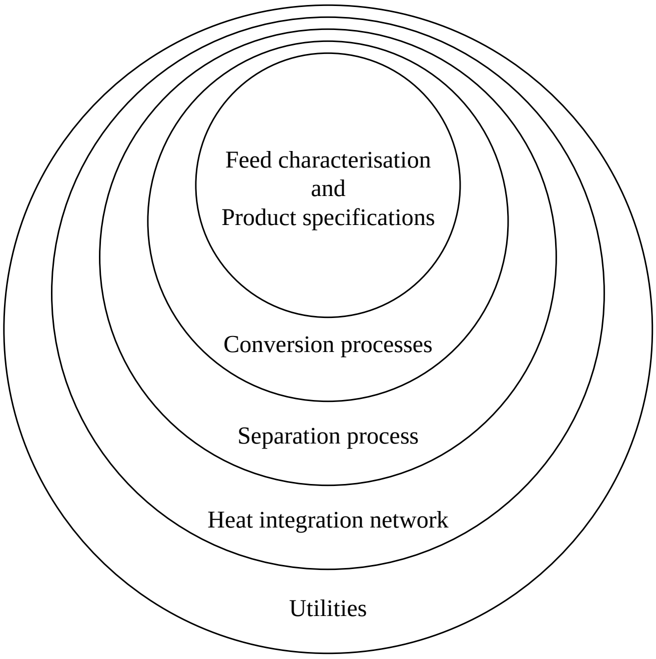

Figure 2. General refinery design hierarchy adapted from ref.(11).

c) *Technology pre-selection.*(13) An interesting approach to refinery design has been followed by Nai Y. Chen, one of the ZSM-5 pioneers at Mobil research. Refining technology has been pre-selected based on its environmental footprint and the refinery design was then done based on a logical ordering of the more limited set of technologies. A variation on this is to make use of pre-selection based on technology compatibility to the feed material.(14)

In all instances the design process relies on some underlying refinery design logic that has to be applied. The logic being referred to, is the logic associated with the knowledge of different refining technologies, their feed requirements and their objectives. This has been discussed in the previous chapter (Chapter VII). For example, when a heavy paraffin cut has to be refined, it is logical to look at separation technologies and residue conversion technologies first, while olefin upgrading technologies can be ignored.

3. Real-world refinery design

Real-world refinery designs, as opposed to conceptual studies, have the aim of producing a practical refinery design for a specific purpose. There are many factors influencing real-world refinery designs and when this added layer of detail is considered in the design process, the design becomes unique. It should be emphasised that beyond the conceptual stage, there is no such thing as a generic or even general refinery design, despite many real refinery designs being close to each other.

In this section some of the important factors affecting real-world refinery designs are discussed. It will be shown that this is not just an added layer of detail that is superimposed on the conceptual refinery design, but that it dictates the design by influencing the feed and product description, as well as the process selection. The arbitrary feed, product and process selection that can be made during conceptual designs now becomes a requirement or consequence of factors such as location, market and politics.

3.1. Refinery type

The selection of refinery type is a business decision and constitutes the *primary design objective*. There are three main crude oil refinery types, namely fuels (energy refinery), petrochemicals and lubricants (non-energy refineries).(15) It is also possible to combine these different refinery types to yield a mixed-type of refinery that could have some economic benefits.(16) The decision nevertheless remains one made by the business as an investment decision that fits into its overall business strategy.

3.2. Products and markets

The type of products and the market into which the products will be sold, forms part of the business decision to build a specific type of refinery. The identification of a market gap, or strategic positioning within a specific market may drive this investment decision. The products and markets should be considered together, since the products determine what will be made, while the markets determine the product specifications.[a] For example, a refinery producing fuels for the current Central African market will look considerably different to a refinery with the same product distribution but targeting the European market a decade into the future.

In principle all refinery designs should aim to meet a future demand in a market requiring future fuel specifications. Anticipating changes in fuel specifications is therefore not merely a mental game, but could have a huge impact on the cost and complexity of a refinery design. This places the discussion on future trends in fuel specifications (Chapter II) into perspective. It is inevitable that there will be a number of years' difference between the time at which the refinery design is frozen and the time when the refinery has been constructed, commissioned and is in production. The importance of refinery design flexibility cannot be over emphasised, since it is almost inevitable that the refinery will have to be modified in some way during its existence to keep up with changes in fuel specifications.

3.3. Feedstock

In a crude oil refinery the feedstock, or basket of crudes that is selected, has a significant impact on the profitability of the refinery. The range of crudes that can be processed is determined during the refinery design phase and flexibility to deviate from the design basis is determined by processing constraints. For example, if the distillation units were designed for Arabian Light (54% <350°C material), it is quite possible to exchange it with crudes such as

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[a] Understanding the market may in some instances be much more than adhering to or anticipating specifications. This is especially true of speciality markets for petrochemicals, but may also be true of fuels. A classic example can be found in the history of the oil industry. When Marcus Samuel (founder of Shell) took on Standard Oil (of John D. Rockefeller) in the Far East, the plan hinged on the efficiency of shipping kerosene in bulk, rather than in tins that had to be packed in wooden cases (both the tins and wood being expensive). However, when the kerosene was placed in the market at half the cost of Standard Oil's, nobody wanted it. It turned out that the tins played a vital role in the Far Eastern way of life, since the tins could be re-used for the manufacture of household items like buckets, cups, etc. The tins were therefore more important to the market than the kerosene! See ref.(17) pp.48-49.

Iranian Light (55% <350°C material), but not with Algerian Hassi Messaoud (75% <350°C material) or South American Bachequero (30% < 350°C material).(15) The price differential between low quality heavy crudes and good quality light crudes can exceed US$ 10 per barrel, but the refining infrastructure and operating cost required to process poorer crudes may not justify the selection of cheaper feed.(18)

Since the nature of the feedstock determines the refining effort to produce the required product slate, care should be taken to match the feedstock to the product requirements. For example, it would make better sense to select Venezuelan Tia Juana or Bachequero crudes that naturally yield good lubricating oil properties as feed for a lubricant refinery, rather than selecting a crude oil that requires significant processing to achieve the same result.(19)

It may also happen that exploiting a specific feedstock is driving the decision to build a refinery. This typically happens when energy security features on the political agenda of a country. This is especially true of coal-to-liquids facilities, where energy security issues require a specific type of feedstock to be used. Likewise, when the scare of global warming requires a renewable energy source to be selected, biorefineries leap to mind.(20) In such cases the feedstock is pre-selected and is the driver for the refinery design, rather than a marketing opportunity or specific product demand.[b]

In a Fischer-Tropsch refining environment the feed material has less of an impact on the refinery design. Irrespective of whether it is a biomass-to-liquids (BTL), coal-to-liquids (CTL) or gas-to-liquids (GTL) facility, the feed is first converted to synthesis gas, thereby making all feed materials equivalent. It is therefore the choice of Fischer-Tropsch technology that determines the properties of the syncrude that has to be refined, not the feed. However, the properties of the feed may still influence the refinery design in an indirect manner. For example, if the coal requires low temperature gasification, some tar pyrolysis products will be co-produced, which in turn will require tar refining to be included in the overall refinery design. Similarly, the gas used in a GTL process may have some associated condensates, which requires co-processing in the refinery. Some of these integrated refinery scenarios have been explored previously.(14)

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[b] A word of caution is prudent. When a refinery is designed on political preference or based on a trend, it is critical to ensure that the design is robust enough to weather a reversal in political opinion or change in trend. For every trend there is a potential trend killer. It may be easy to spot the trend, but not always so easy to spot the trend killer. For example, with instability in oil supply, coal-to-liquids becomes fashionable as means of energy security, but the trend killer is the perceived link between CO_2 emissions and climate change.

3.4. Location

The importance of selecting the location of the refinery is like the three P's of property investment – "position, position and position". Generally refineries are located close to the source of the feedstock, or on trade routes with easy access to feedstock. Most crude oil refineries are consequently situated at the coast with easy access to shipping for supply of feed and export of product. Inland refineries are less common and require either a local feed source, or access to a pipeline for supply. In the case of Fischer-Tropsch based refineries it has thus far been the practise to situate the facility close to the feed source. Solids handling is generally more difficult and expensive than fluids handling, making it almost imperative to situate CTL and BTL refineries close to the source of the feedstock. The same applies to GTL refineries, since GTL facilities need to compete with liquefied natural gas (LNG), which is effectively the transportation alternative.

Yet, in selecting a location there are other aspects to consider that may outweigh positioning the refinery based on feedstock only. The location impacts directly on the refinery design and operation in terms of design details and cost. Some of these location specific aspects to consider are:

a) *Climate*. This determines the insulation, heating and cooling requirements. In extreme climates, such as found in the Arctic, or Middle Eastern desert, special measure may be required to deal with either heating or cooling.[c] The material of construction is also influenced by the climate, with atmospheric corrosion in coastal regions generally being higher than for inland locations. The recent spate of hurricanes in the Gulf of Mexico also illustrated the potential effect of extreme weather phenomena on refineries.(21)

b) *Geology*. The geology of the refinery site may require special measures to be taken in site preparation and construction. Examples of such measures include the strengthening of foundations for earthquake protection and the use of deep foundations in marshy ground to ensure that construction is supported by bedrock.

c) *Natural resources*. The lack of sufficient water or water of acceptable quality to make use of a standard cooling water design, may add to the refinery cost. For example, refineries in the Middle East generally employ salt water cooling systems.

d) *Environmental sensitivity*. Working in a sensitive ecology can markedly affect construction and operating practices. This is also true of facilities that are situated close to communities. It may be required to use quiet rotating equipment, ensure that emissions[d] are lower than legal limits and invest in plant beautification. Construction in such areas needs to be especially well-planned, since future expansion possibilities might be limited. Future site remediation and environmental impact of operations may dictate some design decisions, such as on-site effluent treatment and investment in low emission technologies only.

e) *Utility access*. Power and potable water may not be readily available. In locations where the power grid is already taking strain, it may be prudent to invest electricity generation. In remote areas where potable water supply and sewerage works are not available, construction of such utility systems may have to be undertaken.

f) *Location factor*. Cost estimators use the location factor as a measure to indicate the impact of the location on the construction cost. The location factor tends to be higher for inland locations and locations far from a significant skills base. If the refinery is not situated close to a commercial harbour with the infrastructure to off-load large vessels, the supply and transport of equipment can become an issue. Unit sizes may have to be restricted to facilitate road transportation and it will also impact the construction schedule. Although this might seem like a once off impact, it is not. Siting a refinery in a remote location where living conditions are not considered desirable can result in a much higher operating cost too. It may be necessary to pay more for labour (need for "location allowances"), work force productivity may be lower and it may also be more difficult to attract and retain skilled personnel.[e] It may even be necessary to establish new towns.

g) *Legislation*. Refinery design is subject to various laws, such as the environmental legislation. This may require investment in technologies for CO_2 sequestration or even prevent the use of some technologies, such as HF alkylation. The intellectual property protection provided by the legislature is also an important consideration, since inadequate licensor protection might limit the basket of technologies that can be licensed for the refinery design. Legislation will also govern future operation of the refinery, noting that the profitability of the refinery will be affected by labour laws, tax laws,(23) competition laws, etc.

h) *Politics*. The local, national and international politics of the region could have an impact on the refinery design. Preferred suppliers and boycoting of suppliers will affect the technology selection. Global politics may also influence the refinery design. For example,

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[c] These measures transcend the equipment design. For example, the lubricating oils for rotational equipment needs to be suited for the climate.

[d] Communities may even rebel at perceived emissions, such a steam.

[e] This can be a very serious consideration. The significant performance deterioration seen at Sasol 1 after 1976 has been directly attributed to the loss of key personnel to the Sasol 2 and 3 projects. Ref.(22)

the United States government placed restrictions on the supply of technology to countries like Iran, which implies that a refinery design for Iran will be limited in its technology selection. Other issues that may affect refinery construction and operation include security, crime, labour unrest, government integrity and local bribery practices.

i) *Marketing logistics*. Although the product and market selection can be done independently of the refinery site selection (product can be exported), the latter will impact the refinery design. The location will impart a location advantage or disadvantage for the different products. For example, a fuels refinery close to an international airport will have a location advantage for jet fuel, which will outweigh that of diesel fuel, with its more diffuse market distribution and a refinery design favouring jet fuel over diesel fuel production would make more sense. The refinery configuration is not only affected by the market for final products, but it may also be affected by the market for intermediates and blending components. When a refinery is close to other refineries and petrochemical producers, business agreements can be put in place to simplify the refinery design. By inter-refinery exchange of intermediate products, which cannot be sold to consumers, final products can be prepared by blending. In this way refineries can decrease the capital investment required to refine products to specification. It may also be beneficial to deliberately sell a specific product as an intermediate, rather than refining it at all. For example, the Oryx GTL facility in Qatar produces a Fischer-Tropsch naphtha that is not refined to motor-gasoline, but rather sold as naphtha feed to the nearby naphtha crackers. Conversely, when the refinery is far from petrochemical markets, it may be necessary to convert high value olefins such as ethylene and propylene into fuel. In a Fischer-Tropsch refinery the same may apply to the reaction water oxygenates.(24) Transportation of reactive intermediates over long distances could also present problems, with routing being dictated by local legislation and possibly the need for re-purification closer to the market.[f]

j) *Patents*. Unless protection for a technology is filed very widely, some countries may have been omitted. The presence or absence of relevant patents in a specific country may either create an opportunity or provide an obstacle to the refinery design. This is especially relevant to Fischer-Tropsch refining, where “freedom to operate” in South Africa is virtually guaranteed by the commercial South African Fischer-Tropsch refineries. This is not true in other countries, where the patent landscape is more involved.

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[f] Transportation of carcinogenic substances such as benzene might be prohibitively expensive and routing benzene through some countries may even be illegal. Other chemicals may have insufficient storage stability and require re-purification, such as 1-pentene for co-monomer use.

3.5. Secondary design objectives

The importance of *secondary design objectives* should not be underestimated, since it is these objectives that influence the details of the design. These should be set by the business to guide the refinery design to meet the current financial situation, strategic direction and even to reflect the corporate culture. Examples of such secondary design objectives, sometimes erroneously called a "wish list", are:

a) *Minimise capital expenditure*. This directive is necessary when the gearing of the company is high and additional capital cannot be raised through share issues. The impact of this on a refinery design is to invest in the least expensive configuration that will meet the primary design objective. Typical side-effects of spending the least amount of capital are reduced flexibility (more units operating at or close to nameplate capacity), increased operating cost (more labour intensive units with less automation[g]), reduced on-line availability (less redundant equipment, such as spare pumps) and increased maintenance cost (less expensive materials of construction and quality of equipment).

b) *Maximise nett present value (NPV)*. In a refinery there is a limited refining margin available to generate profit and in a regulated environment, like South Africa, there is a fixed difference between the feedstock cost and the product price. Any capital spent on the refinery to keep up with changing fuel specifications, per definition has a negative NPV. Such expenditures are seen as part of the cost of staying in business. The NPV can only be positively affected if the yield of final products per unit volume of feed is increased, a cheaper feed stock can be used to produce the same products, or the product slate is changed to contain more high value products. In this respect the options open to the refinery designer are limited by the limitations placed on the refinery type, feed selection and product slate. Generally the highest NPV can be obtained by producing more non-energy products, such as chemicals.

c) *Smallest environmental footprint*. It is wrong to state that more environmentally friendly technologies cost more, although they generally do. In the previous chapter (Chapter VII), the environmental impact of refining technologies were discussed and it should be clear that there are often more than one way to achieve a specific outcome during refinery design.

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[g] The level of automation is a detailed design issue, but some technologies lend themselves to a low degree of automation (like hydrocracking), while others demand a high level of automation (like FCC).

Environmentally friendly design is part of responsible engineering and it should always be a design objective.

d) *Maximum liquid product volume*. In fuels refining this strategy often forms the basis for maximising refinery profitability. Fuels are sold by volume and an increase in the volume of final products per unit volume of feed generally translates into increased profits. This will drive refinery technology selection away from conversion processes that reduce the liquid volume of products and will tend to drive refinery design to maximum motor-gasoline production. In instances where the product slate definition leaves little leeway for a shift to motor-gasoline, the refinery design will tend to focus on hydrogen addition processes, since these would reduce the density and increase the volume of products. Focussing on maximum product volume may also drive refinery design to increase investment in processes for the conversion of light olefins to fuels, such as olefin oligomerisation, etherification and aliphatic alkylation.

e) *Refinery flexibility*. Energy markets are cyclic, as typified by the “summer driving season” and “winter heating market”. The same holds true of chemical markets. Refineries are therefore exposed to these variations. It is a business decision whether it its better to invest in the capital necessary for refinery flexibility, or whether the production surplus will rather be sold at discounted prices. Investing in refinery flexibility also has other benefits, namely, that it will be easier to meet future specification changes (smaller chance of specific units constraining refinery upgrades), plant upsets are easier to deal with (re-routing of streams is possible) and plant shutdowns are less constraining (more capacity to work away product). However, added refinery flexibility may come at the cost of added complexity, but this is not necessarily the case.

f) *Least refinery complexity*. The most elegant refinery designs are those where the refinery has the most flexibility with the least complexity. Unfortunately “complexity” can be an ambiguous term and should be defined. Cost estimators define complexity in terms of the type and/or number of units in a plant or refinery, which can then be used to estimate the capital cost.(25)(26) Although this may sound like a sensible definition for capital cost estimating purposes, it does not capture the interdependency of units and amount of work performed (operating cost) to make a final product. It is suggested that refinery complexity should rather be expressed in terms of the number of refinery units a molecule visits before ending up as a final product. This definition is a measure of the refining efficiency (rather than size), since it is a measure of how much work is performed on a molecule before it can be sold. Such a definition would imply that a refinery with more units, but less inter-unit transfers is less complex than a refinery with fewer units, but more inter-unit transfers.[h] Using this definition it implies that refinery complexity can be reduced by proper molecule management (efficient design),[i] which ensures that the feed to each separation and conversion unit is well matched to that unit. Because this definition gives an indication of inter-dependency, it follows that refinery stability increases with decreasing complexity (an upset in one unit is less likely to affect the operation of the other units). A reduction in refinery complexity therefore has a positive impact on the operability of the refinery, although it may not necessarily imply that the refinery has less units, or that it is a cheaper refinery design to construct. However, it does imply that the cumulative capacity of all units on a feed basis will be less for a refinery with a lower complexity.

g) *Shortest time to completion*. Time pressure on the project schedule is driven by economics, which may be linked to a transient window of opportunity. Whatever the business reason, the construction schedule of a refinery can only be reduced by selecting commercial technologies with a low construction (not refinery) complexity. Technologies requiring specialised manufacturing, exotic materials or highly skilled artisans to construct are automatically disqualified from the design.

3.6. Other issues

Refinery designs may be influenced or restricted by other issues too. Foremost amongst these are agreements and intellectual property rights. Instruments for the protection of intellectual property rights, such as patents, may preclude the use of specific technologies. Conversely, agreements, such as joint ventures, may lock the refinery design into the use of specific technologies. For example, Sasol has a joint venture agreement with Chevron that necessitates the use of Chevron hydrocracking technology for all GTL refineries.

Likewise there may be contractual obligations and restrictions that may lock the refinery production into a specific market or out of a market. For example, until December 2003 the Sasol Synfuels refineries were locked into a supply agreement with the other oil companies in South Africa. On termination of that agreement, the Synfuels production

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[h] In mathematical terms this can be expressed using digraph theory. Ref.(27) If the refinery is represented as a weighted digraph, the weighted indegree of each node (refinery unit) can be calculated (sources and sinks are excluded from this calculation). The refinery complexity can then be expressed as the average indegree per node divided by the cumulative outdegree of all sources.

[i] Molecule management relies heavily on proper separation. Sloppy separation can cause increased refinery complexity or decreased refinery efficiency, because some molecules are routed to the wrong units. This may even necessitate pre- or post-treatment steps that could otherwise have been avoided.

volumes were no longer restricted, but they were no longer guaranteed of a market either. With no guaranteed market, it was found that the motor-gasoline to distillate ratio produced by the refinery was not aligned with the product ratio that could be sold into the local market.

There may also be licensing limitations. The licensors of technologies may have reasons for not licensing their technology for a specific application or to a specific company. This will restrict the refinery design, especially if it is a key technology that cannot be licensed and where there is not an equivalent alternative technology that can be licensed instead.

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CHAPTER IX

Conceptual Fischer-Tropsch refinery designs

Refinery designs were developed for maximum motor-gasoline, jet fuel and diesel fuel production from syncrude. Both high temperature Fischer-Tropsch (HTFT) and low temperature Fischer-Tropsch (LTFT) are considered. In all instances it was possible to present at least one design where the targeted fuel could be produced with a 50% or better yield, without resorting to a very complex design. In most designs seven or less conversion units were required in the oil refinery to refine the syncrude to fuels meeting Euro-4 specifications. When aqueous product refining was added, two additional conversion units were needed. Only diesel fuel refining presented a problem, since it was limited by a cetane-density-yield triangle. The naphthenic compounds required to produce diesel fuel in high yield that meets both cetane and density requirements, are not abundant in syncrude. Significant synthetic effort would be required to produce such compounds from a Fischer-Tropsch feedstock and no technologies are commercially available to do so. It was concluded that syncrude (HTFT and LTFT) is on a molecular level unsuited for maximising Euro-4 type diesel fuel production, which is best achieved by blending the syncrude derived distillate with material from other sources, such as coal pyrolysis products or crude oil.

1. Introduction

The aim of this investigation is to determine the suitability of HTFT and LTFT synthesis for the production of maximum motor-gasoline, jet fuel and diesel fuel. Such an investigation, to explore the possibilities within the field of Fischer-Tropsch refining, rather than developing a refinery for a specific project, has never before been undertaken. Limiting variables will be highlighted in an attempt to better understand the possibilities and the constraints within Fischer-Tropsch refineries. In instances where integration opportunities with other feed sources become apparent, such as crude oil, gas condensates and tars, it will only be noted, but not explored. The development of non-energy chemicals refineries has been covered in literature(1)(2)(3)(4) and will not be considered.

2. Modelling details

2.1. Conceptual design

In the previous chapter (Chapter VIII) it has been pointed out that conceptual refinery design requires three important pieces of information: feed description, product description and a list of the refining processes to be considered. These variables have already been discussed:

a) The feed description has been discussed in Chapter V. Since Fischer-Tropsch based coal-to-liquids (CTL), gas-to-liquids (GTL) and biomass-to-liquids (BTL) processes all imply conversion via synthesis gas to Fischer-Tropsch syncrude, a Fischer-Tropsch refinery design is more dependent on the Fischer-Tropsch technology that has been selected than the type of raw material used as feed.[a] There are two main Fischer-Tropsch technology types, namely high temperature Fischer-Tropsch (HTFT) technology and low temperature Fischer-Tropsch (LTFT) technology. Within each Fischer-Tropsch technology type a multitude of variations are possible. For practical reasons the conceptual refinery designs developed in this chapter are limited to only one HTFT syncrude and one LTFT syncrude composition (Appendix A).

b) The product description for a fuels refinery has been discussed in Chapter II. Fuels are classified based on boiling range and properties. Only the three main transportation fuel types were discussed in detail, namely motor-gasoline, jet fuel and diesel fuel. Other fuel types that can be produced and that were not discussed include synthetic natural gas (SNG), heating fuels, liquefied petroleum gas (LPG) and marine fuels. In addition to these, there are various products that can be produced in non-fuels refineries, such as lubricating oils, greases, hydraulic fluids, heat transfer fluids, waxes and chemicals.(5) In this chapter conceptual refinery designs will be developed to maximise only motor-gasoline, jet fuel and diesel fuel.

c) Refining processes have been discussed and evaluated in Fischer-Tropsch refining context in Chapter VII. The conversion technologies considered during the development of conceptual refinery designs will be limited to those already discussed. Justification for the selection of a specific type of technology will be limited to the specific refinery design being considered.

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[a] This is an over-simplification, since CTL gasification technology and the associated production of coal pyrolysis products, or the recovery of associated gas condensates in the feed to GTL facilities, will influence the feed description.

2.2. Refinery economics

Thus far, little attention has been devoted to refinery economics, although some of the drivers determining refinery economics have been discussed (Chapter VIII). The same principles governing crude oil refinery economics apply to Fischer-Tropsch refineries, with the difference that the syncrude composition is fixed in the design phase by the selection of the Fischer-Tropsch technology. The refinery economics can therefore not be improved by judicious selection of crude oils based on day-to-day spot prices in the market. The Fischer-Tropsch syncrude cost is less volatile and based mainly on raw feed material cost, cost of capital and operating cost.

One could arbitrarily divorce syncrude production from syncrude refining[b] and calculate an effective syncrude cost, analogous to crude oil cost. This is bound to yield a high dollar equivalent crude oil price at which syncrude production becomes economical (about US$ 50),(6) because most of the capital cost involved in constructing a Fischer-Tropsch facility is due to syncrude production (Figure 1).(7) The refinery cost is typically less than 15% of the total capital cost (10% in the case of Figure 1). Yet, the refinery makes the

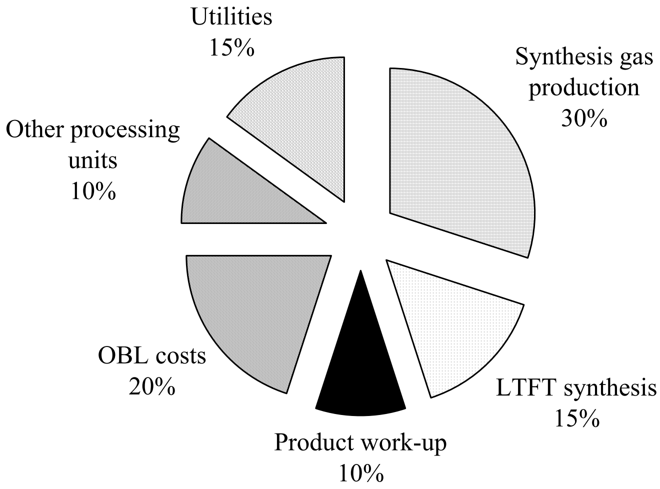

Figure 1. Distribution of capital cost for a gas-to-liquids project in the Middle East.

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[b] In practice divorcing syncrude production and refining negates the synergies between these processes, especially in terms of primary product separation.

difference between selling syncrude as crude oil (like Athabascan tar sand derived syncrude), or final products and is consequently the main value addition step in a Fischer-Tropsch plant.

The key learning point from this is that the yield of final products in a Fischer-Tropsch refinery is pivotal to the economics of the venture. Spending more money in the refinery is less of an issue than in a crude oil refinery, due to its small impact on the overall capital cost of the project. Furthermore, the decision to build a Fischer-Tropsch facility is often driven by a political agenda. In order to realise such a political agenda, economic incentives are provided to investors to offset the high capital cost associated with Fischer-Tropsch facilities for the production of transportation fuels by alternative means. These incentives are generally linked to specific politically desirable final products, not to syncrude production. For this reason, the role of refinery economics will be downplayed during the refinery designs. Nevertheless, the three main refinery types that will be studied are all linked to specific plausible scenarios driven by specific political pressure groups, for example: maximum motor-gasoline (United States Congress); maximum jet fuel (United States Department of Defence); maximum diesel fuel (European Parliament).

3. Motor-gasoline refineries

There are two aspects to consider when aiming for maximum motor-gasoline production from syncrude, namely a) to change the carbon number distribution to maximise the motor-gasoline fraction; and b) to ensure that the molecular composition of this fraction meets motor-gasoline specifications.

The first aspect focuses on the quantity of the syncrude that can be refined in the motor-gasoline boiling range. The maximum amount of motor-gasoline will be determined partly by the amount of straight run syncrude and partly by the amount of syncrude that can be converted to motor-gasoline by conversion processes. The straight run syncrude, which is material already in the correct boiling range, is a function of the Fischer-Tropsch synthesis (Figure 2). From this figure it can be seen that a chain growth probability (α-value) of 0.68-0.72 gives the highest yield of straight run naphtha. This overlaps with the commercial operating window of fused iron-based HTFT synthesis as practised commercially by Sasol and PetroSA. Purely based on straight run yield, it can be said that HTFT syncrude requires less refining effort than LTFT syncrude to produce maximum motor-gasoline. It can also be said the commercial HTFT syncrude is an optimal feed based on straight run motor-gasoline yield. However, this is only part of the picture, since conversion processes resulting in either

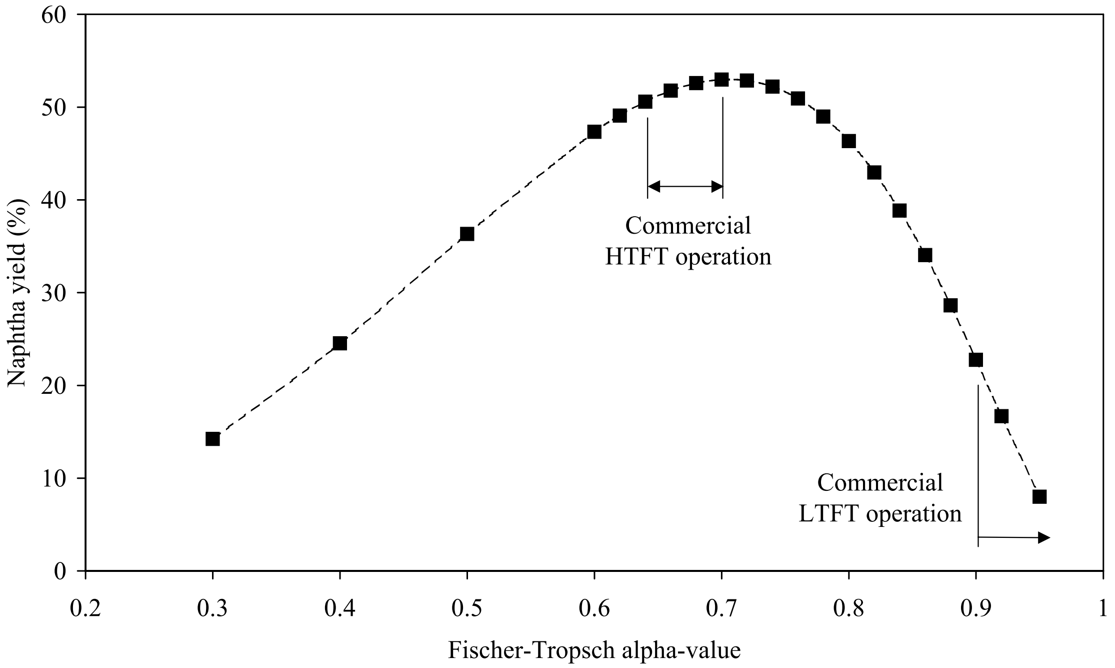

Figure 2. Yield of straight run naphtha (C_5-C_{10}) in the C_3 and heavier hydrocarbon fraction from Fischer-Tropsch as function of the chain growth probability (α-value).

carbon number growth, or in carbon number reduction, can be used to convert lower boiling or higher boiling material to the motor-gasoline range. If this conversion can be done in such a way that it not only increases the quantity of motor-gasoline, but also its quality, it can more than offset any seeming disadvantage based on straight run yield only.

The second aspect focuses on the quality of the refined syncrude. Quality is very important and most refining effort is required for the production of motor-gasoline, a point already made previously (Chapter IV). It is worthwhile to recap the essential qualities needed in motor-gasoline. Octane number is the key refining specification and a minimum RON of 95 and MON of 85 is typically required. The octane requirement must be met within the limitations imposed on composition (35% aromatics, 18% olefins, 15% oxygenates, 10 $\mu g \cdot g^{-1}$ S) and physical properties, such as vapour pressure. Apart from hydrocarbons, oxygenates are the only compound class allowed in significant quantities in fuel. Aromatics and oxygenates can be considered high-octane compounds, with octane numbers generally exceeding that required by fuel specifications. Olefins can be considered as octane “neutral” compounds, with octane numbers generally close to that required by fuel specifications. However, olefins with a low degree of branching and especially linear α-olefins, are low-octane compounds. The octane number of paraffins is very structure sensitive and ranges from less than 0 to more than 100. Since paraffins are the only compound class not limited by fuel specifications, it stands to reason that the crux of motor-gasoline refining is to produce high-octane paraffins.[c] When we compare these quality requirements with the properties of straight run syncrude(8) (Table 1) it is clear that syncrude naphtha refining to motor-gasoline requires:

a) Synthesis of aromatics.
b) Reduction of the olefin content.
c) Improvement of olefin fuel quality.
d) Purification and/or synthesis of appropriate oxygenates.
e) Improvement of paraffin fuel quality.

Table 1. Comparison of straight run iron-based HTFT and LTFT naphtha to specifications and quality requirements for motor-gasoline.

Compound class	HTFT naphtha	LTFT naphtha	Euro-4	Comments
Aromatics	5	0	35% max	Most aromatics are desirable (high RON), but benzene is limited to less than 1% in fuel.
Olefins	70	64	18% max	Branched internal olefins are octane neutral, the linear α-olefins are low in octane.
Oxygenates	12	7	5-15% max	Alcohols or ethers required, FT oxygenates are mainly alcohols, carbonyls and acids.
Paraffins	13	29	unlimited	Highly branched paraffins needed for good octane, but FT paraffins are very linear.

A more detailed analysis of these requirements reveals that the quality issues can be grouped into three categories, although such a grouping may not be immediately obvious.

This first category is the production of *aromatics*. It is possible to aromatise olefins, oxygenates and paraffins by judicious selection of an appropriate aromatisation technology. Since aromatisation needn't be feed dependent, it provides a degree of freedom in the refinery design. Any undesirable material that does not have another natural refining pathway, may be upgraded in this way.

The second category is the production of *oxygenates*. It has previously been pointed out that the nature of the oxygenates that may be included in the fuel is subject to political

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[c] This is somewhat of an over-simplification, but it is much easier to increase the octane number of motor-gasoline by adding appropriate aromatics, olefins and oxygenates than it is by adding paraffins.

pressures. Despite syncrude being rich in oxygenates, only some of these oxygenates are acceptable as fuel oxygenates. Such oxygenates may be separated from the syncrude, for example the production of fuel ethanol by purification of the Fischer-Tropsch aqueous product fraction. Oxygenates may also be obtained from other sources, for example, importing oxygenates from an external source to meet a bio-fuels requirement. Optionally oxygenates may also be synthesised in the refinery, for example the production of fuel ethers, which are compounds not normally found in syncrude. In all instances it is prudent to avoid a tight integration of oxygenate production within the refinery design, since legislation governing oxygenate inclusion has to be considered ever changing.

The third category is the production of *aliphatics*. This is governed by the production of high-octane paraffins. The first guiding principle is that skeletal isomerisation can only be used to upgrade paraffins in the C_4-C_6 range. The C_7 and heavier paraffins are readily cracked(9) before the tri- and tetra-branched species needed for high octane are formed. The second guiding principle is that the production of C_7 and heavier high-octane paraffins can only be accomplished by the addition reaction of two shorter chain aliphatic molecules, either as practised in aliphatic alkylation or as practised in olefin oligomerisation. The third guiding principle is that hydrogenation of excess olefins in the fuel should target those molecules with the smallest octane number difference between the olefin and iso-structural paraffin. The fourth guiding principle is that it is hardly ever worthwhile to upgrade olefins by isomerisation only in order to retain them as olefins in the motor-gasoline.

A last aspect to consider, which has not been touched on, is the preferred way of dealing with material that cannot be accommodated in the motor-gasoline. This may be due to quality issues, or because it does not always make refining (an economic) sense to convert material that is already a transportation fuel into a different transportation fuel. The latter is an important consideration, since the aim is to produce final products. In general it can be said that any product that meets final product specifications, either as chemical, or as fuel, can in principle be retained as such.

3.1. HTFT motor-gasoline refinery development

In order to develop a conceptual design for an HTFT refinery producing maximum motor-gasoline, each boiling fraction will be considered separately. The idea is not to repeat the technology screening (Chapter VII), nor to duplicate literature.(10) This approach just seems to work well for the development of a motor-gasoline refinery.

a) *Residue (C_{22}+).* HTFT syncrude contains about 3% material boiling above 360°C.[d] Using the residue as a fuel oil is tempting from a design perspective, since it avoids the inclusion of any residue upgrading units. However, the aim is to maximise motor-gasoline and some form of cracking is required to reduce the average carbon number of the residue.

b) *C_{15}-C_{22} distillate.* Since HTFT material is sulphur free and low in polynuclear aromatics, the traditional refining approach would be to hydrogenate this material and incorporate it into diesel fuel. The hydrogenated product has a good cetane number, typically >51, and meets all diesel fuel specifications except density. The density of this material is typically around 810 $kg \cdot m^{-3}$, which is lower than the 820 $kg \cdot m^{-3}$ minimum density requirement for diesel. This shortcoming may be overcome by either blending from an external source, or exploiting synergies with tar refining or crude refining. Optionally it may be considered to use a carbon number reduction technology to crack this material into lower boiling material and increase the motor-gasoline production.

c) *C_{11}-C_{14} kerosene.* The straight run kerosene fraction from HTFT can be hydrogenated and used as a Jet A-1 component.(11) Optionally this fraction can be cracked to produce more lower boiling material to increase motor-gasoline production.

d) *C_9-C_{10} naphtha.* Traditionally this naphtha fraction is refined by catalytic reforming to produce aromatics. Despite the low N+2A value, the Sasol and PetroSA HTFT refineries make use of this approach. The main drawback of this approach is that aromatics production is limited, since this fraction constitutes only 5% of the HTFT syncrude. The inclusion of more than one aromatics producing technology can be considered, but such an approach would be costly. However, as straight run motor-gasoline, the C_9-C_{10} naphtha has a low octane value, which becomes worse on hydrogenation. It is not amenable to upgrading by skeletal isomerisation, due to its cracking propensity and oligomerisation would result in a distillate range product, thereby reducing the motor-gasoline product and still leaving the low octane C_9-C_{10} paraffins to be dealt with. After hydrogenation it can be used as jet fuel component, but this also reduces the motor-gasoline production. It can therefore be said that there are numerous upgrading pathways for C_9-C_{10} naphtha, but it is a problematic cut to deal within the context of a motor-gasoline refinery of least complexity.

e) *C_8 naphtha.* This fraction is also traditionally upgraded by catalytic reforming and possibilities for its upgrading can be discussed along similar lines as that for the C_9-C_{10} naphtha. The ability to include C_8 naphtha in jet fuel, however, is limited by its flash point.

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[d] All references to refinery yield are expressed as a mass percentage of C_2 and heavier material in the syncrude.

f) *C_7 naphtha*. In syncrude, like in crude oil refining, this is the most difficult naphtha cut to upgrade.$^{(10)}$ Unlike C_8-C_{10} naphtha, it is poorly converted by catalytic reforming, unless non-acidic Pt/L-zeolite based technology is considered. It cannot be skeletally isomerised efficiently, due to cracking and its hydrogenated straight run octane number (RON<50) makes it a poor motor-gasoline component. High temperature processes, such as aromatisation and catalytic cracking (the latter route having been recently selected by Sasol),[e] can be used as effective refining pathways for C_7 naphtha. These technologies are expensive and considering that the C_7 naphtha constitutes only 7% of HTFT syncrude, it may be difficult to justify from an economic and complexity perspective just for refining the C_7 naphtha.

g) *C_6 naphtha*. Although this cut has a low straight run octane number, there are many ways to refine it to good quality motor-gasoline. The most obvious refining pathway is skeletal isomerisation. Another option is to refine it to aromatics.

h) *C_5 naphtha*. The straight run C_5 naphtha has an octane number of around 90-95 on account of its high olefin content (85%) and can be blended directly into motor-gasoline. The pentenes can also be skeletally isomerised and used as feed for etherification, as is the case at the Sasol Synfuels refineries where it is used for TAME production. More importantly, there is little octane penalty when the C_5 naphtha is hydroisomerised before it is blended into motor-gasoline, which has the advantage of not limiting the inclusion of other olefins into the fuel.

i) *C_4 hydrocarbons*. The C_4 hydrocarbon fraction of HTFT syncrude contains about 85% olefins. Olefin oligomerisation by a motor-gasoline selective technology, such as solid phosphoric acid based oligomerisation, is a natural choice. The remaining butanes can be directly blended into the motor-gasoline and their inclusion is only limited by the vapour pressure constraints placed on the final fuel. Other upgrading pathways that can be considered are aliphatic alkylation and etherification. However, these pathways are less attractive for HTFT syncrude due to the olefin to paraffin (85:15) imbalance, high degree of linearity (n-C_4:iso-$C_4 \approx 9{:}1$) and large volume (13% of HTFT syncrude).

j) *C_3 hydrocarbons*. The HTFT derived C_3 hydrocarbons have a propylene to propane ratio of 87:13 and constitutes about 15% of the syncrude. This makes it the most abundant carbon number in HTFT syncrude. In order to maximise motor-gasoline, the olefin-based transformations would typically be motor-gasoline selective olefin oligomerisation (SPA), or

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[e] Superflex™ Catalytic Cracker (SCC) technology of KBR, commissioned at Sasol Synfuels in 2007.

alkylation to produce mainly motor-gasoline range products. Propane is normally used for liquid petroleum gas (LPG), but may also be upgraded by an appropriate aromatisation technology to boost motor-gasoline production.

k) *C_2 hydrocarbons*. HTFT syncrude contains about 11% C_2 hydrocarbons and even more if the oxygenates (ethanol, acetaldehyde and acetic acid) are included. The ethylene to ethane ratio is 55:45. Ethylene is not generally considered for motor-gasoline production, but depending on the refinery location, it may not be possible to sell the ethylene as chemical. Some technologies are available for the conversion of ethylene into liquid products, although these technologies are not generally associated with fuels refining, for example hydration, olefin oligomerisation and aromatic alkylation. The ethane can be upgraded by thermal cracking, but this is an expensive technology. Alternatively it can be considered a fuel gas at the expense of reducing the yield of final products from the refinery.

l) *Aqueous phase oxygenates*. About 11% of the HTFT syncrude is on condensation dissolved in the water that was co-produced during HTFT synthesis. These oxygenates can partly be recovered by distillation and sold as chemicals, or it can be refined to fuels. One way of simplifying the aqueous product refining to motor-gasoline is to partially hydrogenate the carbonyls to alcohols and then dehydrating the alcohol-water mixture to olefins.(12) The olefins thus produced can then be refined with the other olefins in the refinery.

3.1.1. HTFT paraffinic motor-gasoline

It has been pointed out that the crux of meeting motor-gasoline specifications is ensuring that the paraffins in the motor-gasoline have a sufficiently high octane number, since the other compound classes are either octane neutral or high-octane compounds. Since the volume of paraffins is not limited, but determines the volume of other compounds that can be included, it is a logical place to start refinery design for maximum motor-gasoline. The easiest high-octane paraffin producing technologies are those that upgrade the C_4-C_6 naphtha.

The first design decision is to evaluate the value of installing a butane isomerisation unit. This may be considered for two reasons, namely a) to boost the octane of the straight run butanes that can be blended into the fuel up to its vapour pressure limit; and b) to produce iso-butane for aliphatic alkylation.

Although iso-butane (RON = 101.3; MON = 97.6) has a 7-8 point higher octane number than *n*-butane (RON = 93.8 ; MON = 89.6), the vapour pressure of iso-butane (RVP = 500 kPa) is also much higher than that of *n*-butane (RVP = 357 kPa). Since the volumetric inclusion of the C_4's are limited by the vapour pressure specification and vapour pressure of the base fuel, the volume of iso-butane to *n*-butane that can be included can be calculated (Equation 1).

$$\frac{V_{iso-C4}}{V_{n-C4}} = \frac{\left(RVP_{n-C4} - RVP_{fuel}\right)}{\left(RVP_{iso-C4} - RVP_{fuel}\right)} \qquad \dots (1)$$

Based on equation 1, it is possible to blend 40% less iso-butane than *n*-butane into the fuel. It is consequently not worthwhile to hydroisomerise the butanes for direct inclusion into the fuel.

The next design decision is to evaluate the value of installing an aliphatic alkylation unit in conjunction with butane hydroisomerisation. Aliphatic alkylation is not considered environmentally friendly, but is an effective way to improve the paraffinic octane. In general HF-based alkylation processes yield higher octane products(13) (RON=90-91 with propene and RON=94-95 with FT butenes), although H_2SO_4-based alkylation has a better technology fit with syncrude.

Alkylate production is limited by the butane availability in HTFT syncrude and different scenarios have been considered to maximise alkylate production (Table 2). The alkylate production can be considerably increased if some of the butenes are hydrogenated, especially if alkylation is performed with propylene, which is not a limiting feedstock. Additionally, even more C_4 hydrocarbons can be made available by selective hydrogenation and dehydration of the oxygenates in the aqueous product. In this way, up to 23% of the HTFT syncrude can be converted into alkylate.

Table 2. Maximum production of alkylate as mass percentage of the C_2 and heavier straight run HTFT syncrude by an HF-based aliphathic alkylation process in conjunction with butene hydrogenation and butane hydroisomerisation.

Conversion unit	Using only straight run butanes		Butene hydrogenation optimised		Aqueous product C_4's included	
	C_3-alky	C_4-alky	C_3-alky	C_4-alky	C_3-alky	C_4-alky
Butene hydrogenation	0	0	11.1	4.9	12	5.3
Butane isomerisation	1.6	1.6	12.7	6.5	13.6	6.9
Aliphatic alkylation	2.8	3.2	21.9	12.7	23.4	13.6

Another possibility that can be considered is the production of an alkylate equivalent product by butene oligomerisation. This can be accomplished in more than one way. The easiest method is to make use of the unique low temperature butene skeletal isomerisation pathway on solid phosphoric acid, which yields a product with a hydrogenated octane number of 86-88 from straight run HTFT butenes.(14) Another possibility is to include a butene skeletal isomerisation unit before the olefin oligomerisation process. This would enable the production of an alkylate equivalent with a hydrogenated octane number of around 96. These options are limited to the butene availability. In this way, when the C_4 oxygenates in the reaction water are also converted to olefins, up to 12% of the HTFT syncrude can be converted into alkylate.

Table 3. Hydroisomerisation of hydrogenated C_5-C_6 HTFT naphtha by different processing pathways showing typical composition and fuel quality values. (Cyclo-paraffin composition is not shown due to the low cyclo-paraffin content of Fischer-Tropsch syncrude).

Description	Syncrude		Once-through operation				Recycle operation	
	C_5-only	C_5-C_6	C_5-only	C_5-only	C_5-C_6	C_5-C_6	C_5-only	C_5-C_6
			Pt/Al_2O_3	Pt-MOR	Pt/Al_2O_3	Pt-MOR	Pt-MOR	Pt-MOR
% of HTFT syncrude	10.6	19.2	10.6	10.6	19.2	19.2	10.6	19.2
Typical C_5 composition								
n-pentane	79	79	29	37	29	37	3	3
2-methylbutane	21	21	71	63	71	63	97	97
Typical C_6 composition								
n-hexane		76			11	15		0
2-methylpentane		11			31	34		39
3-methylpentane		11			17	22		26
2,2-dimethylbutane		0			30	20		23
2,3-dimethylbutane		1			10	8		11
Typical fuel properties								
RON	68	54	84	81	81	77	91	87
MON	68	55	82	80	80	77	90	86
Density ($kg \cdot m^{-3}$)	630	645	627	627	641	642	625	640
RVP (kPa)	114	83	131	129	99	96	140	104

In crude oil refineries the mixed C_5-C_6 naphtha cut from the atmospheric distillation unit is known as light straight run (LSR) naphtha. These carbon fractions are often not separated and hydroisomerisation of the C_5-C_6 naphtha is performed in a single conversion unit. This needn't be the case. As discussed previously (Chapter VII) there are a variety of processes and process configurations available, with recycling of the unconverted material that can be considered. When C_5 naphtha is processed separately, recycling of the *n*-pentane is easy and can be accomplished by distillation. This separation becomes more involved when mixed C_5-C_6 naphtha is hydroisomerised, requiring multiple distillation columns or selective adsorption. On account of the slower rate of hydroisomerisation of hexanes compared to pentanes, units processing C_5-C_6 naphtha operate at the thermodynamic equilibrium of the C_5's, but not the C_6's.(15) Different scenarios have been considered for HTFT refining (Table 3). When C_5 hydroisomerisation is considered, the octane number of hydrogenated C_5 syncrude can be improved by more than 20 points using recycle operation, yielding an isomerate with octane numbers above 90. Although the isomerate quality that can be achieved with recycle operation using C_5-C_6 naphtha has a lower octane value (86-87), the octane gain exceeds 30 points and 19% of the HTFT syncrude can be converted to isomerate.

Based on the data presented in Tables 2 and 3, it can be said that there scope to convert up to 42% of the total C_2 and heavier HTFT syncrude to paraffinic motor-gasoline with octane numbers in the range of 85-95. This excludes additional conversion that may be possible from C_4-C_6 material generated by other conversion processes in the refinery.

3.1.2. HTFT aromatic motor-gasoline

The main source of high octane compounds in motor-gasoline is aromatics. In choosing an aromatics production technology, apart from the technology issues already covered (Chapter VII), there are three important aspects to consider from a motor-gasoline refinery development perspective:

a) *Feed*. Aromatics production has three functions in a refinery, namely to provide high-octane motor-gasoline, hydrogen production and as a sink for low octane or otherwise unwanted material. The latter aspect is quite important, since the technology can be selected in such a way that a refining pathway is created for the upgrading of material to improve motor-gasoline yield, or for the upgrading of material that could be detrimental to the quality of the motor-gasoline. In this respect metal promoted H-ZSM-5 based aromatisation technology is the best, since it is capable of converting material in the C_3-C_{10} range. Conversely, platinum promoted non-acidic L-zeolite based aromatisation is by far the most efficient aromatisation process, having a high yield of liquid products and hydrogen, but it is restricted to processing feed in the C_6-C_{10} range (preferably C_6-C_8 naphtha). Ironically, one of the key crude oil refining units, namely catalytic reforming (chlorided Pt/alumina), is the least flexible in terms of feed, being efficient only at converting C_8-C_{10} naphtha, although low conversion of C_6-C_7 naphtha is possible.[f]

b) *Yield structure*. The yield structure of the different aromatisation technologies has been discussed previously (Chapter VII). Of special importance is the co-production of paraffins in the same boiling range as the aromatics, typically C_7 and heavier aliphatics. These hydrocarbons have low octane numbers and are difficult to separate from the aromatics. The octane number of the aromatic motor-gasoline is adversely affected by the presence of these paraffins and such co-production should be minimised. This is a drawback associated mainly with chlorided Pt/alumina based catalytic reforming, which produces the lowest octane aromatic motor-gasoline (RON = 95-100).[g] The octane number of the reformate is controlled by temperature and can be increased by increasing the temperature, but this results in a lower liquid yield.

A low liquid yield is the main drawback of ZSM-5 based aromatisation, which necessitates recycling of the C_3-C_4 paraffins to reduce the overall motor-gasoline yield loss. The octane number that can be obtained from such a process is nevertheless higher (RON = 100-105). An even higher octane number can be achieved with L-zeolite based aromatisation (RON = 105-110), but this brings us to another important selectivity issue, the co-production of benzene.

c) *Benzene*. The benzene content of motor-gasoline is limited to less than 1% by volume in most countries, because it is a known human carcinogen. Although benzene selectivity is low in chlorided Pt/alumina catalytic reforming and ZSM-5 based technologies, it is co-produced, especially if benzene precursors are present in the feed. Conversely, in platinum promoted non-acid L-zeolite based technology, benzene selectivity from C_6 naphtha is very high (>90%). In any event, benzene co-production may exceed the maximum allowable limit in motor-gasoline, in which case something must be done to reduce the

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[f] Conversion of heavier than C_{10} hydrocarbons is possible with all three aromatisation technologies, but falls outside the design intent of such technologies.

[g] Due to the low *N*+2*A* content of Fischer-Tropsch syncrude, it requires quite severe operation to maintain a RON 95 product. Although it has been shown that with heavier feed materials higher octane numbers can be obtained, such figures cannot be used for conceptual design purposes.

benzene content.(16) In a Fischer-Tropsch refinery, where olefins are abundant, the alkylation of benzene with olefins is an obvious possibility.

It is therefore possible to convert any material in the C_3-C_{10} range to aromatic motor-gasoline with an octane number above RON 95 by an appropriate selection of aromatisation technology.

3.1.3. HTFT olefinic motor-gasoline

Olefinic motor-gasoline is a blending component that is considered mainly due to the inherently high olefin content of straight run HTFT naphtha (Table 1). All olefin oligomerisation technologies are able to produce an olefinic motor-gasoline, but not all of these technologies produce a good olefinic motor-gasoline. Only in exceptional cases can the olefinic motor-gasoline be hydrogenated without much octane loss. Nevertheless, olefin oligomerisation is a convenient way to increase the average carbon number of a feed material and it enables the conversion of C_2-C_4 olefins to motor-gasoline. In this respect SPA based oligomerisation is by far the best oligomerisation technology for motor-gasoline production from straight run syncrude.

3.1.4. HTFT oxygenated motor-gasoline

There are three natural ways in which the oxygenate content of the motor-gasoline can be increased, apart from importing oxygenates:

a) *Alcohol recovery from syncrude*. The aqueous product from HTFT synthesis contains dissolved ethanol and iso-propanol that can be recovered for use as fuel alcohols. These alcohols constitute 3-4% of the C_2 and heavier syncrude fraction. It should be noted though, that iso-propanol is less commonly used as fuel alcohol. Production of fuel alcohols can be increased by selective hydrogenation of acetaldehyde and acetone to their corresponding alcohols. This increases the overall yield of ethanol and iso-propanol to 6% of the C_2 and heavier syncrude fraction.

b) *Hydration of syncrude olefins*. The oxygenate content of the motor-gasoline can be further increased by hydration of ethylene to ethanol or even propylene to iso-propanol. These technologies are not found in fuels refineries. Ethylene hydration is especially interesting for fuel refineries far from markets where ethylene can be sold as a chemical. It is also a convenient way of moving a normally gaseous olefin into motor-gasoline.

c) *Etherification.* Etherification of branched olefins with an alcohol, or even etherification of alcohols, are two ways in which fuel ethers can be prepared. The alcohols may be imported, recovered from the HTFT aqueous product or produced by hydration. Some branched olefins are present in the syncrude, but not all are active for etherification, since the C=C double bond is not always on the tertiary carbon atom. Furthermore, not all alcohols produce high-octane ethers and care should be taken in the selection of etherification products. For example, di-*sec*-butylether (1-methyl-propoxy-2-butane) has blending octane number below 100.(17)

It is possible to produce the necessary oxygenated motor-gasoline components by separation and/or synthesis from HTFT syncrude. The preferred oxygenates will depend on legislation and currently ethanol is favoured as fuel oxygenate.

3.2. HTFT motor-gasoline refinery flowschemes

3.2.1. Flowscheme 1

The first refinery flowscheme that was developed, focused on the upgrading of C_4-C_6 naphtha to high-octane paraffinic motor-gasoline (Figure 3). Based on environmental considerations,

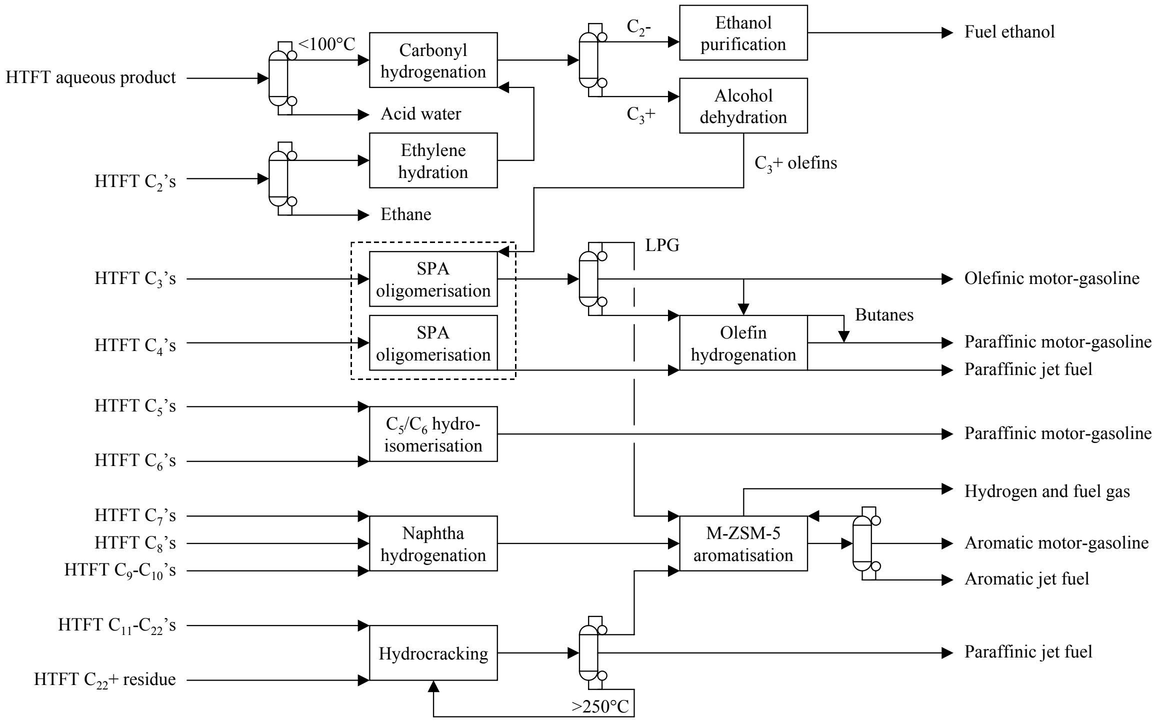

Figure 3. HTFT motor-gasoline refinery, flowscheme 1.

aliphatic alkylation was not considered and the C_4 naphtha was converted to paraffinic motor-gasoline by direct blending of the butanes, while the butenes were oligomerised in a process based on a SPA catalyst and the product was hydrogenated. The C_5-C_6 naphtha was hydroisomerised with full recycle, in a typical commercial total isomerisation process (TIP) configuration. These conversion processes converted 30% of the refinery feed to an 86 octane paraffinic motor-gasoline.

The refining of the Fischer-Tropsch aqueous product was integrated with the refining of the lighter than C_4 compounds. Ethanol was recovered from the aqueous product and combined with the ethanol produced by hydration of ethylene. The combined ethanol-water mixture was then further refined to produce fuel ethanol. Ethanol was blended as oxygenated motor-gasoline component. The C_3 and heavier oxygenates in the aqueous product were selectively hydrogenated to alcohols and dehydrated to olefins.(12) These olefins were combined with the C_3 hydrocarbons and oligomerised in a SPA-based process. The product was mainly retained as an olefinic motor-gasoline component.

The aromatic motor-gasoline was produced by ZSM-5 based aromatisation of a mixture of the residual light paraffins and C_7-C_{10} naphtha. Some of this material originated from hydrocracking, since the heavier syncrude fraction was hydroisomerised and hydrocracked at high severity to produce mainly a C_{16} and lighter product. A ZSM-5 based aromatisation process was selected specifically to reduce the yield loss associated with high severity hydrocracking, since such a process is able to convert the LPG fraction to aromatics. The aromatic product from aromatisation was fractionated in such a way that the kerosene range material could be blended to produce jet A-1, with the rest of the aromatics being used as high-octane motor-gasoline.

The yield structure of the refinery is given in Table 4.[h] The refinery yield of liquid fuels was 92%, while the motor-gasoline yield was 62%. The design was successful in terms of the yield structure, but the motor-gasoline did not meet Euro-4 specifications (Table 5). The RON was too low (93 versus 95 required), benzene exceeded the specification (1.5% versus 1% required) and the motor-gasoline density was too low (718 $kg \cdot m^{-3}$ versus 720-775 $kg \cdot m^{-3}$ required). The low density is understandable, since more than a third of the motor-gasoline was C_4-C_6 material (35% of the motor-gasoline by mass and 40% by volume), which also helped to boost the volumetric yield of the refinery. Liquid fuels production was about 94 000 bpd.

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[h] Unrecovered organics are mainly carboxylic acids that are present in the aqueous effluent (acid water).

Table 4. Yield structure of the HTFT motor-gasoline refinery shown in Figure 3 having a liquid fuel yield of 92% (mass) and a motor-gasoline yield of 60% (mass).

Product	Refinery production			
	$(kg\cdot h^{-1})$	$(m^3\cdot h^{-1})$	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	309090	430	64951	69.0
Excess fuel ethanol	49391	62	9390	10.0
Jet fuel	100817	130	19639	20.9
Diesel fuel	0	0	0	0.0
LPG	647	1	177	0.2
Other products				
Fuel gas	38027			
Unrecovered organics	15801			
Hydrogen	-3461			
Water	-10313			
Σ	500000	624	94157	100

Looking at Table 5, it is immediately apparent that there is scope for aromatic and oxygenated gasoline addition to boost the octane number.

Table 5. Motor-gasoline quality from the HTFT motor-gasoline refinery shown in Figure 3.

Fuel properties	Refinery	Euro-4	
RON	93	95	Min
MON	87	85	Min
Vapour pressure (kPa)	59	60	Max
Density $(kg\cdot m^{-3})$	718	720-775	Range
Olefins (vol %)	18.0	18	Max
Aromatics (vol %)	18.4	35	Max
Oxygenates (vol %)	5.0	15	Max
Benzene (vol %)	1.5	1	Max
Ethanol (vol %)	5.0	5	Max

Further aromatics production from syncrude is limited to re-routing some of the C_5-C_6 naphtha to the aromatisation unit, or aromatising some of the already refined product, such as olefin oligomers and/or jet A-1. The latter would not only result in an overall yield loss, but also make little sense from an economic perspective. Furthermore, the benzene content of the motor-gasoline is already an issue and increasing the aromatics production would make this worse, since the flowscheme (Figure 3) does not make provision for benzene mitigation. However, a decrease in the benzene content of the motor-gasoline can be accomplished by modifying the flowscheme to extract the benzene as chemical, hydrogenate the benzene to cyclohexane or to alkylate the benzene with an olefin.

Additional fuel ethanol is available to increase the octane number, but adding it as oxygenated fuel component can only be considered in countries that have higher vapour pressure and ethanol specifications than Euro-4. Some of the ethanol may be used for etherification to produce ETBE or TAEE, which would overcome these shortcomings, but this would require a modification to the flowscheme.

3.2.2. Flowscheme 2

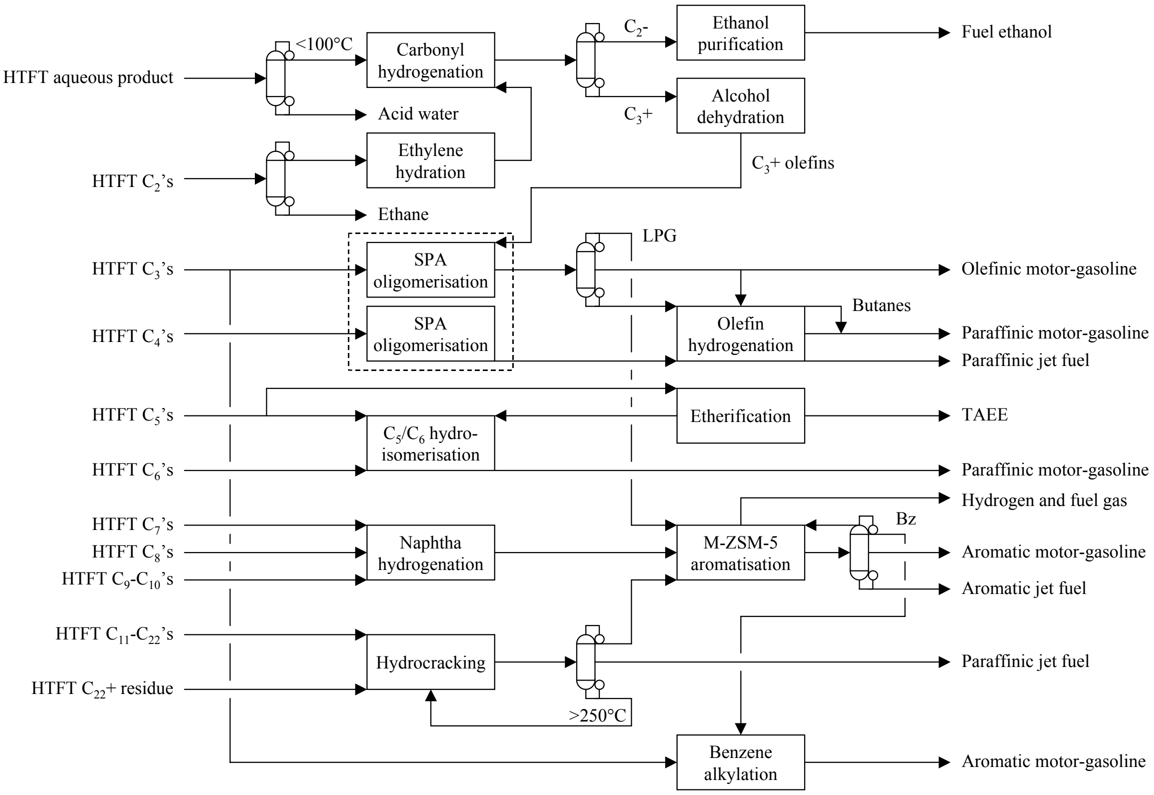

Figure 4. HTFT motor-gasoline refinery, flowscheme 2.

Incremental improvements to the previous flowscheme (Figure 3) in order to meet the Euro-4 specifications, can result in a rapid proliferation of units. It is possible to address the deficient motor-gasoline octane, benzene and density specifications by adding an etherification unit and an aromatic alkylation unit as previously suggested (Figure 4). These changes increase the refinery complexity and reduce the yields, but ensure that the motor-gasoline and jet fuel meet specifications. Although a benzene alkylation unit has been added to the flowscheme as a separate unit, there is a more efficient way of doing this alkylation. It has been shown that it is possible to alkylate the benzene in the SPA based oligomerisation process by directly co-feeding the benzene with the propylene rich feed.(18)

Different scenarios have been investigated to understand the trade-offs involved in meeting the motor-gasoline specifications:

a) The aromatics production was increased by routing 20% of the C_6 naphtha to the ZSM-5 based aromatisation unit. Oxygenated gasoline production was increased by routing the olefinic C_5 naphtha to the etherification unit, where it was converted to tertiary amyl ethyl ether (TAEE). This reduced the light naphtha inclusion, thereby solving the density issue and lowering the RVP, while the additional aromatics and fuel ethers boosted the octane of the motor-gasoline. The benzene specification was addressed by alkylation with propylene to produce cumene, which is also a high-octane aromatic that could be blended into the motor-gasoline. The yield structure (Table 6) did not change much, although the overall refinery yield decreased to 93 000 bpd, which is a little less compared to the 94 000 bpd of the previous design (Table 4).

b) It was found that the C_6 naphtha could be substituted by 6% of the motor-gasoline from C_3 oligomerisation. This fraction would otherwise have to be hydrogenated to meet the olefin specification. Re-routing this material removed RON 50 paraffins from the fuel pool and converted them to high-octane aromatics. The other aspects of the refinery design being the same as in scenario (a). The yield structure (Table 7) changed only marginally compared to the previous scenario, with the refinery yield increasing to 93 500 bpd.

c) Surprisingly it was found that when 60% of the C_6 naphtha is routed to the ZSM-5 based aromatisation unit, sufficient octane was generated by the aromatic motor-gasoline to meet the octane requirements. This has the advantage of eliminating the etherification unit. This implies that if the benzene alkylation is performed in the C_3 SPA-based oligomerisation unit, the present flowscheme (Figure 4) can again be simplified to flowscheme 1 (Figure 3)! The effect of this on the yield structure (Table 8) was to reduce the overall yield to 92 000 bpd on account of the higher density of the increased aromatic motor-gasoline.

Table 6. Yield structure of the HTFT motor-gasoline refinery shown in Figure 4 with 20% C_6 naphtha routed to aromatisation. It has a liquid fuel yield of 92% (mass) and a motor-gasoline yield of 62% (mass).

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	311895	428	64649	69.5
Excess fuel ethanol	43806	55	8328	8.9
Jet fuel	101505	131	19779	21.3
Diesel fuel	0	0	0	0.0
LPG	1169	2	319	0.3
Other products				
Fuel gas	38809			
Unrecovered organics	15991			
Hydrogen	-2862			
Water	-10313			
Σ	500000	617	93075	100

Table 7. Yield structure of the HTFT motor-gasoline refinery shown in Figure 4 with 6% of the motor-gasoline from C_3 oligomerisation routed to aromatisation. It has a liquid fuel yield of 92% (mass) and a motor-gasoline yield of 63% (mass).

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	312927	432	65179	69.7
Excess fuel ethanol	43806	55	8328	8.9
Jet fuel	101199	131	19718	21.1
Diesel fuel	0	0	0	0.0
LPG	1169	2	319	0.3
Other products				
Fuel gas	38300			
Unrecovered organics	15983			
Hydrogen	-3072			
Water	-10313			
Σ	500000	620	93544	100

Table 8. Yield structure of the HTFT motor-gasoline refinery shown in Figure 4 with 60% C_6 naphtha routed to aromatisation and no etherification (TAEE) unit. It has a liquid fuel yield of 91% (mass) and a motor-gasoline yield of 60% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	301553	412	62141	67.4
Excess fuel ethanol	50100	63	9525	10.3
Jet fuel	103435	133	20148	21.9
Diesel fuel	0	0	0	0.0
LPG	1274	2	348	0.4
Other products				
Fuel gas	40455			
Unrecovered organics	16017			
Hydrogen	-2522			
Water	-10313			
Σ	500000	611	92162	100

Table 9. Motor-gasoline quality from scenarios (a) to (c) of the HTFT motor-gasoline refinery shown in Figure 4.

Fuel properties	Different refinery configurations			Euro-4	
	(a)	(b)	(c)		
RON	95	95	95	95	Min
MON	88	88	88	85	Min
Vapour pressure (kPa)	51	52	56	60	Max
Density ($kg \cdot m^{-3}$)	728	725	733	720-775	Range
Olefins (vol %)	18.0	17.7	17.9	18	Max
Aromatics (vol %)	20.6	19.3	24.8	35	Max
Oxygenates (vol %)	9.2	9.1	5.0	15	Max
Benzene (vol %)	0.0	0.0	0.0	1	Max
Ethanol (vol %)	5.0	5.0	5.0	5	Max
TAEE (vol %)	4.2	4.1	0.0	15	Max

Although these are all workable designs, they have two important shortcomings, namely a significant hydrogen deficit and a close approach to the fuel specifications on more than one account (Table 9). The hydrogen deficit implies that hydrogen has to be taken from the Fischer-Tropsch gas loop, which will effectively reduce the production of syncrude. This is less of a concern than a similar situation in a crude oil refinery, but nevertheless a shortcoming. When fuel specifications are just being met after considerable tweaking of the refinery design, the refinery is very inflexible in dealing with upsets. This is not a conceptual design problem, but will become an issue if such a design is to be built. With RON, olefin content and ethanol content being close to specification, there is little room to solve problems in the blending operation.[i]

3.2.3. Flowscheme 3

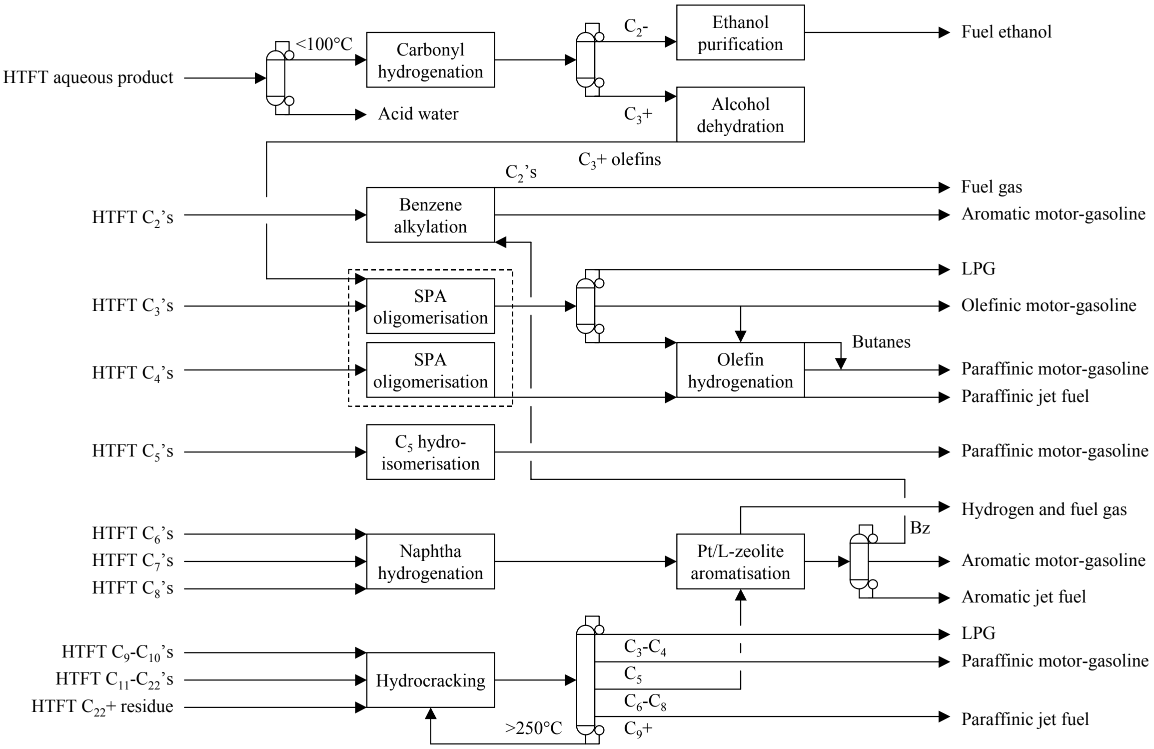

Figure 5. HTFT motor-gasoline refinery, flowscheme 3.

To address the issue of hydrogen availability and tightness in meeting motor-gasoline specifications, the refinery design should be approached differently. Hydrogen availability and octane limitations can be resolved simultaneously by producing more aromatics.[j] By changing the aromatisation technology to an L-zeolite based process, maximum aromatics

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[i] A close approach to fuel specifications can be viewed in a positive light too, since it implies that there is little refinery give-away. However, since this is a conceptual refinery design, it will be viewed in a negative light.

[j] It is for exactly this reason that a catalytic reformer is the central conversion unit (and often the limiting conversion unit) in a crude oil refinery.

and hydrogen selectivity can be achieved (Figure 5). Since the need for aromatic alkylation has already been shown, the high benzene selectivity of the L-zeolite based process is not a new concern. As a matter of fact, this can be put to good advantage to eliminate the ethylene-splitter and ethylene hydration unit, by selecting ethylene as alkylating olefin for benzene alkylation. The feed to the L-zeolite based aromatisation has been limited to C_6-C_8 naphtha. One implication of restricting the feed to C_6-C_8 naphtha is that there is flexibility left to route heavier naphtha to this unit, should it be needed.[k] Another implication is that the C_5/C_6 hydroisomerisation unit in the previous flowschemes (Figures 3 and 4) becomes just a C_5 hydroisomerisation unit. This simplifies the hydroisomerisation unit design and efficiency, because recycle operation is made easier. The rest of the conversion units are similar to that in flowschemes 1 and 2, although the feed routing to the hydrocracker now includes C_9-C_{10} naphtha.

Table 10. Yield structure of the HTFT motor-gasoline refinery shown in Figure 5 having a liquid fuel yield of 89% (mass) and a motor-gasoline yield of 53% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	267078	364	54957	60.4
Excess fuel ethanol	17624	22	3351	3.7
Jet fuel	140447	181	27363	30.1
Diesel fuel	0	0	0	0.0
LPG	18592	35	5256	5.8
Other products				
Fuel gas	32466			
Unrecovered organics	14894			
Hydrogen	-379			
Water	9277			
Σ	500000	602	90927	100

The yield structure (Table 10) shows liquid fuel production of 91 000 bpd, which is equivalent to an overall refinery yield of 89%. Compared to the previous motor-gasoline

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[k] In practise this would imply that the necessary transfer lines and spare capacity on the unit should be included in the design. Conceptually it implies that there is a degree of freedom in the design that is not being used.

flowschemes there is a significant increase in LPG and jet fuel production. The increase in LPG production was expected, since more feed material is hydrocracked and the L-zeolite based aromatisation technology is not capable of converting the LPG into aromatics. The increase in jet fuel production was also expected, since the hydrocraker, which doubles as a kerosene hydroisomerisation unit, is also one an important source of jet fuel. By routing the C_9-C_{10} naphtha to the hydrocracker, production of both kerosene and LPG range material is increased at the expense of naphtha production. Although this is contrary to the aim of maximising motor-gasoline, the refinery complexity was reduced and some flexibility was gained. The fuel quality has been improved to such an extent that the motor-gasoline meets Euro-4 specifications before ethanol addition (Table 11). It indicated that the basic refinery design was decoupled from the politically sensitive oxygenate mandate. The ability to use blending to vary the relationship between octane number, oxygenate content and olefin content, is a measure of the flexibility of the design. The design is also flexible with respect to the jet fuel and the motor-gasoline blending operation, which can be further be deconstrained by blending more of the C_3 SPA derived motor-gasoline into jet fuel (not shown).

Table 11. Motor-gasoline quality from the HTFT motor-gasoline refinery shown in Figure 5 showing (a) the blend without oxygenates, (b) the blend with the addition of ethanol and less C_4's, and (c) the blend with addition of ethanol and maximum olefins.

Fuel properties	Refinery operating scenarios			Euro-4	
	(a)	(b)	(c)		
RON	95	96	98	95	Min
MON	89	89	90	85	Min
Vapour pressure (kPa)	60	60	60	60	Max
Density ($kg{\cdot}m^{-3}$)	734	738	738	720-775	Range
Olefins (vol %)	16.3	15.6	18.0	18	Max
Aromatics (vol %)	27.2	26.1	26.0	35	Max
Oxygenates (vol %)	0.0	5.0	5.0	15	Max
Benzene (vol %)	0.3	0.3	0.3	1	Max
Ethanol (vol %)	0.0	5.0	5.0	5	Max

Despite the lower refinery yield, the refinery is less reliant on imported hydrogen and the basic refinery design is robust.

3.3. LTFT motor-gasoline refinery development

The carbon number distribution of LTFT syncrude (Figure 2) is far from optimal for motor-gasoline production. Most of the syncrude is heavier boiling than naphtha, which implies that residue upgrading will be an important aspect of the refinery design. Although the main aim of residue upgrading will be to change the carbon number distribution to increase the quantity of naphtha, the technology selection may be driven by quality considerations. From the preceding discussion on HTFT motor-gasoline refinery development, the production of high-octane paraffinic motor-gasoline components and aromatic motor-gasoline emerged as key aspects of a successful refinery design. The refining of the various carbon number fractions will be discussed, as was discussed for HTFT syncrude:

a) *Residue* C_{22}*+*. The residue (>360°C boiling) fraction contains 52% of the LTFT syncrude, making it the largest fraction to refine. Although hydrocracking and thermal cracking have a better technology fit with LTFT syncrude (Chapter VII), catalytic cracking is quite efficient at cracking Fischer-Tropsch waxes. The reason for considering catalytic cracking in this specific instance, is related to the nature of its products in relation to the aim of the refinery, namely motor-gasoline production. Catalytic cracking produces a product that is rich in iso-olefinic material, which has significant synthetic value for motor-gasoline production. Furthermore, the product from catalytic cracking of wax consists mostly of products in the C_3-C_{11} range.(19) Although thermal cracking can also be used to produce olefins, the product from thermal cracking is rich in linear α-olefins, which are less desirable for motor-gasoline production than the iso-olefins produced by catalytic cracking. Hydrocracking yields the least desirable product for further refining to motor-gasoline, since it is mainly paraffinic.

b) C_{15}-C_{22} *distillate*. The density of the distillate range material from LTFT syncrude is around 780 $kg{\cdot}m^{-3}$, which is well below the minimum diesel fuel density specification. The low density of LTFT distillate is due to its low aromatics content (<1%). Although this makes it suitable for special uses, such as indoor heating and lighting, refining it to meet diesel fuel specifications presents a challenge. Since the aim of the refinery design is to maximise motor-gasoline production and not to produce diesel fuel, this cut can rather be converted to naphtha range material by catalytic cracking.

c) C_{11}-C_{14} *kerosene*. The straight run LTFT kerosene will not meet the freezing point specification of jet fuel on account of its significant *n*-paraffin content. This shortcoming can be addressed by mild hydroisomerisation. Alternatively this material can also be converted by catalytic cracking to lighter material for refining to motor-gasoline. When pushing for maximum motor-gasoline production, the latter course of action is probably the best, although it may be less efficient than refining it to jet fuel.

d) *C_9-C_{10} naphtha*. The discussion on the refining of this HTFT syncrude cut is equally applicable to LTFT syncrude. Although it is already in the motor-gasoline boiling range, it has a low octane value and in the absence of a catalytic reformer, its refining pathway is less clear. It can be used as a jet fuel component, at the loss of motor-gasoline, or it can be co-processed with the heavier fractions in a catalytic cracker to make it more amenable to motor-gasoline refining.

e) *C_2-C_8 material*. Less than 20% of the LTFT syncrude is contained in this fraction, which is very olefinic (>60% olefins), unlike the heavier material. It can be upgraded to motor-gasoline in a similar fashion as discussed for HTFT, but ethylene refining is less of a problem, since ethylene constitutes only 1% of the LTFT syncrude.

f) *Aqueous phase oxygenates*. About 4-5% of the LTFT syncrude is dissolved in the water produced during Fischer-Tropsch synthesis. Methanol and ethanol are the main products and can be recovered by the appropriate separation processes. However, it should be noted that no aqueous phase oxygenates are recovered in the current commercial LTFT refinery designs, since it is considered uneconomical.

3.3.1. Catalytic cracking of LTFT wax

The selection of the cracking technology for the upgrading the LTFT residue fraction is central to the success of the refinery design when motor-gasoline has to be maximised. By selecting a catalytic cracker for the conversion of the bulk of the syncrude, the feedstock that has to be refined to motor-gasoline loses much of its Fischer-Tropsch character. However, it would be wrong to say that the yield structure from fluid catalytic cracking of wax is similar to that from crude oil FCC. The yield of motor-gasoline and gas is substantial (Table 12)(19)(20) and the motor-gasoline contains less aromatics than the product from the FCC of crude oil. As a matter of fact, the FCC derived naphtha from LTFT syncrude resembles HTFT syncrude, although there are no oxygenates and the hydrocarbons are more branched. One would therefore expect that a similar refining strategy could be followed as was devised for the development of an HTFT motor-gasoline refinery.

Table 12. Yield structure of fluid catalytic cracking (FCC) of wax as determined at 90% conversion on a commercial equilibrium catalyst (Ecat) at 525°C and 4 s residence time in a microriser reactor. This is compared to a typical yield structure from FCC of crude oil.

Products	Selectivity to cracking products (mass %)			
	FCC of wax. Ref.(19)		FCC of crude oil. Ref.(20)	
Dry gas (H_2, CH_4, C_2's)	0.9		3.42	
propylene	6.0		3.9	
propane	0.6		1.1	
n-butenes	3.5		4.38	
iso-butene	4.2		1.82	
butanes	0.5		2.48	
C_5-C_{11} naphtha	83.9		47.6	
- *n*-olefins		19.3		23.2
- iso-olefins		42.8		
- *n*-paraffins		0.4		7.7
- iso-paraffins		14.3		
- cyclo-olefins		4.2		1.1
- cyclo-paraffins		0.4		
- aromatics		2.5		15.6
Distillate (LCO)	0.0		16.3	
Residue (HCO)	0.0		14.6	
Coke	0.4[‡]		4.4	

[‡] Reported as 2.6%, but for mass balance closure it must be 0.4%. The latter number makes more sense, since it is known that FT feed is non-coking.

3.3.2. Hydrocracking of LTFT wax

When hydrocracking technology is used to upgrade the residue, as is being done commercially, the distillate production is maximised, not the naphtha production. By increasing the severity, more naphtha and gas can be produced, but it is paraffinic. The C_4-C_6 naphtha can be upgraded as naphtha, but to counteract the high vapour pressure of this high-octane motor-gasoline, some heavier material is also needed. This presents a problem, because the LTFT syncrude contains less than 1% butenes, which are an important feed material for heavier high-octane motor-gasoline production.

Aromatic motor-gasoline can be produced to counteract the high vapour pressure of the C_4-C_6 motor-gasoline, but the inclusion of aromatics is limited by the fuel specifications. The type of aromatisation technology that can be used is also somewhat dependent on the selection of hydrocracking for residue upgrading. When a platinum promoted non-acidic L-zeolite based technology is selected, the feed is limited to the C_6 and heavier naphtha. However, inclusion of the C_6 naphtha in the feed not only removes material from the C_4-C_6 motor-gasoline, but also results in a high benzene production. In an HTFT refinery benzene production is not a problem, since it can be alkylated with short chain olefins, but in a hydrocracker based LTFT refinery the availability of such olefins is limited. The volume of benzene that can be alkylated is consequently also limited. Selection of a ZSM-5 based aromatisation technology is better suited to a hydrocracker based LTFT refinery, since the LPG fraction can be converted to aromatics. Nevertheless, the volume of on-specification motor-gasoline that can be produced in this way is rather limited and such a design is better suited to jet fuel production.

3.4. LTFT motor-gasoline refinery flowschemes

3.4.1. Flowscheme 4

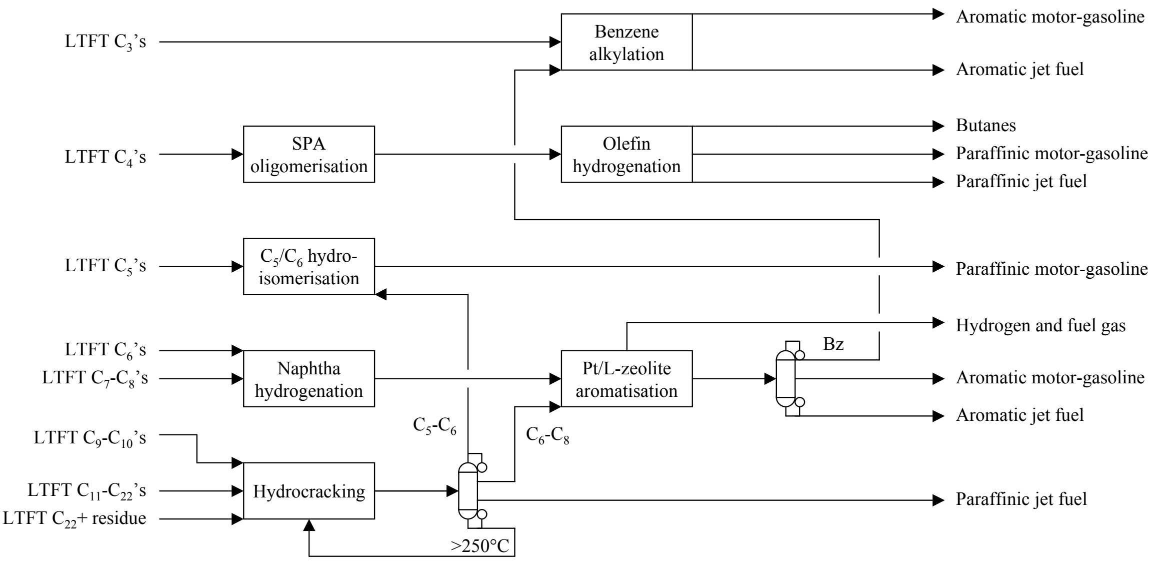

Figure 6. LTFT motor-gasoline refinery, flowscheme 4.

The aim with this refinery design was to explore to what extent hydrocracking can be used as residue upgrading technology for an LTFT motor-gasoline refinery. The selection is based on the good technology fit with syncrude, despite the arguments already raised against its applicability to motor-gasoline production. This train of thought, namely to select the technology with the best fit to Fischer-Tropsch syncrude, was continued with the selection of the aromatisation technology. A platinum promoted non-acidic L-zeolite based process is employed. The resulting refinery design is shown in Figure 6. The flowscheme does not include recovery of the C_2 hydrocarbons and the oxygenates dissolved in the aqueous product. This is in line with the practise at current commercial LTFT facilities such as Shell's Bintulu plant in Malaysia and Sasol's Oryx facility in Qatar.

All C_9 and heavier material is hydrocracked to material lighter boiling than 250°C by operating the hydrocracker in kerosene-mode. The C_6-C_8 product from hydrocracking is combined with the hydrotreated C_6-C_8 LTFT syncrude fraction and aromatised. The C_5-C_6 product from hydrocracking is combined with the C_5 LTFT syncrude fraction and hydroisomerised. It will be noted that C_6 hydrocarbons from the hydrocracker are only partly routed to the aromatisation unit. The split of C_6 material between aromatisation and hydroisomerisation is determined by the benzene processing capability of the refinery. The benzene is alkylated with propylene to produce cumene, typically on a SPA catalyst. Since the amount of propylene in the LTFT syncrude is limited, benzene alkylation capacity is constrained by olefin availability. Although it is in principle possible to use butene as alkylating olefin too, it is not only less efficient, but the butenes are also needed for the production of heavier high-octane non-aromatic motor-gasoline.

The refinery design (Figure 6) resulted in a low motor-gasoline yield (Table 13) and significant production of LPG and jet fuel. The quality of the motor-gasoline was borderline with respect to some fuel specifications (Table 14), while the jet fuel failed to meet the density specification for Jet A-1. However, the jet fuel could easily be upgraded to either Jet A-1 or even BUFF (flash point specification of 60°C) by routing more heavy aromatics to the jet fuel. Some benefits of L-zeolite aromatisation could be seen, such as the high octane number of the motor-gasoline and the small refinery hydrogen requirement. Surprisingly, the design showed that an L-zeolite based aromatisation process could be combined with hydrocracking in an LTFT refinery, despite expectations to the contrary.

Table 13. Yield structure of the LTFT motor-gasoline refinery shown in Figure 6 using L-zeolite based aromatisation. It has a liquid fuel yield of 92% (mass), a motor-gasoline yield of 28% (mass) and a jet fuel yield of 52% (mass).

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	140157	189	28585	29.7
Jet fuel	261121	340	51290	53.2
Diesel fuel	0	0	0	0.0
LPG	59403	109	16484	17.1
Other products				
Fuel gas	16006			
Unrecovered organics	22396			
Hydrogen	-573			
Water	1490			
Σ	500000	638	96359	100

Table 14. Motor-gasoline and jet fuel quality from the LTFT motor-gasoline refinery shown in Figure 6.

Fuel properties	Refinery	Fuel specification	
Motor-gasoline		*Euro-4*	
RON	98	95	Min
MON	92	85	Min
Vapour pressure (kPa)	61	60	Max
Density ($kg\cdot m^{-3}$)	740	720-775	Range
Olefins (vol %)	0.5	18	Max
Aromatics (vol %)	35.0	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.7	1	Max
Jet fuel		*Jet A-1*	
Density ($kg\cdot m^{-3}$)	768	775-840	Range
Aromatics (vol %)	12.1	8-25	Range
Flash point (°C)	57	38	Min
Vapour pressure (kPa)	0.5	-	

3.4.2. Flowscheme 5

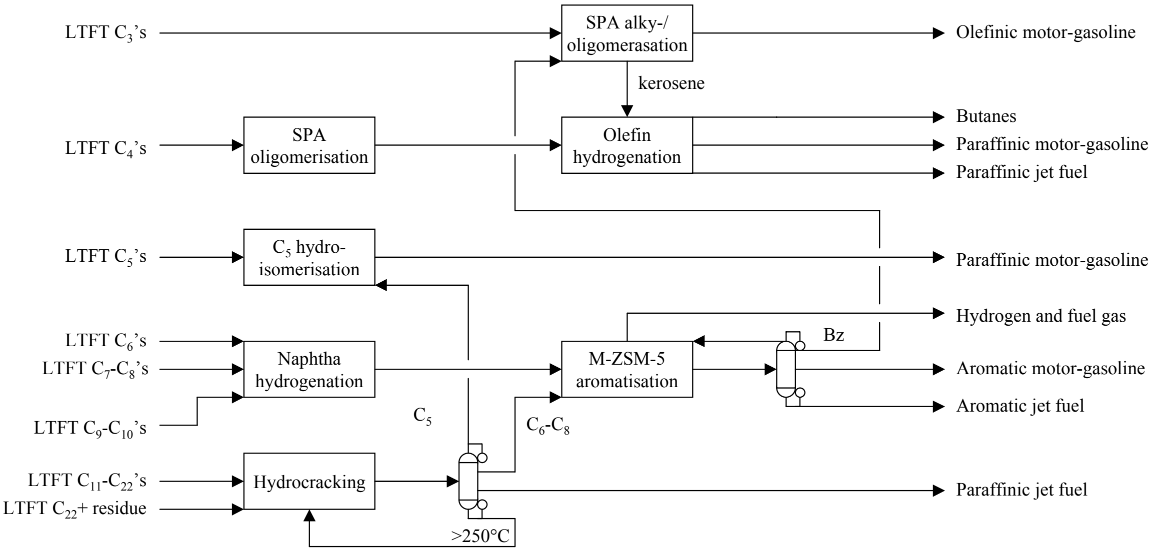

Figure 7. LTFT motor-gasoline refinery, flowscheme 5.

The same design principles as in flowscheme 4 was used to develop a hydrocracker based refinery design employing a metal promoted H-ZSM-5 based aromatisation technology (Figure 7). It was hoped that the ZSM-5 based aromatisation unit could reduce the LPG production, as well as offer a more direct upgrading pathway for the C_9-C_{10} naphtha. In general the design is very similar to flowscheme 4, apart from the aromatisation technology and the operation of the benzene alkylation unit. The latter unit was operated as a C_3 SPA based oligomerisation unit, with benzene being co-fed to enable alkylation.(18) Unlike conventional aromatic alkylation units, this mode of operation entails a low aromatics to olefin ratio in the feed. Oligomerisation is therefore not suppressed and may even be the main reaction.

The C_5's from the hydrocracker serve as feed for hydroisomerisation and aromatisation and the vapour pressure of the motor-gasoline determines the split being used. The design of the hydroisomerisation unit is thereby simplified, since it takes only C_5 hydrocarbons as feed and *n*-pentane recycle can be achieved by distillation.

The yield structure (Table 15) changed and the yield of motor-gasoline decreased to 22% compared to the 28% of the previous design! Although the LPG production was reduced by the use of ZSM-5 based aromatisation, most of the gain was reflected in jet fuel production. Nevertheless, the design was less quality constrained, with both motor-gasoline and jet fuel meeting specifications (Table 16).

Table 15. Yield structure of the LTFT motor-gasoline refinery shown in Figure 7 using ZSM-5 based aromatisation. It has a liquid fuel yield of 91% (mass), a motor-gasoline yield of 22% (mass) and a jet fuel yield of 59% (mass).

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	108308	148	22309	23.7
Jet fuel	293867	377	56979	60.5
Diesel fuel	0	0	0	0.0
LPG	53744	98	14835	15.8
Other products				
Fuel gas	23957			
Unrecovered organics	22614			
Hydrogen	-3805			
Water	1315			
Σ	500000	624	94122	100

Table 16. Motor-gasoline and jet fuel quality from the LTFT motor-gasoline refinery shown in Figure 7.

Fuel properties	Refinery	Fuel specification	
Motor-gasoline		*Euro-4*	
RON	96	95	Min
MON	89	85	Min
Vapour pressure (kPa)	60	60	Max
Density ($kg\cdot m^{-3}$)	733	720-775	Range
Olefins (vol %)	5.1	18	Max
Aromatics (vol %)	34.7	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.1	1	Max
Jet fuel		*Jet A-1*	
Density ($kg\cdot m^{-3}$)	779	775-840	Range
Aromatics (vol %)	20.3	8-25	Range
Flash point (°C)	54	38	Min
Vapour pressure (kPa)	0.7	-	

The vapour pressure of the motor-gasoline was a limiting specification in flowscheme 4 (Figure 6) and flowscheme 5 (Figure 7). This excluded the butanes from being blended into the motor-gasoline and even resulted in some C_5 naphtha not being hydroisomerised to keep the RVP within specification limits. The vapour pressure of the fuel could not be lowered by further aromatics blending, since the aromatic content was already close to its limit. A lack of short chain olefins precluded production of heavier olefinic motor-gasoline, which left oxygenated motor-gasoline as the only lever remaining in order to introduce more flexibility in the fuel pool. Since vapour pressure was limiting, only fuel ethers such as TAME and TAEE could be considered as oxygenate motor-gasoline additives. Unfortunately the C_5 olefin fraction in LTFT syncrude that is amenable to etherification (2-methyl-1-butene and 2-methyl-2-butene) is too small for meaningful syncrude based etherification. A significant modification of the refinery flowscheme was therefore required to enable syncrude based ether production. Alcohols would have to be recovered from the aqueous product, a pentene skeletal isomerisation unit would have to be added to increase the yield of reactive isoamylenes and an etherification unit would have to be included. These additions would increase the refinery complexity and cost considerably, yet, it would be able to convert only 2% of the syncrude to fuel ethers. This avenue of refinery development was consequently not explored any further.

From the designs (flowschemes 4 and 5) it was clear that a hydrocracker based LTFT refinery is not good for maximum motor-gasoline production.

3.4.3. Flowscheme 6

When catalytic cracking is used as residue conversion unit in the refinery design (Figure 8), the refinery contains the same conversion units as in the previous two LTFT refinery designs (Figures 6 and 7), but the motor-gasoline yield is significantly increased (Table 17). The almost doubling of motor-gasoline yield comes at the expense of some overall liquid fuel yield loss. This is to be expected from a carbon rejection technology such as FCC.

Without repeating the discussion on feed and product routing, some of the differences in this design will be highlighted.

The C_4 product from the FCC contains about 50% iso-butene. This allows the SPA based oligomerisation process to be operated at a lower temperature to produce a product rich in trimethylpentenes. The negative impact of the excess propylene (11% of olefins) that is co-fed to this unit is more than offset by the positive impact of the iso-butene. The calculated

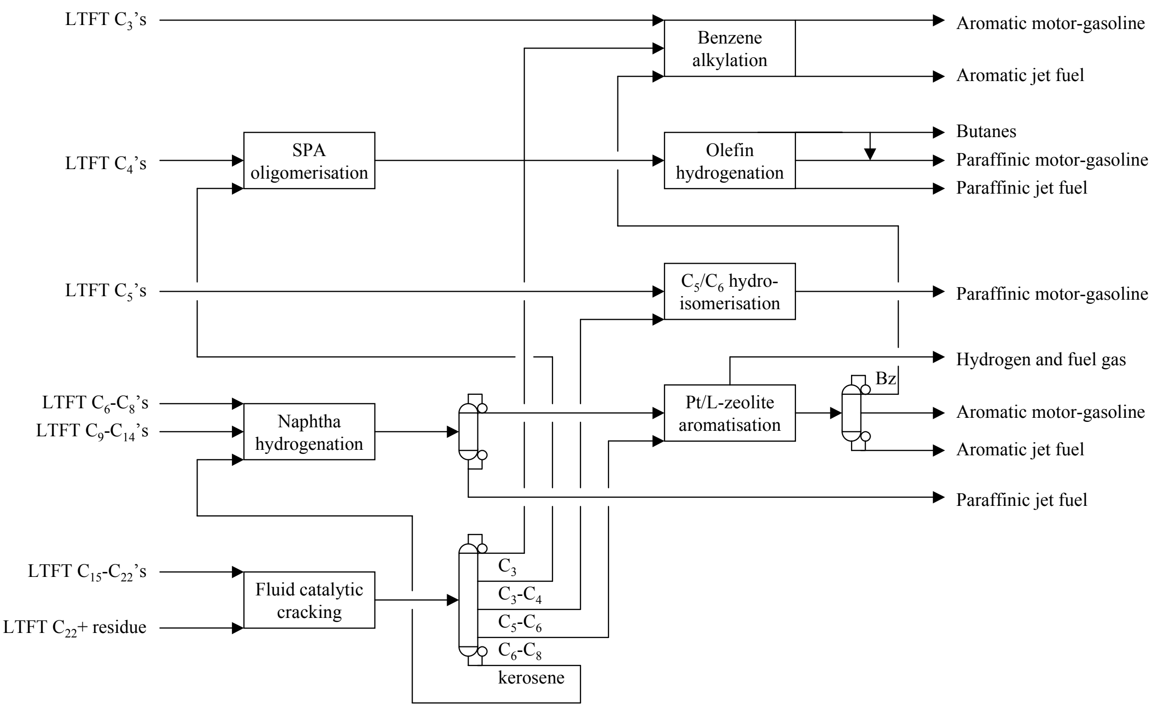

Figure 8. LTFT motor-gasoline refinery, flowscheme 6.

hydrogenated motor-gasoline properties are RON 91 and MON 86, which are better than can be achieved with C_4-only HTFT feed.(14) The short chain olefin shortage that limited benzene alkylation capacity (as noted in the discussion of flowscheme 4) has been addressed by the FCC. Some propylene could therefore be routed to the olefin oligomerisation unit.

Platinum promoted non-acidic L-zeolite based aromatisation technology has been selected to convert the C_6-C_8 LTFT naphtha and most of the C_6-C_8 FCC derived naphtha to aromatics. Since FCC increased the naphtha volume and is not a hydrogen consumer like hydrocracking, the refinery has a significant surplus of hydrogen (Table 17).

The motor-gasoline and jet fuel produced by this design meet fuel specifications (Table 18). The motor-gasoline production is vapour pressure constrained and only a limited fraction of the butanes could be blended into the motor-gasoline. However, the high iso-olefin content of the FCC naphtha makes it possible to consider etherification without the need for an olefin skeletal isomerisation unit as would be required for flowschemes 4 and 5. This reduces the vapour pressure in the motor-gasoline (Table 18) and opens possibilities to further increase the motor-gasoline yield by blending in butanes, etc. In addition to the beneficial effect on vapour pressure, ether addition also adds further blending flexibility with respect to octane and aromatics content.

Table 17. Yield structure of the LTFT motor-gasoline refinery shown in Figure 8. It has a liquid fuel yield of 90% (mass) and a motor-gasoline yield of 51% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	254329	344	51936	56.4
Jet fuel	177030	228	34462	37.4
Diesel fuel	0	0	0	0.0
LPG	20228	37	5659	6.1
Other products				
Fuel gas	20488			
Unrecovered organics	23710			
Hydrogen	2746			
Water	1471			
Σ	500000	610	92058	100

Table 18. Motor-gasoline quality from the LTFT motor-gasoline refinery shown in Figure 8 showing (a) the blend without oxygenates, and (b) the blend with the addition of TAME from an additional etherification unit (not shown in Figure 8).

Fuel properties	Refinery scenarios		Euro-4	
	(a)	(b)		
RON	98	102	95	Min
MON	92	93	85	Min
Vapour pressure (kPa)	60	52	60	Max
Density ($kg \cdot m^{-3}$)	739	750	720-775	Range
Olefins (vol %)	0.8	0.8	18	Max
Aromatics (vol %)	33.9	32.2	35	Max
Oxygenates (vol %)	0.0	14.9	15	Max
Benzene (vol %)	0.2	0.0	1	Max
Ethanol (vol %)	0.0	0.0	5	Max
TAME (vol %)	0.0	14.6	15	Max

From this refinery design it should be clear that residue upgrading by FCC is much better than hydrocracking for maximising motor-gasoline production from LTFT syncrude.

However, the improvement is not only limited to motor-gasoline yield, but also in terms of motor-gasoline quality and refinery flexibility.

4. Jet fuel refineries

When maximum jet fuel production is considered, it is important to adjust the carbon number distribution, as well as the properties of the material. In this respect it is not different from maximum motor-gasoline refining. The carbon number distribution determines the yield, while the properties determine whether jet fuel specifications will be met.

Kerosene range material is typically in the carbon number range C_9-C_{14},[1] which overlaps with motor-gasoline and diesel fuel. Using this range, it can be shown that the maximum straight run kerosene from syncrude is produced when the Fischer-Tropsch catalyst has chain growth probability (α-value) of 0.80-0.84 (Figure 9). In practise, the distillation range of straight run Fischer-Tropsch syncrude that can be included in jet fuel is determined by the flash point (minimum 38°C) and freezing point (maximum –47°C) specifications on account of its high linear hydrocarbon content (Table 19).(21)

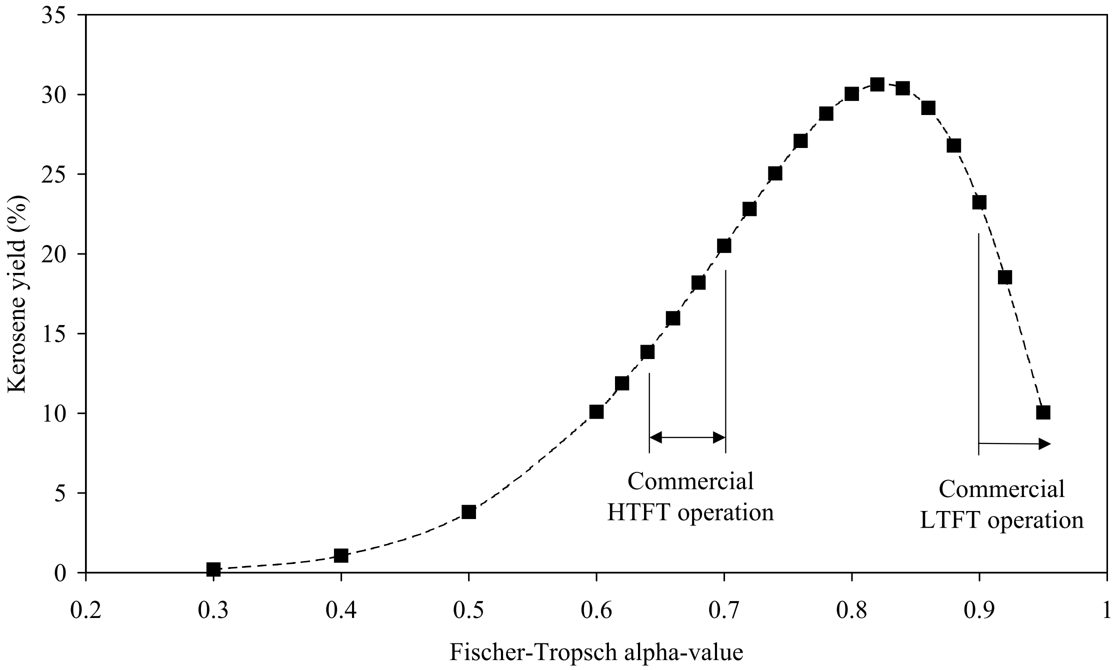

Figure 9. Yield of straight run kerosene (C_9-C_{14}) in the C_3 and heavier hydrocarbon fraction from Fischer-Tropsch as function of the chain growth probability (α-value).

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[1] The Jet A-1 specification limits the maximum final boiling point temperature to 300°C, but it does not prescribe a minimum initial boiling point temperature. The initial boiling point temperature is indirectly regulated by specifying a minimum flash point of 38°C and maximum T10 temperature of 205°C.

Table 19. Physical properties relevant to jet fuel of some hydrocarbons, namely freezing point (T_m), normal boiling point (T_b), flash point (T_{fp}) and vapour pressure at 15.6°C (RVP).

Compound	T_m (°C)	T_b (°C)	T_{fp} (°C)	RVP (kPa)
Linear paraffins				
n-nonane	-53.5	150.8	31.1	1.2
n-decane	-29.6	174.2	46.1	0.4
n-undecane	-25.6	195.9	65.0	0.1
n-dodecane	-9.6	216.3	73.9	<0.1
n-tridecane	-5.4	235.2	-	<0.1
n-tetradecane	5.9	253.8	100.0	<0.1
n-pentadecane	9.9	270.7	-	<0.1
n-hexadecane	18.2	286.9	-	<0.1
Branched paraffins				
2-methyloctane	-80.4	143.3	-	1.7
2,2,5-trimethylhexane	-105.8	124.1	12.8	4.3
2-methylnonane	-74.7	167.0	-	0.6
Aromatics				
benzene	5.5	80.1	-11.1	22.1
toluene	-95.0	110.6	4.4	7.1
ethylbenzene	-95.0	136.2	15.0	2.6
o-xylene	-25.2	144.4	17.2	1.8
m-xylene	-47.8	139.1	25.0	2.3
p-xylene	13.3	138.4	25.0	2.4
cumene	-96.0	152.4	43.9	1.3
sec-butylbenzene	-75.5	173.3	52.2	0.5
tert-butylbenzene	-57.9	169.1	60.0	0.6
o-cymene	-71.5	178.2	-	0.4
m-cymene	-63.7	175.1	-	0.5
p-cymene	-67.9	177.1	47.2	0.4
o-diethylbenzene	-31.2	183.4	57.2	0.3
m-diethylbenzene	-83.9	181.1	56.1	0.3
p-diethylbenzene	-42.8	183.8	56.7	0.3
n-hexylbenzene	-61.0	226.1	71.7	<0.1

Quality-wise jet fuel requires neither a high octane number, nor a high cetane number. Since Fischer-Tropsch syncrude is naturally low in sulphur and dinuclear aromatics, it requires only some hydroisomerisation to meet the freezing point specification and the inclusion of aromatics to meet the aromatic content (8-25%) and density (775-840 kg·m^{-3}) specifications.[m] Jet fuel therefore does not require much refining to achieve specification. The basic steps involved in producing maximum jet fuel from syncrude are:

a) Adjust the carbon number distribution to maximise kerosene.

b) Synthesise appropriate kerosene range aromatics.

c) Skeletally isomerise the linear hydrocarbons to lower their freezing point.

d) Hydrogenate the syncrude to reduce the olefin and oxygenate content.

The development of a syncrude refinery that produces just jet fuel is not practical and it is expected that some material will end up as LPG, naphtha and heavy distillate. An important aspect of the refinery design, which is less obvious, is to ensure that these non-kerosene range fractions are of sufficient quality that the naphtha can be sold as motor-gasoline and that the heavy distillate can be sold as diesel fuel. This was also tacitly done in the flowschemes for maximum motor-gasoline production.

4.1. HTFT jet fuel refinery development

The synergy between motor-gasoline refining and jet fuel refining has indirectly been explored with flowschemes 1-3, where jet fuel was the main secondary product. If we compare the requirements for motor-gasoline and jet fuel, two aspects of commonality are obvious, namely the need for alkyl aromatics and the undesirability of linear paraffins. The requirements for upgrading of the different fractions are discussed on a carbon number basis:

a) *Residue (C_{22}+).* Despite the HTFT residue fraction being small, the need to hydroisomerise the kerosene range material and the possibility to convert heavy distillate to kerosene, strongly argues for the inclusion of a hydrocracker. The hydrocracker should be operated in kerosene mode to maximise the kerosene range products and avoid over-cracking to naphtha and gas.

b) *C_{15}-C_{22} distillate.* Considering that the inclusion of a hydrocracking unit is likely, the distillate can be partly converted into a branched paraffinic kerosene component that should have good cold flow properties. In doing so, the main shortcoming of using HTFT

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[m] Full syn-jet has not yet been approved, but in anticipation, maximum aromatics has been set at 25%, not 22%.

distillate as diesel fuel, namely its low density, is overcome by moving the material out of the diesel boiling range.

c) *C_{11}-C_{14} kerosene*. The straight run HTFT kerosene does not meet jet fuel specifications, but can easily be converted to a fully synthetic jet fuel. Hydrogenation of the oxygenates and hydroisomerisation of the hydrocarbons render a product that meets all the jet A-1 specifications, including aromatics content and density.[n] This is best achieved by operating a hydrocracking unit in such a way that the kerosene range material is only hydroisomerised, although some material will inevitably be lost due to hydrocracking.

d) *C_9-C_{10} naphtha*. This heavy naphtha fraction also falls within the kerosene range and can be refined in a similar way to the C_{11}-C_{14} kerosene, namely by hydroisomerisation in a hydrocracking unit. Strictly speaking it is not even necessary to hydroisomerise the C_9-C_{10} naphtha, which only requires hydrotreating, since it will be present in low enough concentration for the freezing point of the *n*-decane not to be a problem. Two benefits can be gained by only hydrotreating, rather than hydroisomerising this fraction. The flash point is not worsened and no material is lost to lighter products. The inclusion of the C_9-C_{10} naphtha in jet fuel effectively rules out catalytic reforming as technology to produce aromatics. This is not of concern, because it has previously been argued that the low $N+2A$ value of HTFT syncrude makes it a poor feed material for chlorided Pt/alumina catalytic reforming.

e) *C_7-C_8 naphtha*. The inclusion of C_7-C_8 naphtha in jet fuel is limited by the flash point specification, while its inclusion in motor-gasoline is limited by its poor octane value. The bulk of this fraction must therefore be converted in some way and aromatisation is the logical refining pathway. Olefin oligomerisation can also be considered as way to move some of this material into the kerosene boiling range.

f) *C_6 naphtha*. The two obvious upgrading pathways for the C_6 naphtha are hydroisomerisasion and aromatisation. The former results in a product destined exclusively for motor-gasoline, while the latter results in the production of aromatics that can potentially be refined to jet fuel. Since the aim is to produce maximum jet fuel, aromatisation is the preferred choice. Nevertheless, some refinery designs may dictate otherwise depending on the motor-gasoline quality requirements. Although olefin oligomerisation is a less obvious way to refine the C_6 olefin fraction, it may be considered as a method to increase the kerosene production.

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[n] It was shown that the preparation of Jet A-1 from a hydrogenated HTFT kerosene fraction and iso-paraffinic kerosene from short chain olefin oligomerisation over SPA meets all the Jet A-1 specifications. Ref.(11). Certification of fully synthetic jet fuel from HTFT is expected in 2007/8.

g) *C_5 naphtha*. The C_5 naphtha is primarily a motor-gasoline component, with hydroisomerisation yielding high-octane C_5 isomerate. Depending on the constraining motor-gasoline specifications, olefin skeletal isomerisation followed by etherification may also be considered. Optionally the pentene fraction can be used as feed for aromatic alkylation or olefin oligomerisation to increase the kerosene production.

h) *C_4 hydrocarbons*. Butene oligomerisation on SPA forms the basis for the production of heavier high-octane hydrogenated motor-gasoline. Some kerosene is co-produced during this process. The butenes can also be oligomerised on other types of acid catalysts to boost kerosene production. Aromatic alkylation is a less preferred refining pathway. However, it is anticipated that the technology selection for C_4 upgrading will be determined by motor-gasoline quality requirements.

i) *C_3 hydrocarbons*. SPA based propylene oligomerisation is an ideal jet fuel technology. The SPA catalyst restricts oligomer formation to the kerosene range (no heavier material is being co-produced) and kerosene is the main product. The resultant iso-paraffinic kerosene (IPK) produced by hydrogenation of the oligomers is known to be an excellent jet fuel component.(11) It is therefore ironic that benzene alkylation with propylene is also an efficient way to produce an aromatic component that is well suited for inclusion in both motor-gasoline and jet fuel. These processes can in principle be combined to produce a fully synthetic jet fuel in a single step.(18)

j) *C_2 hydrocarbons*. In the context of a maximum jet fuel refinery, ethylene should preferably be used for aromatic alkylation. Other refining pathways include hydration and purification for chemical use.

l) *Aqueous phase oxygenates*. The possibilities for the refining of the oxygenates dissolved in the aqueous product from HTFT synthesis has already been discussed. From a fuels refining perspective the easiest and least complex pathway is selective hydrogenation and dehydration to increase the production of mainly C_2-C_5 olefins that can be co-refined with the rest of such material.(12)

4.2. HTFT jet fuel refinery flowschemes

4.2.1. Flowscheme 7

The recommendations made in the previous section were applied to the development of an HTFT refinery to maximise jet fuel (Figure 10). This resulted in a refinery design very similar to that of flowscheme 3. The main differences being the routing of the products from C_3 SPA oligomerisation, which is included *in toto* in the jet fuel, and the hydrogenation of the C_9-C_{10} naphtha that is also included in the jet fuel.

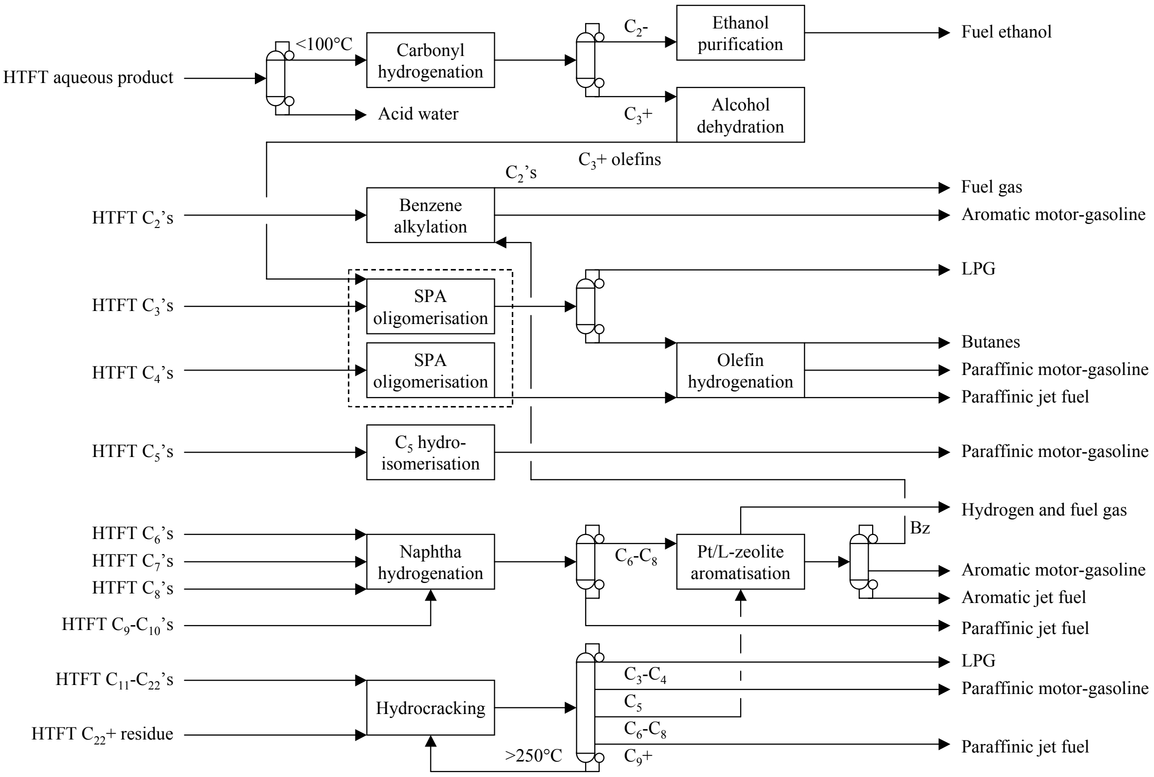

Figure 10. HTFT jet fuel refinery, flowscheme 7.

The yield structure (Table 20) shows a motor-gasoline to jet fuel volume ratio of 47:53, but once the motor-gasoline is blended with either butanes or ethanol to its vapour pressure limit, the ratio is closer to 50:50. The refinery design required no tweaking to meet motor-gasoline and jet fuel specifications (Table 21), indicating that it is a robust design for real-world situations.

The main drawback of flowscheme 7 is its jet fuel yield, which is low considering that the aim was to maximise jet fuel production. The refining pathways for the different syncrude fractions were analysed to determine in what way the jet fuel yield could be improved. It was found that the C_4, C_5, C_7 and C_8 naphtha fractions were refined mainly to motor-gasoline. It was also realised that these fractions were used to produce good quality high-octane motor-gasoline blending components and that care would have to be taken not to make motor-gasoline that does not meet specifications.

Table 20. Yield structure of the HTFT jet fuel refinery shown in Figure 10, which has a liquid fuel yield of 89% (mass) and jet fuel yield of 43% (mass).

Product	Refinery production			
	($kg{\cdot}h^{-1}$)	($m^3{\cdot}h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	183049	249	37598	41.5
Excess fuel ethanol	17624	22	3351	3.7
Jet fuel	214417	275	41560	45.9
Diesel fuel	0	0	0	0.0
LPG	29054	54	8122	9.0
Other products				
Fuel gas	32612			
Unrecovered organics	14894			
Hydrogen	-928			
Water	9277			
Σ	500000	600	90631	100

Table 21. Jet fuel and motor-gasoline quality from the HTFT jet fuel refinery in Figure 10.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density ($kg{\cdot}m^{-3}$)	779	775-840	Range
Aromatics (vol %)	24.2	8-25	Range
Flash point (°C)	52	38	Min
Vapour pressure (kPa)	0.7	-	
Motor-gasoline		*Euro-4*	
RON	96	95	Min
MON	91	85	Min
Vapour pressure (kPa)	56	60	Max
Density ($kg{\cdot}m^{-3}$)	735	720-775	Range
Olefins (vol %)	1.3	18	Max
Aromatics (vol %)	29.2	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.5	1	Max
Ethanol (vol %)	0.0	5	Max

4.2.2. Flowscheme 8

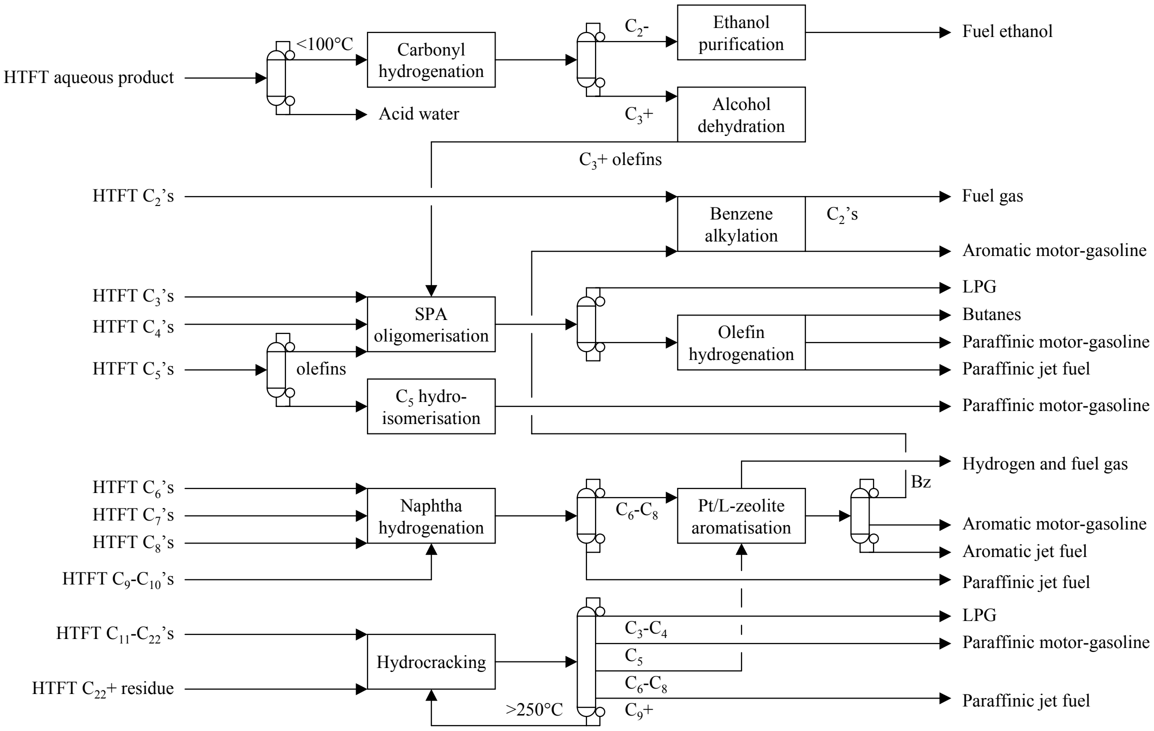

Figure 11. HTFT jet fuel refinery, flowscheme 8.

The objective of this refinery design was to find a way of incorporating more of the syncrude into jet fuel. The development of the refinery design focussed specifically on the routing of the C_4 and C_5 naphtha, since these fractions constitute 23% of the syncrude. The crux of the design (Figure 11) was the selective conversion of these cuts into jet fuel, by exploiting the unique properties of SPA catalysis. The rest of the design is similar to that of flowscheme 7.

When a mixture of propylene, butenes and pentenes are oligomerised, conjunct polymerisation results (the products are not integer multiples of the feed carbon number). On a mechanistic level, propylene dominates reaction initiation due to its ability to form a strong phosphoric acid ester.(22) The C_8-rich product fraction found during C_4-only oligomerisation is thereby greatly reduced, with most of the oligomers being in the C_9-C_{14} range. The SPA catalysed oligomerisation of a mixed C_3-C_5 syncrude naphtha yields a significant kerosene fraction, especially if the distillation cut point is between C_8 and C_9. This allowed the present flowscheme to convert more than 80% of the olefinic C_3-C_5 material into jet fuel, compared to only around 50% in the previous design, flowscheme 7. Since the hydrogenated kerosene fraction from SPA oligomerisation is iso-paraffinic kerosene, aromatics can be blended into the kerosene to further increase the jet fuel volume.

Table 22. Yield structure of the HTFT jet fuel refinery shown in Figure 11, which has a liquid fuel yield of 89% (mass) and jet fuel yield of 61% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	98880	131	19742	22.4
Excess fuel ethanol	17624	22	3351	3.8
Jet fuel	302863	389	58650	66.5
Diesel fuel	0	0	0	0.0
LPG	23568	42	6410	7.3
Other products				
Fuel gas	32612			
Unrecovered organics	14894			
Hydrogen	281			
Water	9277			
Σ	500000	584	88152	100

Table 23. Jet fuel and motor-gasoline quality from the HTFT jet fuel refinery in Figure 11.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density ($kg \cdot m^{-3}$)	780	775-840	Range
Aromatics (vol %)	24.9	8-25	Range
Flash point (°C)	50	38	Min
Vapour pressure (kPa)	0.8	-	
Motor-gasoline		*Euro-4*	
RON	99	95	Min
MON	90	85	Min
Vapour pressure (kPa)	60	60	Max
Density ($kg \cdot m^{-3}$)	756	720-775	Range
Olefins (vol %)	15.6	18	Max
Aromatics (vol %)	32.6	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.9	1	Max
Ethanol (vol %)	0.0	5	Max

Another benefit realised by the conversion of the pentenes to heavier products was that the vapour pressure of the motor-gasoline was reduced. This allowed more butanes to be blended into the fuel, thereby reducing the LPG production. It is also possible to blend in fuel ethanol in exchange for some of the butanes.

The yield structure of the design reflected the significant increase in jet fuel production (Table 22). The design was robust and the quality of the motor-gasoline was not compromised (Table 23) by meeting jet fuel specifications. As a matter of fact, the motor-gasoline quality was sufficient to exclude the C_5 hydroisomerisation unit from the design and still meet the motor-gasoline octane specifications! Another important benefit of this design is that it is hydrogen self-sufficient.

4.2.3. Flowscheme 9

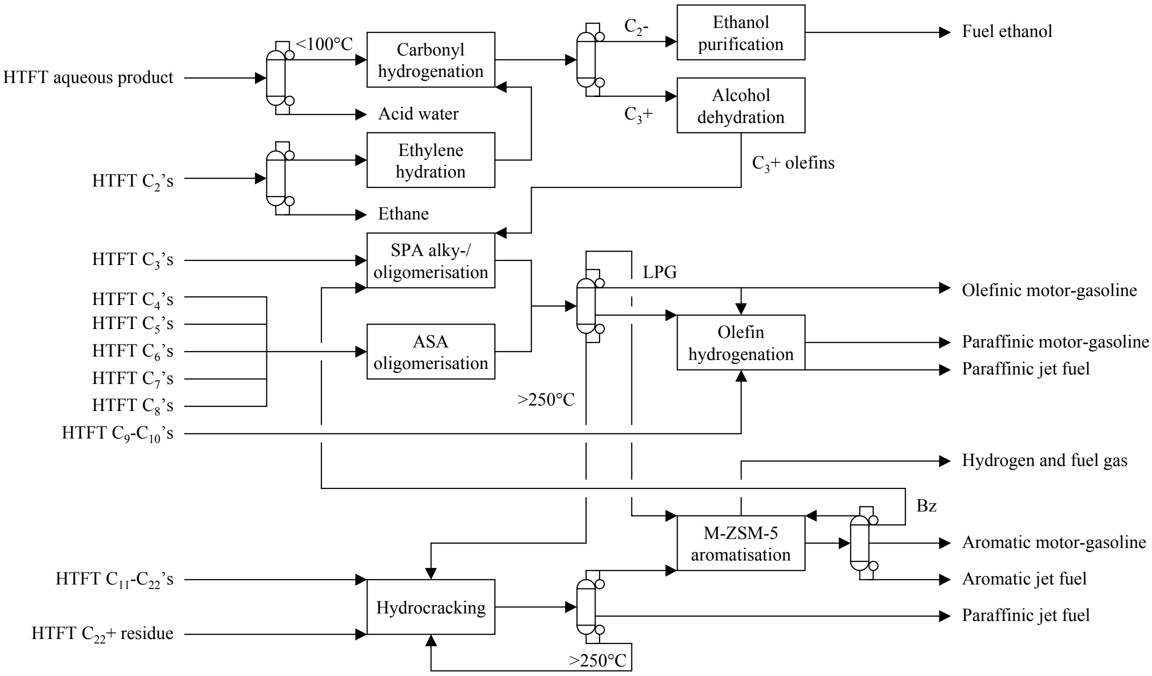

Figure 12. HTFT jet fuel refinery, flowscheme 9.

Despite the robustness and high jet fuel yield of flowscheme 8, the possibility to increase the jet fuel yield even further was explored by changing the oligomerisation and aromatisation technologies. In this design (Figure 12), oligomerisation by amorphous silica-alumina and aromatisation with a metal promoted H-ZSM-5 catalyst were employed, because both technologies are capable of converting material within a wide carbon number range. It was hoped that the combination of the kerosene-mode hydrocracker and ZSM-5 based aromatisation would be able to force most of the material into the kerosene range by cracking the heavier material and aromatising the light material. These changes in technology necessitated a change in alkylation technology too, since ZSM-5 based aromatisation has a low selectivity to benzene. Alkylation of the benzene with ethylene using a zeolite based alkylation technology would have been sub-optimal and combined alkylation/oligomerisation on SPA was better suited to the task. This still left the HTFT ethylene to be refined. Ethylene hydration was used in order to convert the ethylene to fuel ethanol, although by doing so the ethanol production far exceeded motor-gasoline requirements. This flowscheme (Figure 12) is consequently different in many respects from flowscheme 7 (Figure 10) and flowscheme 8 (Figure 11).

Table 24. Yield structure of the HTFT jet fuel refinery shown in Figure 12, which has a liquid fuel yield of 91% (mass) and jet fuel yield of 69% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	46287	59	8914	10.2
Excess fuel ethanol	66405	84	12625	14.4
Jet fuel	343887	437	65979	75.4
Diesel fuel	0	0	0	0.0
LPG	0	0	0	0.0
Other products				
Fuel gas	38772			
Unrecovered organics	17836			
Hydrogen	-2876			
Water	-10311			
Σ	500000	580	87518	100

This approach was a successful refining strategy for increasing jet fuel production (Table 24), with a volumetric motor-gasoline to jet fuel ratio of 13:87 being obtained. However, it was less successful from the point of view of motor-gasoline quality, with only the jet fuel meeting specifications (Table 25). The motor-gasoline resembled a petrochemical feedstock, being high in olefins and aromatics and further refining in a non-energy refinery would make more economic sense.

Table 25. Jet fuel and motor-gasoline quality from the HTFT jet fuel refinery in Figure 12.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	787	775-840	Range
Aromatics (vol %)	25.0	8-25	Range
Flash point (°C)	52	38	Min
Vapour pressure (kPa)	0.8	-	
Motor-gasoline		*Euro-4*	
RON	96	95	Min
MON	84	85	Min
Vapour pressure (kPa)	8	60	Max
Density (kg·m^{-3})	784	720-775	Range
Olefins (vol %)	31.9	18	Max
Aromatics (vol %)	45.3	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.3	1	Max
Ethanol (vol %)	0.0	5	Max

On a conceptual level one could consider recycling most of the motor-gasoline to extinction. One could also consider fluid catalytic cracking as an alternative to hydrocracking for converting the unwanted naphtha range material into olefins and paraffins that can be converted in the oligomerisation and aromatisation units. However, further recycling and processing by energy intensive conversion units were seen as steps in the wrong direction, although it could potentially result in a higher jet fuel yield.

4.3. LTFT jet fuel refinery development

During the development of the LTFT motor-gasoline refineries, some good pointers were obtained on how to develop a jet fuel refinery. As a matter of fact, flowscheme 5 (Figure 7) is a good example of an LTFT jet fuel refinery, meeting both motor-gasoline and jet fuel specifications and having a 59% jet fuel yield.

The lack of olefins for motor-gasoline production is less of an issue when jet fuel is maximised and in general LTFT syncrude is better suited for jet fuel production than for motor-gasoline production. This can be understood in terms of the molecular requirements of jet fuel, with jet fuel consisting mainly of iso-paraffins, naphthenes and alkyl aromatics. Iso-paraffins are easily prepared by the hydroisomerisation and hydrocracking of the linear paraffins present in LTFT syncrude to yield a good quality jet fuel component.(23) Aromatics are also easily produced from paraffins, with the aromatisation technology influencing the feed range that can be converted and the product distribution that can be expected.

The motor-gasoline that is co-produced during jet fuel refining must still meet specifications. Aromatics production is common requirement to both motor-gasoline and jet fuel, while the availability of olefins are important mostly for the production of motor-gasoline. Increasing the jet fuel yield should consequently be beneficial for motor-gasoline production, since it indirectly increases olefin availability for motor-gasoline refining. Details of the refining requirements for motor-gasoline and jet fuel production have already been covered in the previous sections and it serves no purpose rehashing this discussion on a carbon number basis in the present context.

4.4. LTFT jet fuel refinery flowschemes

4.4.1. Flowscheme 10

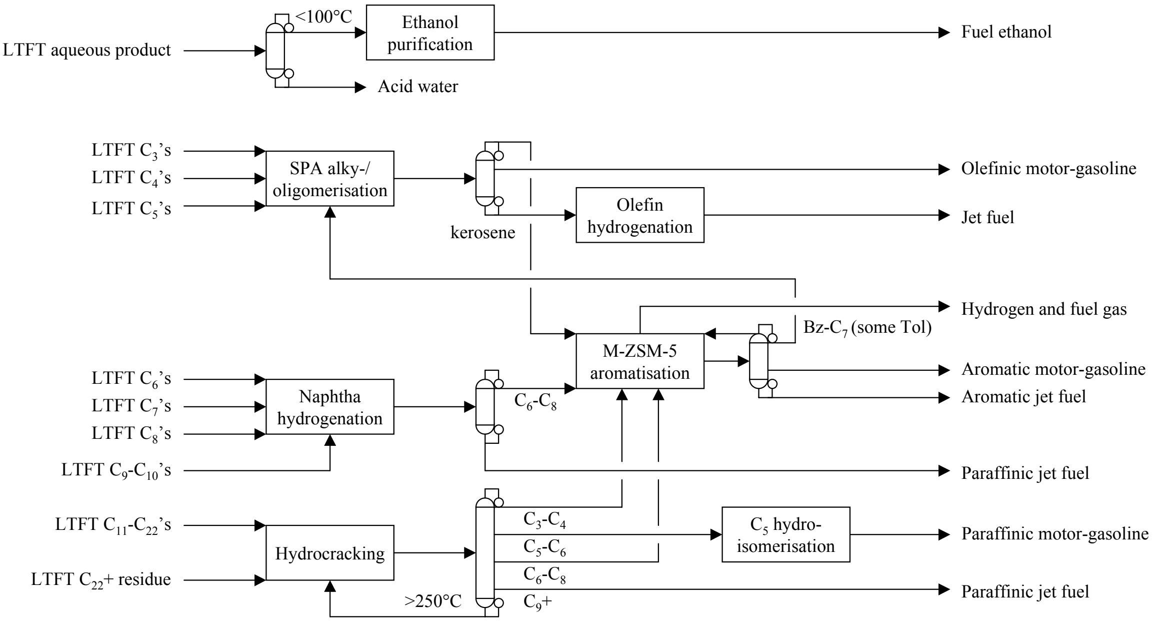

Figure 13. LTFT jet fuel refinery, flowscheme 10.

It has been demonstrated in flowscheme 5 (Figure 7) that the combination of hydrocracking and ZSM-5 based aromatisation is well-suited to jet fuel production. It has further been shown in flowscheme 8 (Figure 11) that SPA catalysed oligomerisation of mixed C_3-C_5 olefins produces good jet fuel and good motor-gasoline if the distillation cutpoint is between C_8 and C_9. Yet, it is also known that when there is not too much benzene in the refinery, that the benzene can be alkylated in a SPA catalysed oligomerisation process without disrupting the olefin oligomerisation. A new LTFT jet fuel refinery was developed by combining these ideas into a single refinery design (Figure 13). The main aim of this design was to maximise jet fuel production, while still meeting the motor-gasoline specifications.

As in the previous LTFT refinery designs, due to economic reasons the C_2 hydrocarbons were not recovered. Contrary to the previous LTFT designs, some aqueous product refining was included in this design (Figure 13), since the motor-gasoline required ethanol addition to meet fuel specifications. The ethanol, or another type of fuel oxygenate can also be obtained from an external source and the inclusion of some aqueous product refining is not central to the design.

The mixed C_3-C_5 hydrocarbons from the LTFT syncrude are used as feed to a SPA based oligomerisation unit, where it is partly oligomerised and partly used to alkylate benzene and some toluene from the aromatisation unit. The kerosene fraction of the product, which contains alkyl aromatics and olefin oligomers, is hydrotreated to produce jet fuel. The naphtha fraction is directly included in the motor-gasoline, while the unconverted C_3-C_5 olefins and paraffins are used as feed for the aromatisation unit.

The LTFT C_6-C_{10} naphtha is hydrotreated before being fractionated into kerosene (C_9-C_{10}) for jet fuel and naphtha (C_6-C_8) for aromatisation.

The heavier LTFT syncrude (C_{11} and heavier) fraction that consists of the straight run distillate and wax, is fed to the hydrocracker. The hydrocracker is operated in kerosene-mode, with the material that is higher boiling than 250°C being recycled to extinction. The product is fractionated into kerosene, C_6-C_8 naphtha, C_5-C_6 naphtha and LPG fractions. The C_5-rich fraction is hydroisomerised in a C_5 hydroisomerisation unit and the C_6 content of this fraction (about 15% of the C_6 hydrocracker product) is determined by the paraffin requirements of the motor-gasoline. The LPG and C_6-C_8 naphtha fractions are employed as feeds to the aromatisation unit.

The aromatisation unit has to make use of metal promoted H-ZSM-5 based technology in order to convert the C_3-C_5 hydrocarbons and keep the benzene production low.

The aromatic-rich product is fractionated, with the toluene rich fraction being used for motor-gasoline and the C_8 and heavier aromatics being blended into the jet fuel.

The refinery design has a volumetric motor-gasoline to jet fuel ratio of 22:78 and yielded 71% jet fuel (Table 26), while meeting both jet fuel and motor-gasoline specifications (Table 27). The motor-gasoline blending is tight, with RON and aromatics being borderline. The refinery as a whole is at its limit with respect to aromatics and it is clear that any additional aromatics production would decrease the yield of jet fuel.[o] There is some leeway for more olefinic motor-gasoline production, but considering the RON of the motor-gasoline, the design is very close to the maximum amount of jet fuel that can be obtained with the conversion unit selection made for this flowscheme. Since this is the highest yield of jet fuel (71%) obtained in any of the HTFT and LTFT flowschemes presented and the blending is very constrained, it may well be close to the maximum yield that can be achieved before significantly increasing the complexity of the refinery.

Table 26. Yield structure of the LTFT jet fuel refinery shown in Figure 13, which has a liquid fuel yield of 92% (mass) and jet fuel yield of 71% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	101328	137	20641	23.0
Excess fuel ethanol	2272	3	432	0.5
Jet fuel	355912	455	68720	76.5
Diesel fuel	0	0	0	0.0
LPG	0	0	0	0.0
Other products				
Fuel gas	26781			
Unrecovered organics	15634			
Hydrogen	-3243			
Water	1315			
Σ	500000	595	89793	100

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[o] The maximum aromatic content in jet fuel is 25%, but in motor-gasoline it is 35%. Since both fuels are blended to their respective aromatics limits, any further aromatics production has to be included in the fuel with the higher aromatics limit. This implies that excess aromatics would have to be diluted with jet fuel and added to the motor-gasoline.

Table 27. Jet fuel and motor-gasoline quality from the LTFT jet fuel refinery in Figure 13.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	782	775-840	Range
Aromatics (vol %)	24.8	8-25	Range
Flash point (°C)	52	38	Min
Vapour pressure (kPa)	0.8	-	
Motor-gasoline		*Euro-4*	
RON	95	95	Min
MON	87	85	Min
Vapour pressure (kPa)	58	60	Max
Density (kg·m^{-3})	741	720-775	Range
Olefins (vol %)	6.5	18	Max
Aromatics (vol %)	34.9	35	Max
Oxygenates (vol %)	4.6	15	Max
Benzene (vol %)	0.2	1	Max
Ethanol (vol %)	4.6	5	Max

5. Diesel fuel refineries

Thus far the production of diesel fuel has been studiously avoided. The aim in the previous designs had been to maximise motor-gasoline and jet fuel production, and convenient refining pathways could be found to refine all distillates to those products. Nevertheless, considering the marketing hype surrounding the GTL ventures of Sasol and Shell, it may have been surprising that no attempt was made to produce diesel fuel in any of the previous flowschemes.

It is true that HTFT and LTFT syncrude have good straight run cetane numbers and being sulphur-free, are high quality distillates. However, there is one diesel fuel specification that is not easily met by syncrude, namely diesel density (820-845 kg·m^{-3}). Acyclic aliphatic hydrocarbons in the distillate boiling range typically have densities in the range 740-800 kg·m^{-3}, which are well below the diesel density specification. One may instinctively think that the density shortfall can be overcome by aromatics addition, just like aromatics had been used to boost the octane number of motor-gasoline and were required to meet jet fuel specifications. Unfortunately this is not the case. For example, if we select a typical mid-range syncrude distillate hydrocarbon such as *n*-hexadecane (777.2 kg·m^{-3}) and co-boiling aromatic such as *n*-nonylbenzene (859.9 kg·m^{-3}), the diesel fuel requires a 52% aromatic content to meet the minimum density specification!

In this respect HTFT syncrude is better suited to diesel fuel production than LTFT syncrude, since the distillate range material contains aromatics and naphthenes, giving it a straight run density close to the diesel specification. When the straight run HTFT distillate is processed in a distillate hydrotreater (such as the Sasol Synfuels U35/235 DHT), the light diesel has a cetane number of 54-58, kinematic viscosity of 2.1-2.4 cSt and density of 804-813 kg·m^{-3}.(24) Unfortunately the HTFT straight run C_{11}-C_{22} distillate is only 8% of the HTFT syncrude and hardly enough to form the base stock for a maximum diesel fuel refinery. More material is needed in the diesel fuel range and this material is not only required to increase the density, but also to increase the overall diesel fuel yield.[p] In order to address some of these shortcomings, the Kölbel-Engelhardt conversion of CO and H_2O into an aromatic-rich Fischer-Tropsch-type of product, may have an advantage over normal Fischer-Tropsch synthesis, since the aromatics fraction includes bicyclic species, such as indanes and naphthalenes.(25)(26)

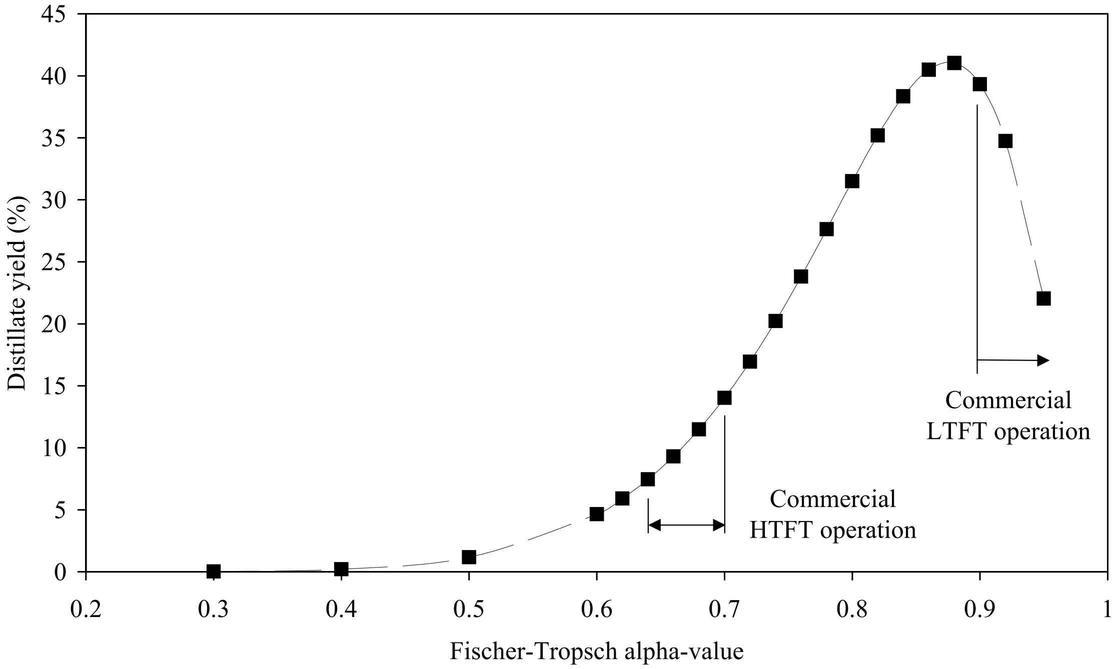

Figure 14. Yield of straight run distillate (C_{11}-C_{22}) in the C_3 and heavier hydrocarbon fraction from Fischer-Tropsch as function of the chain growth probability (α-value).

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[p] It is ironic that in Fischer-Tropsch refineries it is difficult to meet the minimum density requirement for diesel fuel, while the opposite is true in crude oil refineries. There is synergy in combining these two refinery types.

The carbon number distribution of LTFT syncrude is such that it has much more distillate range material than HTFT syncrude (Figure 14), with an α-value of 0.88 being close to the optimum for maximum straight run distillate production. However, the distillate from an LTFT process, such as the Sasol SPD™ process, has a high cetane number, typically >70, but it has a density of less than 780 kg·m^{-3}.(10) Producing a high volume of distillate with a high cetane number is therefore not an issue, but in terms of meeting the density requirement, the situation is precarious.

From the preceding discussion on HTFT and LTFT straight run distillate properties the conundrum of Fischer-Tropsch diesel fuel refining emerges. It seems straightforward to refine syncrude to distillate, but how to refine syncrude to maximise distillate volume, as well as meet the diesel properties required by fuels specifications, is far from obvious.(27)

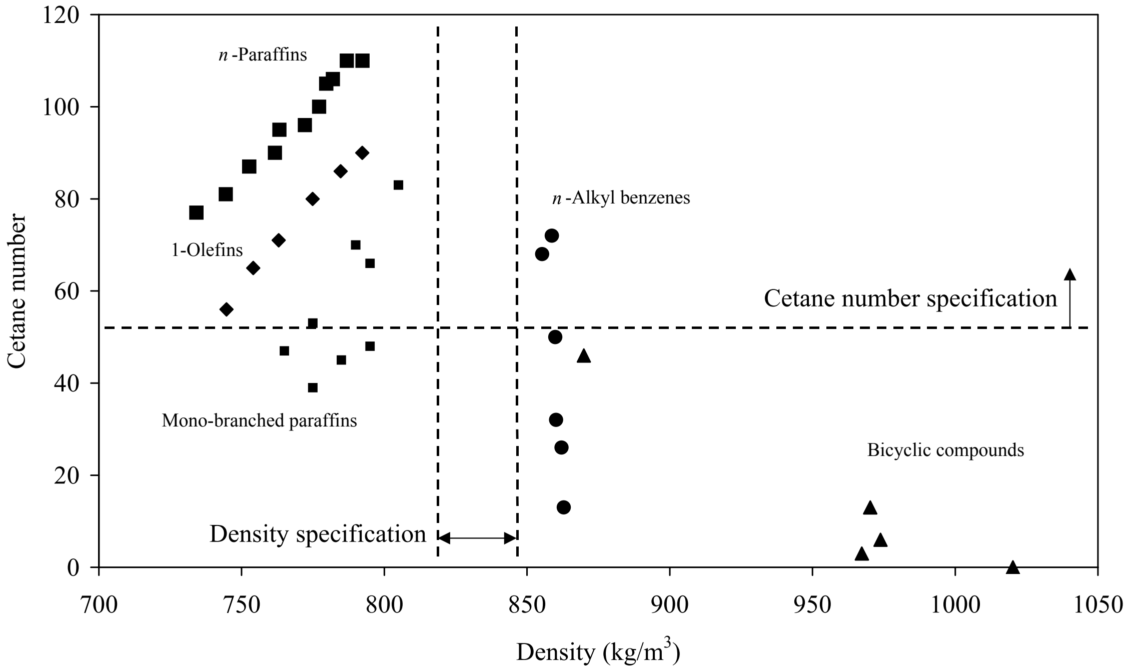
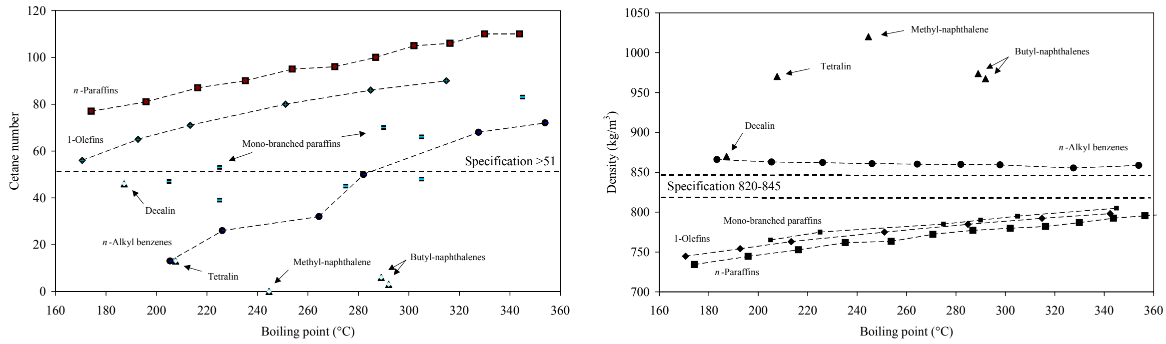


Figure 15. Cetane-density relationship of various compounds in the distillate boiling range from 170 to 360°C.

The key to maximum diesel fuel refining from Fischer-Tropsch syncrude lies in a refining problem that I will call the *density-cetane-yield triangle*. It is possible to meet any two of these three requirements without too much refining effort, but meeting all three is very difficult. This may not be apparent from the discussion thus far, since the cetane number of the distillate has never been an issue. However, if one compares the relationship of cetane number and density of different hydrocarbons in the distillate boiling range, a very disheartening picture emerges (Figure 15).(21)(28) The relationship between cetane number, density and molecular composition is not a new insight - it forms the basis for many predictive equations for cetane number.(29)(30) At this point it is worthwhile mentioning that diesel viscosity may also become a constraint, since a minimum viscosity of 2 cSt is required. However, viscosity is more closely related to the distillation profile than to the nature of the hydrocarbons in the distillate.(31)

There is potential for a cetane number versus density trade-off in order to increase the density of the syncrude derived diesel fuel. Depending on what compound class is used, this may result in a cetane deficient diesel fuel, despite Fischer-Tropsch distillate being known for its high cetane number. With the abundance of olefins in a Fischer-Tropsch refinery, the production of alkylbenzenes (860 kg·m^{-3}) to increase diesel density is a natural choice, but from a cetane number perspective they are the worst compounds to use. Monocycloalkanes in the diesel boiling range have cetane values close to that of acyclic paraffins, but their density (mean density of 815 kg·m^{-3}) is insufficient to densify the diesel. Although benzocycloalkanes and benzodicycloalkanes have slightly lower cetane numbers, they have much higher densities (>950 kg·m^{-3}) and are good compounds to use for densification.(29) Dicycloalkanes can also be considered on account of their high density, but they have worse cetane numbers than the cycloalkanes having one aromatic ring.(29)



(a) (b)

Figure 16. Relationship of cetane number and density to the boiling point temperature of compounds in the distillate boiling range.

The first general trend that is of benefit in increasing diesel quality is realising that with increasing boiling point the cetane number (Figure 16a) and density (Figure 16b) increases within each compound class. A heavier distillate is therefore preferable to a light distillate and the co-production of jet fuel in a Fischer-Tropsch refinery will improve the diesel quality. However, even a very heavy distillate derived from syncrude will require the addition of a significant volume of cyclic compounds to meet the density specification.

Cookson, Lloyd and Smith(32) described the compositional prerequisites for acceptable diesel fuel in an insightful manner. They have not used density as a key constraining variable in their discussion or analyses, but they have successfully modelled most other composition-property relationships by a simple linear correlation (Equation 2).

$$P = \kappa_1 \cdot [\mathrm{n}] + \kappa_2 \cdot [\mathrm{BC}] + \kappa_3 \cdot [\mathrm{Ar}] \qquad \ldots (2)$$

The property value, P, is expressed as a function of the abundance of *n*-paraffins, [n], branched and cyclic aliphatics, [BC], and aromatics [Ar]. In a simple example it was shown that a diesel fuel consisting mostly of branched and cyclic aliphatics would meet diesel fuel specifications more readily than a fuel in which either *n*-paraffins or aromatics are the dominant compound classes.(32) Some additional pointers for the improvement of diesel fuel quality can be found in the work of industrial research laboratories, like those of ConocoPhillips(28) and ExxonMobil.(33) In these studies the problem is approached from the opposite angle, namely a high density and low cetane number, which is typical of crude oil derived distillates. Although not specifically highlighted by any of these studies, the importance of naphthenes becomes quite clear when read in conjunction with Figures 15 and 16. This supports the previous analysis by showing that distillate base stock that is rich in naphthenes has a reasonable cetane and density. Such a base stock can more easily be blended to on-specification diesel fuel by the addition of heavier *n*-paraffins for cetane number improvement, and some aromatics and partially saturated aromatics for density improvement.

It is possible that in future the fuel specifications may change to mandate a 5% *bio-diesel* addition. This would be beneficial for syncrude derived distillate, since it will increase the synthetic diesel density by 3-4 $\mathrm{kg \cdot m^{-3}}$ without any cetane penalty.

Commercial bio-diesel consists of a mixture of fatty acid methyl esters (FAME) in the C_{16}-C_{18} range. Property values reported for bio-diesel from different suppliers seem to be close to each other, with a cetane number of 54,(34) kinematic viscosity of 4.2 cSt(34) and density of 878 $\mathrm{kg \cdot m^{-3}}$.(35) The properties of such bio-diesel mixtures are poorer than that reported for bio-diesel derived from pure oils, which have cetane numbers of 57-65, viscosities of 4.4-4.7 cSt and densities of 880-886 $\mathrm{kg \cdot m^{-3}}$.(36)

Additive packages can be used to increase the cetane number, which allows more leeway for the inclusion of low cetane, but high density compounds in the Fischer-Tropsch derived diesel fuel. This may be a more efficient way of satisfying the density-cetane-yield triangle than just refining syncrude molecules to reach the cetane number specification. Nevertheless, it should be noted that specifications such as Euro-4 also include a cetane index requirement, which in the case of Euro-4 is a minimum of 46. The cetane index is calculated based on the distillation properties of the diesel fuel, which by its definition cannot be improved by a cetane booster.

5.1. HTFT diesel fuel refinery development

The importance of generating a good quality base stock for blending to diesel fuel has already been highlighted. The straight run HTFT distillate range material is a good base stock, but its yield is far too little for a maximum diesel fuel refinery. One or more conversion processes are needed for carbon number growth to push the naphtha and gas into the distillate range.

A comparison of the distillate properties of three olefin industrial oligomerisation processes, solid phosphoric acid (SPA), amorphous silica alumina (ASA) and H-ZSM-5 based, show that from a density perspective, ASA based oligomerisation is the best.(37),[q] It is capable of producing a 60-70% distillate yield with the distillate having a density of 809-816 kg·m^{-3}, kinematic viscosity of 2.8-3.6 cSt and cetane number of 28-30. The product contains distillate range aromatics and naphthenes to provide density. Unfortunately the cetane number is low and the hydrogenated distillate from ASA oligomerisation makes a poorer quality base stock than hydrogenated straight run HTFT distillate. A refinery design based on ASA oligomerisation is therefore expected to be cetane constrained.

Since the crude oil refining industry has never had to increase the density of distillate, no refining technologies have been developed for this purpose. It is speculated that if such a technology was to be developed, that it is likely to exploit the selective ring closing behaviour of supported non-acidic noble metal catalysts,(38) typically using supports with an open pore structure. More conventional alternatives would include refining to aromatics with subsequent hydrotreating and it may well be possible to use standard reforming technology with heavy (C_{10}+) feed to produce compounds of the naphthalene and indene families. These binuclear compounds could provide density. Hydrotreating could restore the cetane loss, without compromising density, for example, *trans*-decalin has a density of 869.9 kg·m^{-3} and a cetane number of 46.

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[q] It is ironic that the one technology recently developed for the conversion of HTFT olefins to distillate, namely the COD-process, is based on H-ZSM-5, which produces a distillate with high cetane number (>51), but low density (787-801 kg·m^{-3}).

Nevertheless, the prognosis for the development of a maximum diesel refinery based on HTFT syncrude to produce diesel fuel that meets specification is not good when only commercial refining technologies are considered. Blending with coal pyrolysis products or crude oil derived distillates provide technically less challenging solutions than the development of a standalone HTFT syncrude based diesel refinery. In this sense Fischer-Tropsch derived diesel fuel is like diesel made from renewables – it is excellent in mixtures with crude derived products, but it is not so good just on its own.

The refining pathways for diesel fuel production will be explored on a carbon number basis:

a) *Residue (C_{22}+)*. The HTFT residue is a good source of heavy material to improve the density of the diesel fuel. This can be achieved by moderate hydrocracking, taking care not to over-crack the material.

b) *C_{11}-C_{22} distillate*. Hydrotreating of this fraction yields a product with good diesel fuel properties. Commercial HTFT distillate hydrogenation is quite severe and the product is completely hydrodeoxygenated. In this respect the advantages of moderate hydrotreating has not yet been realised. Much of the potential lubricity and storage stability characteristics imparted by long chain carboxylic acids and alkylated phenols are destroyed by severe hydrotreating. It may be beneficial from a density and cetane point of view to use the C_{11}-C_{14} fraction of the distillate for jet fuel. If this approach is to be followed, the C_{11}-C_{14} fraction will have to be hydroisomerised. However, the hydrogenated straight run HTFT distillate is good diesel base stock and should be retained as such considering that the aim of the refinery design is to maximise diesel fuel production.

c) *C_9-C_{10} naphtha*. This naphtha fraction yields poor motor-gasoline, but can be hydrotreated with the distillate to give a good quality kerosene component for jet fuel production. It is not necessary to hydroisomerise this cut. Alternatively it can be used as feed for ASA oligomerisation to increase distillate production. The use of such material for the production of linear alkyl benzenes as high density and cetane diesel fuel additives has also been considered, but it is doubtful whether this would be realistic in refining context.

d) *C_3-C_8 hydrocarbons*. The selection of the aromatisation technology determines the way in which the different carbon number fractions will be utilised. If a platinum promoted non-acidic L-zeolite based technology is used, then the C_6-C_8 naphtha cut would be the most appropriate feed for it. There is more feed flexibility if metal promoted H-ZSM-5 based technology is selected. In order to maximise the distillate blend stock, a significant part of the olefins in the C_3-C_8 fraction may be oligomerised on ASA. Whatever routing is selected, there is some trade-off involved, not only in terms of the density-cetane-yield triangle, but also in terms of the aromatics that are needed for motor-gasoline, jet fuel and diesel fuel.

e) *C_2 hydrocarbons*. Ethylene is a convenient aromatic alkylation agent to produce alkyl aromatics for all the transportation fuel types. This should be qualified though, because cetane numbers of such short chain alkyl aromatics are low, which may limit inclusion in diesel fuel. Pathways such as hydration and purification for chemical use can be considered, but in general it can be said that refining of ethylene to diesel fuel is limited. One exception that may be considered, is using ethylene oligomerisation technology for the production of linear α-olefins.(39) These linear α-olefins can the be co-refined with the HTFT syncrude, which is in any case rich in such material.

f) *Aqueous phase oxygenates*. The conversion of oxygenates dissolved in the aqueous phase by selective hydrogenation and dehydration to olefins, has already been noted.(12) The olefins thus produced can be co-refined with the HTFT syncrude. One modification to this idea that may be considered, is the production of heavier ethers from the alcohols. Distillate range ethers are high cetane diesel additives.(40) Unfortunately the production of heavier ethers will be limited due to the small C_5+ fraction being present in the aqueous phase and it is unlikely to be cost effective. Another possibility that may be considered is esterification of the carboxylic acids in the aqueous product with heavier alcohols in the oil product. This would produce shorter chain FAME-equivalents, which may be beneficial from both a cetane number and density perspective.[r]

5.2. HTFT diesel fuel refinery flowschemes

5.2.1. Flowscheme 11

In order to establish a baseline for HTFT refinery designs to maximise diesel fuel production, a design was developed that incorporated aspects of the preceding discussion (Figure 17). The design strategy was to convert most of the olefins in the gas and naphtha range into distillate range oligomers, thereby increasing the distillate yield (albeit not quality). Some incremental distillate yield improvement was gained by cracking the small residue fraction.

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[r] Esterification ($RCOOH + {}'ROH \rightleftharpoons RCOO`R + H_2O$) is an equilibrium limited reaction and using a dilute acid solution may not be economical. On the other hand, the use of an alcohol in a non-polar medium may result in extraction of the ester into the non-polar medium, thereby favouring the equilibrium. In any event, whatever the dominating equilibrium effect, mass transfer will probably be the main limitation.

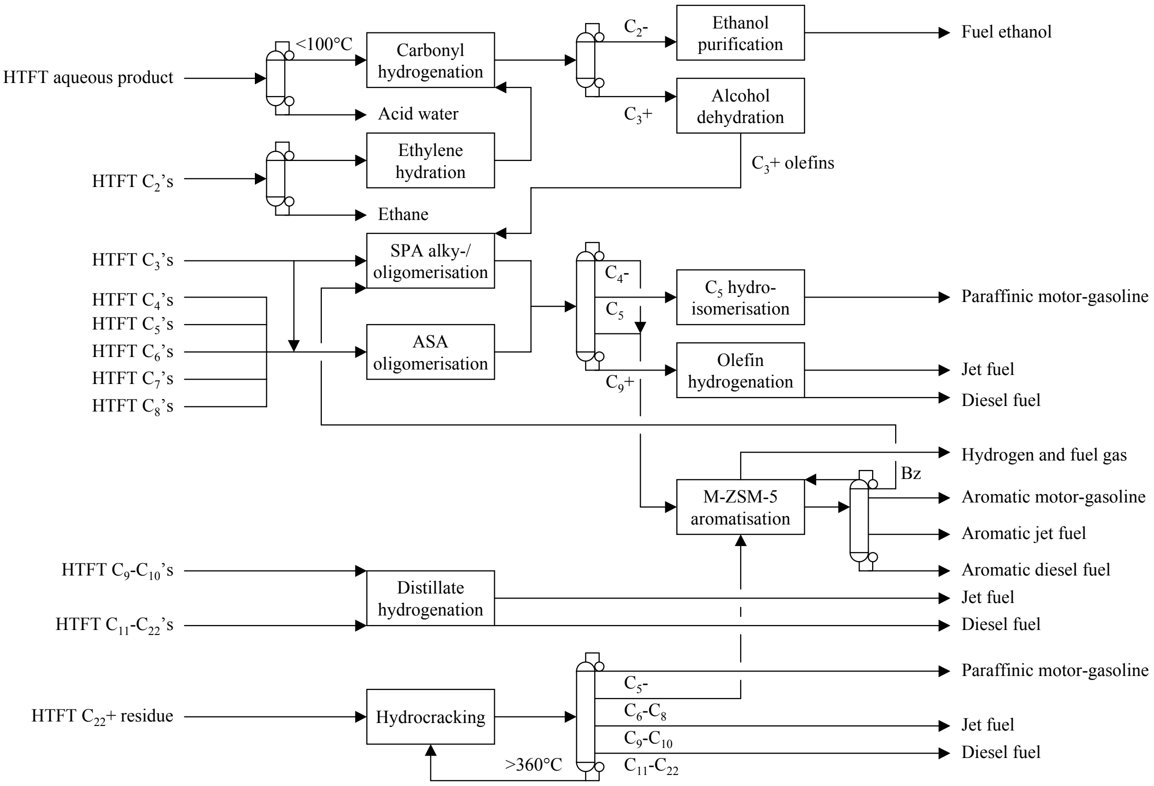

Figure 17. HTFT diesel fuel refinery, flowscheme 11.

Table 28. Yield structure of the HTFT diesel fuel refinery shown in Figure 17, which has a liquid fuel yield of 93% (mass) and diesel fuel yield of 42% (mass).

Product	Refinery production			
	($kg{\cdot}h^{-1}$)	($m^3{\cdot}h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	58491	79	11890	13.4
Excess fuel ethanol	63304	80	12035	13.6
Jet fuel	132975	171	25866	29.1
Diesel fuel	208392	256	38709	43.6
LPG	1100	2	304	0.3
Other products				
Fuel gas	34543			
Unrecovered organics	14369			
Hydrogen	-2863			
Water	-10311			
Σ	500000	588	88804	100

The residue is converted mostly to distillate by hydrocracking, while the kerosene and distillate range material is just hydrotreated and fractionated into jet fuel (C_9-C_{10}) and diesel fuel (C_{11}-C_{22}). Most of the olefins in the C_3-C_8 range are oligomerised in an ASA based process. Some of the C_3 olefins and the olefins that were obtained from the selective hydrogenation and dehydration of the aqueous phase oxygenates, are used to alkylate the benzene in a SPA based combined alkylation and oligomerisation process. The products from the ASA and SPA based processes are combined. The kerosene and distillate fractions are hydrogenated and fractionated into jet fuel and diesel fuel. Most of the C_3-C_8 fraction is used as feed for metal promoted ZSM-5 based aromatisation, with only the C_5 cut being reserved for hydroisomerisation to produce motor-gasoline.

Table 29. Diesel fuel, jet fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 17.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	813	820-845	Range
Cetane number	31	51	Min
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	776	775-840	Range
Aromatics (vol %)	22.2	8-25	Range
Flash point (°C)	42	38	Min
Vapour pressure (kPa)	1.2	-	
Motor-gasoline		*Euro-4*	
RON	97	95	Min
MON	88	85	Min
Vapour pressure (kPa)	55	60	Max
Density (kg·m^{-3})	743	720-775	Range
Olefins (vol %)	14.4	18	Max
Aromatics (vol %)	34.8	35	Max
Oxygenates (vol %)	5.0	15	Max
Benzene (vol %)	0.1	1	Max
Ethanol (vol %)	5.0	5	Max

The refinery yield structure (Table 28) indicates a high overall refinery yield (93%), but expressed on a volumetric basis it is equivalent to only around 89 000 bpd. A significant fraction of the liquid production is due to excess fuel ethanol from ethylene hydration. The distillate yield was more than the combined motor-gasoline and jet fuel yields, but only marginally so. It can nevertheless be seen as a maximum diesel fuel refinery design.

Ironically the motor-gasoline and jet fuel meet specifications, but not the diesel fuel (Table 29). The diesel fuel density is only 813 kg·m^{-3}, while the cetane number is only 31, which is clearly unacceptable! Despite these serious shortcomings, the refinery design is instructive by demonstrating the impact of the inherent low density of syncrude. A suitable synthetic pathway to meet density, cetane and yield is unfortunately not obvious.

5.2.2. Flowscheme 12

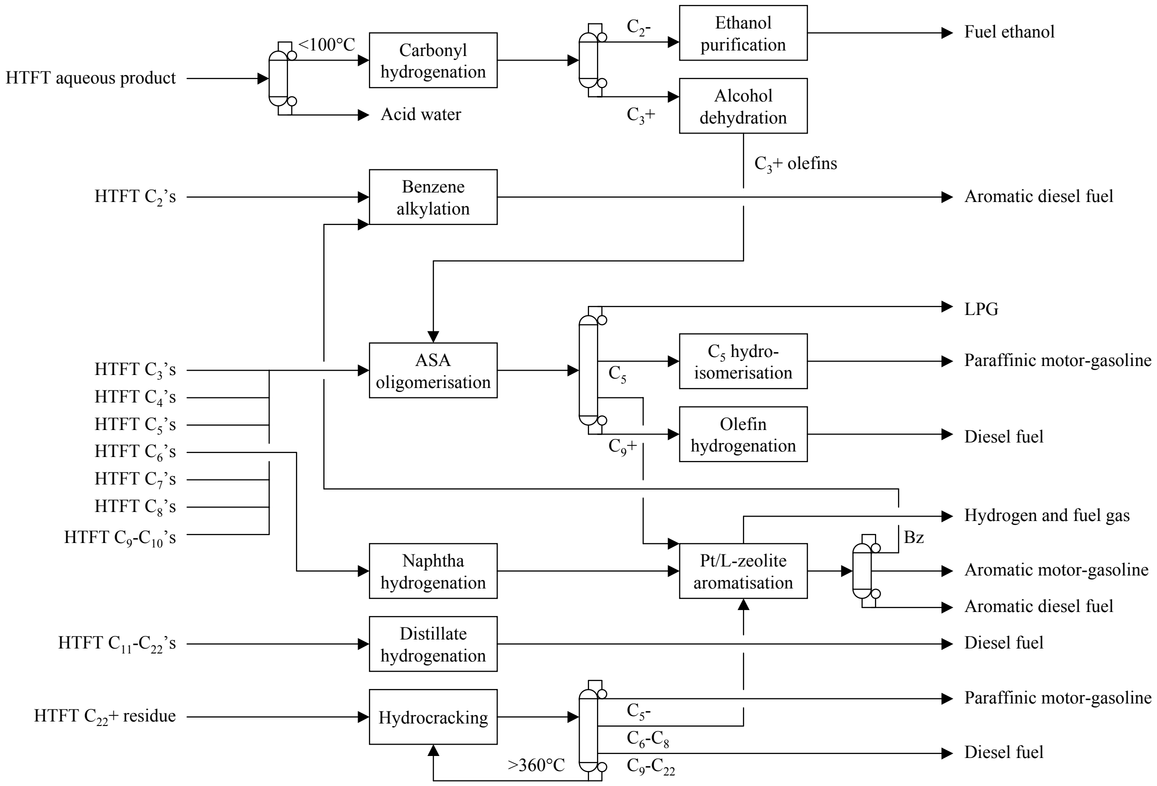

Figure 18. HTFT diesel fuel refinery, flowscheme 12.

It has been shown that HTFT syncrude has considerably less straight run distillate than LTFT syncrude (Figure 14) and the tacit assumption is sometimes made that HTFT technology cannot be used to produce a high yield of distillate. The previous design (flowscheme 11) indicated that it is difficult to produce diesel fuel meeting specification, despite trying to do so and the yield structure was constrained by the deliberate attempt to meet specification for all transportation fuel types. In the present flowscheme (Figure 18) the focus was shifted to the yield structure to explore to what extent diesel fuel yield can be maximised. In order to achieve this objective all kerosene range material has been included in the diesel fuel as a light diesel component.

The aqueous phase oxygenates were selectively hydrogenated to alcohols and dehydrated to olefins. These olefins were combined with the HTFT syncrude and all C_3-C_5 and C_7-C_{10} olefins from the HTFT syncrude and alcohol dehydration were converted in an ASA based oligomerisation unit. The C_6-C_8 naphtha thus produced was combined with the C_6 HTFT syncrude naphtha and used as feed for aromatisation on a platinum promoted non-acidic L-zeolite. Since this technology is very selective for the conversion of C_6 naphtha to benzene, the aromatic product contained more than 50% benzene. The benzene was alkylated with ethylene to produce a mixture of ethylbenzene and diethylbenzenes, thereby utilising most of the ethylene. The C_{11}-C_{22} straight run distillate was hydrotreated and the C_{22}+ material was hydrocracked in a similar way as the previous flowscheme.

Table 30. Yield structure of the HTFT diesel fuel refinery shown in Figure 18, which has a liquid fuel yield of 89% (mass) and diesel fuel yield of 69% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	60895	80	12064	14.1
Excess fuel ethanol	17624	22	3351	3.9
Jet fuel	0	0	0	0.0
Diesel fuel	343358	417	62958	73.8
LPG	25188	46	6944	8.1
Other products				
Fuel gas	29823			
Unrecovered organics	13307			
Hydrogen	824			
Water	8982			
Σ	500000	565	85317	100

Table 31. Diesel fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 18.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	823	820-845	Range
Cetane number	27	51	Min
Motor-gasoline		*Euro-4*	
RON	98	95	Min
MON	91	85	Min
Vapour pressure (kPa)	57	60	Max
Density (kg·m^{-3})	762	720-775	Range
Olefins (vol %)	0.0	18	Max
Aromatics (vol %)	38.2	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	1.7	1	Max
Ethanol (vol %)	0.0	5	Max

This refining approach resulted in a distillate yield of 69% from the C_2+ syncrude (Table 30), while the overall refinery yield was 89%. This demonstrated that it is possible to devise a refinery design to convert HTFT syncrude with high yield to distillate. It was also surprising to note that the motor-gasoline almost met the Euro-4 fuel specifications (Table 31), while the diesel fuel met the density, but not the cetane specification. Since the product meets the density specification, some lower density high cetane material can conceivably be blended into the diesel to increase the cetane number and lower the density. This train of thought was explored for the new South African CTL project, which employs a combined HTFT and LTFT refinery design.(27)

One salient point worth highlighting is that flowscheme 12 contains the same conversion units as flowscheme 11. The only difference is in the technology selection of the conversion units and the routing of the various streams. Yet, the way in which the design was developed resulted in a refinery that met the density and yield requirements of the density-cetane-yield triangle.

5.2.3. Flowscheme 13

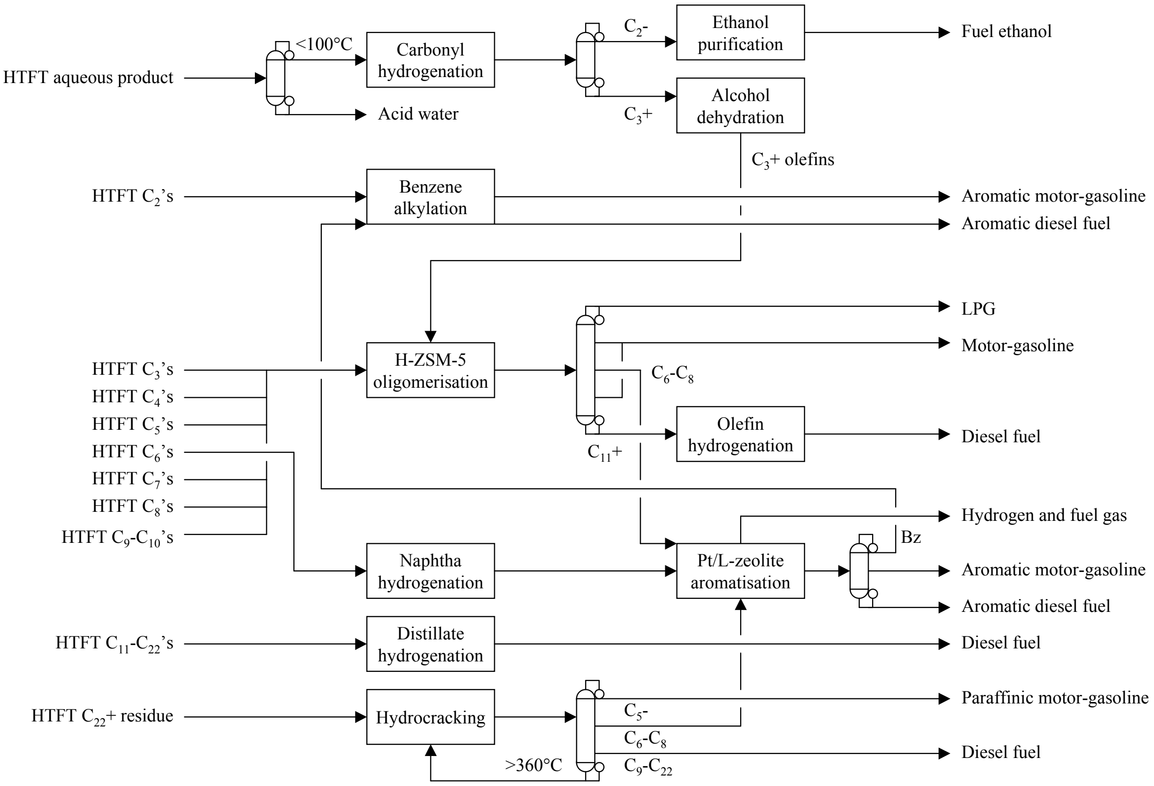

Figure 19. HTFT diesel fuel refinery, flowscheme 13.

Based on the outcome of flowscheme 12, it should also be possible to devise a refinery that would maximise diesel yield and have a high cetane. By exploring this side of the density-cetane-yield triangle, it may be possible to calculate the lever necessary to meet all three requirements simultaneously. The aim of flowscheme 13 was therefore to find a refinery that would maximise diesel yield, but rather have a high cetane than a high density (Figure 19).

In doing so the basic strategy remained the same, but the oligomerisation technology was changed. The pore constrained geometry of the ZSM-5 zeolite is known to limit the degree of branching of the oligomers, thereby increasing the cetane number and decreasing the octane number of the distillate and naphtha respectively.(31)

It was possible to obtain a 24:76 split between naphtha and distillate (Table 32), with a distillate yield of 60% being obtained. The overall liquid yield from the refinery design was 89%, but the contribution of LPG to the yield had been much more than in flowscheme 12 (Figure 18).

Table 32. Yield structure of the HTFT diesel fuel refinery shown in Figure 19, which has a liquid fuel yield of 89% (mass) and diesel fuel yield of 60% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	87839	116	17470	19.9
Excess fuel ethanol	17624	22	3351	3.8
Jet fuel	0	0	0	0.0
Diesel fuel	299223	372	56099	64.0
LPG	38754	71	10700	12.2
Other products				
Fuel gas	33100			
Unrecovered organics	13307			
Hydrogen	1171			
Water	8982			
Σ	500000	580	87619	100

The present design (Figure 19) showed that even with a good cetane distillate from H-ZSM-5 oligomerisation, the cetane number of the base stock (cetane around 51-55) was lowered significantly by the inclusion of aromatics in the diesel fuel (Table 33). The diesel fuel made neither cetane nor density specifications. Furthermore, the considerably lower octane number of the motor-gasoline fraction from H-ZSM-5 based oligomerisation caused the motor-gasoline to fail specifications on numerous accounts (Table 33). Even the inclusion of a C_5 hydroisomerisation, as in flowscheme 12 (Figure 18), failed to remedy the situation (Table 33).[s]

This clearly indicated that ASA based oligomerisation is a better technology for distillate production in a Fischer-Tropsch refinery than H-ZSM-5 based oligomerisation, since the distillate yield is better, the motor-gasoline almost meets specification (aromatics content of 38% exceeding 35% limit) and the diesel meets the density specification. It also demonstrated the importance of C_5 hydroisomerisation technology in upgrading octane-constrained motor-gasoline, resulting in a 6 RON gain in this specific instance.

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[s] Further incremental improvements in motor-gasoline quality can be achieved by blending in ethanol (5% maximum) and butanes (vapour pressure 60 kPa maximum) in tandem with increasing the ethyl benzene inclusion (35% aromatics maximum). However, none of the above results in a motor-gasoline that comes close to meeting the octane number specification.

Table 33. Diesel fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 19, as well as a design with a C_5 hydroisomerisation unit added as in Figure 18.

Fuel properties	Refinery as in Figure 19	Refinery with C_5 hydroisomerisation	Fuel specification	
Diesel fuel			*Euro-4*	
Density (kg·m^{-3})	805	805	820-845	Range
Cetane number	42	42	51	Min
Motor-gasoline			*Euro-4*	
RON	81	87	95	Min
MON	77	82	85	Min
Vapour pressure (kPa)	39	46	60	Max
Density (kg·m^{-3})	759	757	720-775	Range
Olefins (vol %)	33.4	13.9	18	Max
Aromatics (vol %)	35.0	34.8	35	Max
Oxygenates (vol %)	0.0	0.0	15	Max
Benzene (vol %)	1.1	1.1	1	Max
Ethanol (vol %)	0.0	0.0	5	Max

5.3. LTFT diesel fuel refinery development

Commercial LTFT based GTL plants that employ hydroprocessing as the only conversion type can achieve a distillate selectivity of around 70% with a cetane number exceeding 70.(4) The base stock is density constrained, with the density being around 780 kg·m^{-3}. The point that was made during the discussion of HTFT syncrude refining to diesel fuel is therefore equally valid for LTFT syncrude, namely, that it is better to use LTFT syncrude in combination with material derived from other sources, such as crude oil(41) and coal pyrolysis products, in order to meet diesel specifications. However, when a standalone LTFT refinery design for maximum diesel fuel production is considered, the main challenge is to increase the density of the diesel fuel.

On a conceptual level it is important to retain the cetane advantage of the linear paraffin rich LTFT syncrude. This can be achieved by focussing on a carbon number reduction strategy to convert most of the waxy material into the heavy diesel fuel range (260-

360°C) by mild hydrocracking. Hydroisomerisation of the linear paraffins that takes place in tandem with hydrocracking is beneficial in two ways, namely, to improve the cold flow properties and to increase the density slightly (Figure 16b). This could create a base stock with good cetane number (60-70) and reasonable density (790-800 kg·m^{-3}), which may just be good enough to upgrade with alkyl aromatics to meet the density specification, while not decreasing the cetane number too much (Figure 20).

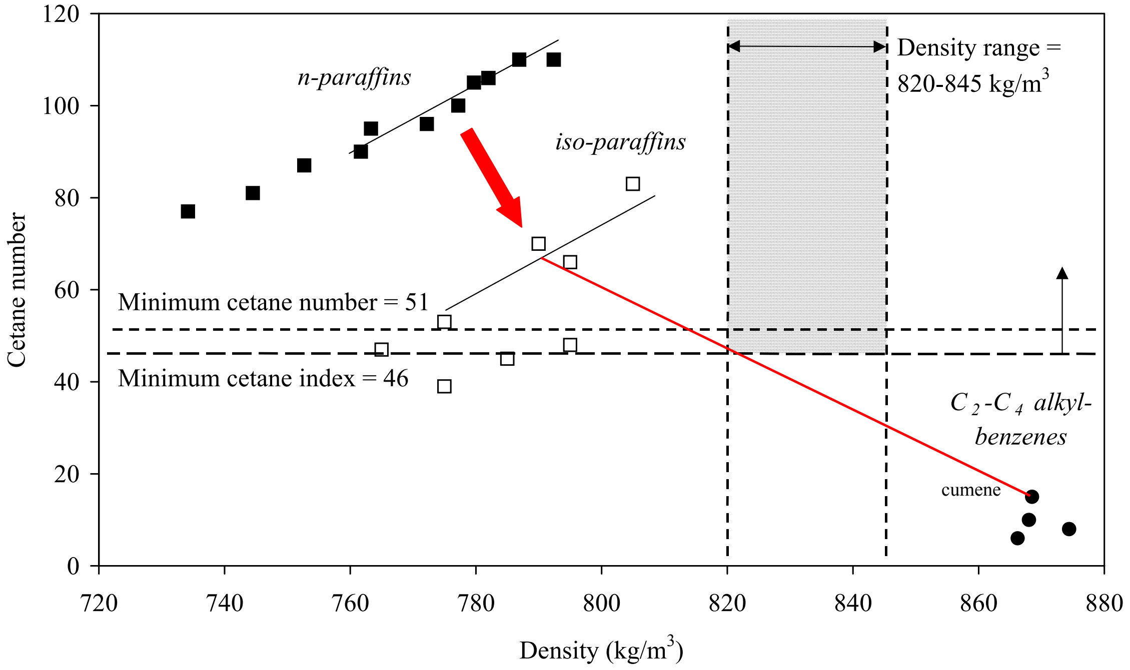

Figure 20. Graphic illustration of a potential refining strategy for the production of diesel fuel from LTFT syncrude that meets fuel specifications.

This is quite important, since a refinery design based on such a concept does not require unconventional refining technologies[t] and may be achievable in practice. Nevertheless, it is clear that alkyl aromatics are not a particularly good compound class to improve density. Furthermore, there will be a yield reduction associated with this approach, since the kerosene range material is not included in the diesel fuel.

The kerosene range material may be used for jet fuel, should enough aromatics be produced to meet the aromatics specification. The product from hydrocracking will be isomerised and is a very good base stock for jet fuel, as was seen in flowscheme 10. The same cannot be said of the motor-gasoline. It is expected that significant refining effort will be required to upgrade the naphtha to motor-gasoline.

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[t] The use of the UOP Pacol process (paraffin conversion to olefin) in combination with LAB (linear alkyl benzene) production can theoretically be considered as means of producing good cetane, high density material, but it would be quite expensive and large volumes would be required.

By discussing the refining pathways for diesel fuel production from LTFT syncrude on a carbon number basis, further constraints emerge:

a) *Residue (C_{22}+)*. The key conversion step in the refinery is the hydrocracking of wax to distillate. Since the aim is to maximise the 260-360°C fraction, the hydrocracker design and operation will have to limit material being lost to the kerosene and naphtha range.

b) *C_{15}-C_{22} distillate*. Unlike hydrotreated HTFT distillate, hydrotreating of this LTFT fraction yields a diesel with a very high cetane number, a low density and poor cold flow properties on account of its high linear paraffin content. It has already been shown that some of these shortcomings can be overcome by hydroisomerisation. This can be accomplished by feeding this fraction to a hydrocracker, but limiting its contact time to reduce cracking losses.

c) *C_{11}-C_{14} kerosene*. The most efficient refining pathway for the kerosene is probably hydroisomerisation in a hydrocracking unit operated in such a way that cracking losses are minimised. In this way the freezing point specification of the jet fuel will be met. The main disadvantage of this approach in the context of maximum diesel fuel refining is that it labels material in the kerosene range as a final jet fuel product, with no further conversion of kerosene to diesel fuel. Arguably this material can be included in the diesel fuel, but its inclusion will be detrimental to cetane and density, which are the main reasons for considering this cut separately. One of the options available is to oligomerise the kerosene range olefins (straight run LTFT kerosene contains about 50% olefins) with the naphtha range olefins to produce distillate. Yet, to fully exploit the kerosene range material, both the olefins and the paraffins will have to be targeted. Two possible refining pathways that can be considered are aromatisation (needed for density) and catalytic cracking (to produce olefins for alkylation and oligomerisation).

d) *C_9-C_{10} naphtha*. This fraction can be hydrotreated and used as jet fuel. However, similar arguments as raised for the C_{11}-C_{14} kerosene fraction are applicable to this material. This fraction may be refined in the same way as the C_{11}-C_{14} cut.

e) *C_3-C_8 naphtha*. The naphtha range material is the source of feed for aromatisation, aromatic alkylation and oligomerisation. The allocation of the various cuts will depend on the refinery design. It is suffice to state that balancing this allocation will be an important aspect of a diesel fuel refinery design.

As in most of the previous LTFT refinery designs, the recovery of C_2 hydrocarbons and oxygenates dissolved in the aqueous product are not considered. It is in principle possible to refine these fractions (for example flowscheme 10), but unless the product slate specifically calls for it, it is not considered cost effective.

5.4. LTFT diesel fuel refinery flowschemes

5.4.1. Flowscheme 14

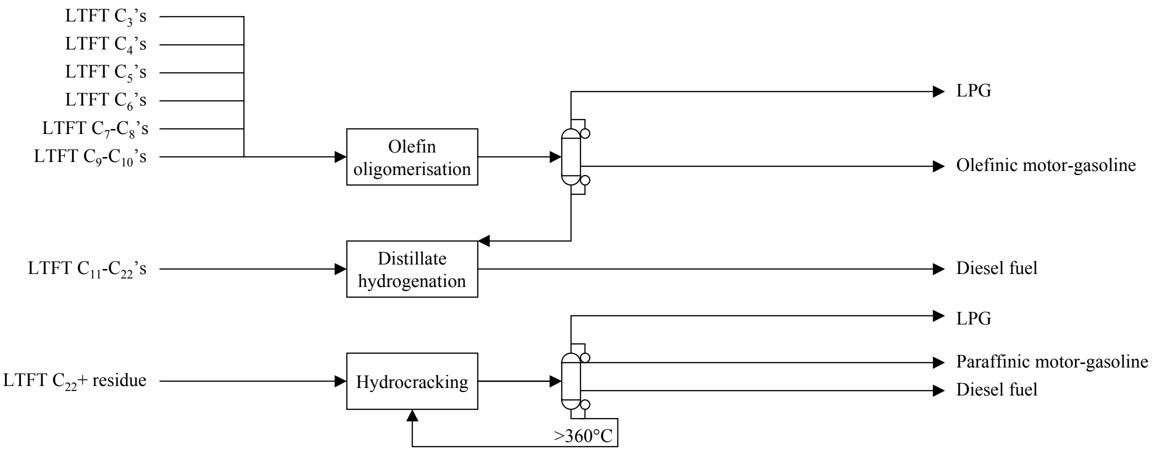

Figure 21. LTFT diesel fuel refinery, flowscheme 14.

The aim of this refinery design (Figure 21) is to establish a base case for LTFT diesel fuel production by maximising the diesel yield when not much attention is paid to the properties of the diesel fuel. Wax hydrocracking, distillate hydrotreating and naphtha oligomerisation are combined to force the carbon number distribution into the distillate boiling range. This is a slightly more complicated refinery design than presently used for commercial LTFT GTL plants that achieve 70% diesel selectivity.

Two oligomerisation technologies have been evaluated for the conversion of the C_3-C_{10} olefins to naphtha and distillate, namely H-ZSM-5 based and ASA based. The properties and yield structure of these two processes differ, although both are considered distillate production processes. The C_{11}-C_{22} distillate fraction is only hydrotreated in order to maximise the distillate yield, full-knowing that the cold flow properties of this product will be poor. The heavier material (heavier than C_{22}) is hydrocracked to produce mainly distillate. The refinery design therefore makes use of carbon number growth, as well as carbon number reduction technologies to maximise distillate yield.

The impact of the oligomerisation technology selection was evaluated, which is reflected in the yield structure (Table 34). The refinery designs using H-ZSM-5 and ASA based oligomerisation process had distillate selectivities of 78% and 76% respectively, indicating the benefit of including a carbon number growth technology to move some material from the naphtha into the distillate boiling range. The diesel yield was 69%.

Table 34. Yield structure of the LTFT diesel fuel refinery shown in Figure 21, with ZSM-5 and ASA based olefin oligomerisation technologies. The refineries have a liquid fuel yield of 94% (mass) and diesel fuel yield of 69% (mass).

Product	H-ZSM-5 based refinery				ASA based refinery			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels								
Motor-gasoline	89848	127	19132	20.1	98123	139	20940	22.1
Jet fuel	0	0	0	0.0	0	0	0	0.0
Diesel fuel	347030	446	67382	70.8	343927	440	66431	70.0
LPG	31238	57	8644	9.1	27095	50	7498	7.9
Other products								
Fuel gas	11375				10287			
Unrecovered organics	22396				22396			
Hydrogen	-3202				-3144			
Water	1316				1316			
Σ	500000	630	95159	100	500000	628	94870	100

Table 35. Diesel fuel and motor-gasoline quality from the LTFT diesel fuel refinery shown in Figure 21 illustrating the impact of oligomerisation technology selection, namely H-ZSM-5 versus ASA.

Fuel properties	Refinery in Figure 21		Fuel specification	
	H-ZSM-5	ASA		
Diesel fuel			*Euro-4*	
Density ($kg\cdot m^{-3}$)	777	782	820-845	Range
Cetane number	78	75	51	Min
Motor-gasoline			*Euro-4*	
RON	28	41	95	Min
MON	26	31	85	Min
Vapour pressure (kPa)	19	33	60	Max
Density ($kg\cdot m^{-3}$)	709	707	720-775	Range
Olefins (vol %)	22.4	46.4	18	Max
Aromatics (vol %)	0	0	35	Max
Oxygenates (vol %)	0	0	15	Max
Benzene (vol %)	0	0	1	Max
Ethanol (vol %)	0	0	5	Max

The oligomerisation technology selection influenced the properties of the products too (Table 35). In both instances the distillate has a cetane number better than 70 and density around 780 kg·m^{-3}, typical of commercial LTFT GTL distillate. Likewise, both H-ZSM-5 based and ASA based refinery designs resulted in a naphtha with poor motor-gasoline quality. The difference in the olefinic motor-gasoline quality between the ASA based (better of the two) and H-ZSM-5 based oligomerisation processes are directly reflected in the properties of the motor-gasoline from the refinery. It is consequently clear why commercial LTFT GTL naphtha is used as naphtha cracker feedstock.

5.4.2. Flowscheme 15

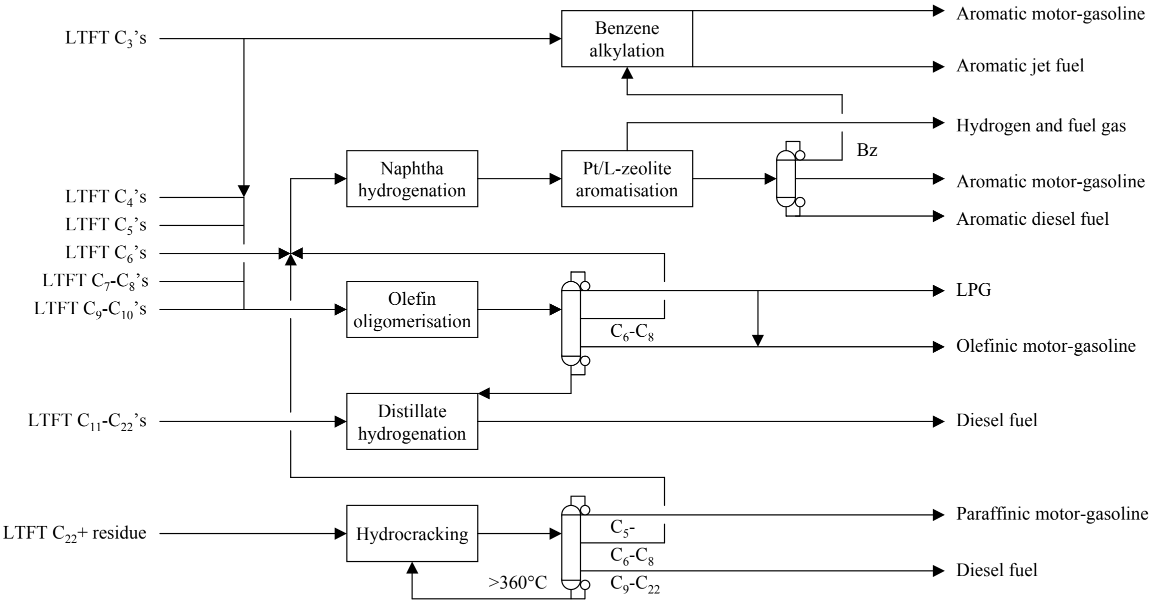

Figure 22. LTFT diesel fuel refinery, flowscheme 15.

The absence of an aromatisation unit in flowscheme 14 (Figure 21) makes the refinery dependent on hydrogen from the Fischer-Tropsch gas loop (Table 34). The inclusion of an appropriate aromatisation unit will not only make the refinery self-sufficient in terms of hydrogen, but also provide aromatics to improve the motor-gasoline quality and increase the diesel density. Furthermore, by converting some of the naphtha into aromatics, the diesel yield may be improved. In this refinery design (Figure 22) these premises were explored by incorporating an aromatisation unit and an aromatic alkylation unit with the objective of increasing the diesel yield beyond that of flowscheme 14, while improving the fuel quality.

It was found that the combination of a platinum promoted non-acidic L-zeolite based aromatisation technology with SPA based cumene production achieves the aforementioned objective. The C_6 LTFT syncrude and C_6-C_8 naphtha fractions from hydrocracking and oligomerisation are used as feed to the aromatisation process, which is benzene selective. The benzene is then alkylated with the LTFT C_3's that is rich in propene, to produce mainly cumene. Although a SPA based cumene process has been selected for benzene alkylation in this design, a slightly better diesel yield is possible if a zeolite-based technology is selected, on account of its lower mono-alkylation selectivity. The rest of the refinery design is similar to flowscheme 14.

The yield structure of the refinery (Table 36) shows that the aim to improve distillate yield was met, with a distillate selectivity of 80% and overall diesel yield 76%. The quality of the naphtha and density of the distillate were also improved (Table 37), but both were far from meeting fuel specifications. Relative to flowscheme 14, the small increase in diesel density (from 782 to 785 $kg \cdot m^{-3}$) that was found, was accompanied by a much larger decrease in cetane number (from 75 to 70). This does not bode well for the possibility to refine syncrude in such a way that operation can be achieved in the small operating window shown in Figure 20 where diesel specifications can theoretically be met.

Table 36. Yield structure of the LTFT diesel fuel refinery shown in Figure 22, which has a liquid fuel yield of 93% (mass) and diesel fuel yield of 76% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	52395	70	10574	11.5
Jet fuel	0	0	0	0.0
Diesel fuel	382193	487	73477	79.7
LPG	29283	54	8164	8.9
Other products				
Fuel gas	12785			
Unrecovered organics	22396			
Hydrogen	-369			
Water	1316			
Σ	500000	611	92214	100

Table 37. Diesel fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 22.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	785	820-845	Range
Cetane number	70	51	Min
Motor-gasoline		*Euro-4*	
RON	77	95	Min
MON	64	85	Min
Vapour pressure (kPa)	33	60	Max
Density (kg·m^{-3})	748	720-775	Range
Olefins (vol %)	39.4	18	Max
Aromatics (vol %)	26.0	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.6	1	Max
Ethanol (vol %)	0.0	5	Max

5.4.3. Flowscheme 16

The quality of the motor-gasoline in flowscheme 15 (Figure 22 and Table 37) is quite poor and despite the limited volume being produced, the refinery complexity may have to be increased in order to meet motor-gasoline specifications. The lowest octane material is typically the heaviest motor-gasoline compounds (C_9-C_{10}), which fall within the kerosene range. Motor-gasoline quality can therefore be improved by producing jet fuel. Diesel fuel quality can likewise be improved by producing jet fuel, since the lightest diesel fuel compounds (C_{11}-C_{14}) have the lowest density and cetane number. The C_{11}-C_{14} material also falls within the kerosene range. However, using the kerosene range material for jet fuel will inevitably reduce the diesel fuel yield, thereby posing a trade-off between yield and overall fuel quality.

In flowschemes 14 and 15 the fuel quality was deliberately ignored in order to maximise diesel fuel production and this design (Figure 23) is an attempt to redress the quality deficiency.

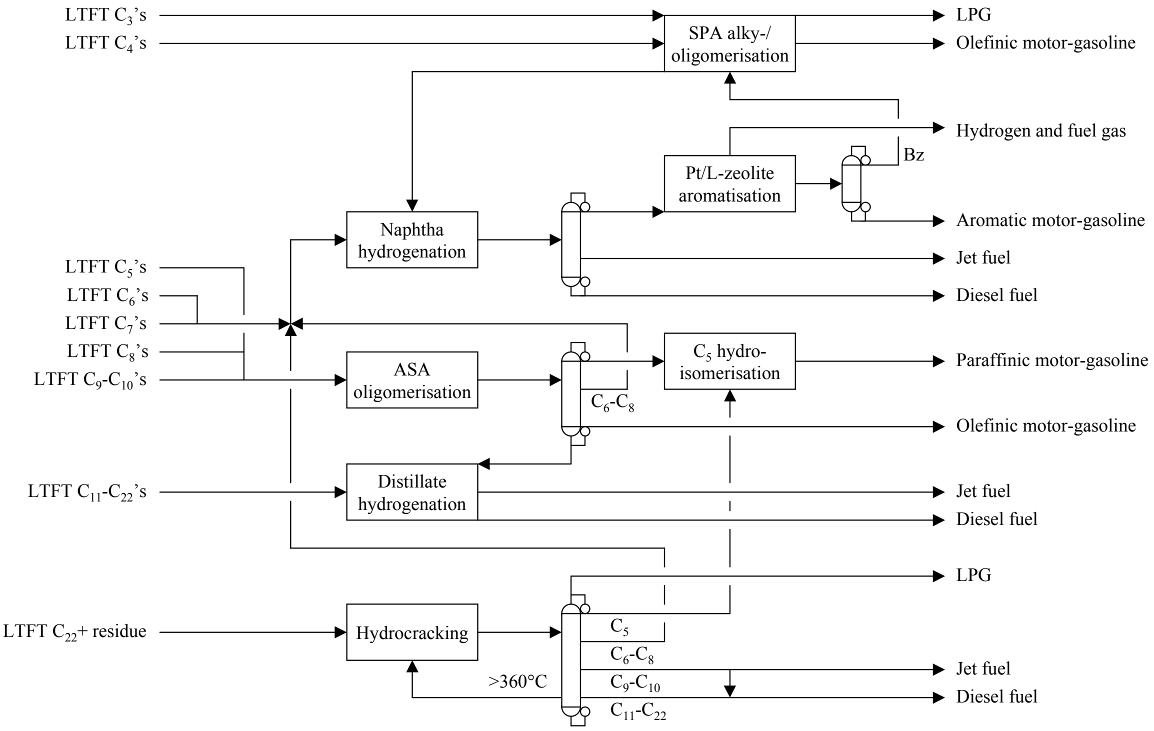

Figure 23. LTFT diesel fuel refinery, flowscheme 16.

Table 38. Yield structure of the LTFT diesel fuel refinery shown in Figure 23, which has a liquid fuel yield of 92% (mass) and diesel fuel yield of 69% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	72183	97	14617	15.8
Jet fuel	18078	23	3518	3.8
Diesel fuel	345119	442	66649	72.2
LPG	27313	50	7504	8.1
Other products				
Fuel gas	13866			
Unrecovered organics	22505			
Hydrogen	-484			
Water	1420			
Σ	500000	611	92288	100

To improve the octane number of the motor-gasoline a C_5 hydroisomerisation unit was included in the refinery design. With the C_6-C_8 naphtha being used as aromatisation feed and the C_9-C_{10} naphtha being used as jet fuel, the motor-gasoline became very light. Good octane C_6-C_8 motor-gasoline had to be produced, which is why SPA based oligomerisation was included in the refinery design. In order not to duplicate oligomerisation units (both SPA and ASA), it was investigated whether only SPA oligomerisation, or a combined SPA oligomerisation and benzene alkylation unit could be used. The latter proved to be a better design optimisation and the final refinery design (Figure 23) required only one more conversion unit than in flowscheme 15 (Figure 22).

As expected, the diesel yield (Table 38) was lower than in the previous design (69% compared to 76%), but it was similar to that of flowscheme 14. The fuel quality (Table 39) was significantly better, with the motor-gasoline and jet fuel meeting fuel specifications. Only the diesel fuel did not meet fuel specifications and resembled a typical commercial LTFT GTL distillate with better than 70 cetane number and density of around 780 kg·m^{-3}.

Table 39. Diesel fuel, jet fuel and motor-gasoline quality from the LTFT diesel fuel refinery shown in Figure 23.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	782	820-845	Range
Cetane number	74	51	Min
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	776	775-840	Range
Aromatics (vol %)	17.9	8-25	Range
Flash point (°C)	38	38	Min
Vapour pressure (kPa)	1.2	-	
Motor-gasoline		*Euro-4*	
RON	95	95	Min
MON	87	85	Min
Vapour pressure (kPa)	60	60	Max
Density (kg·m^{-3})	745	720-775	Range
Olefins (vol %)	18.0	18	Max
Aromatics (vol %)	32.8	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.5	1	Max
Ethanol (vol %)	0.0	5	Max

The refinery design reiterated the difficulty inherent in satisfying the density-cetane-yield triangle. It also illustrated that it is possible to produce on-specification motor-gasoline and jet fuel in a Fischer-Tropsch distillate refinery, but that Fischer-Tropsch syncrude is not suited for the production of on-specification diesel fuel.

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APPENDIX A

Design basis for conceptual refinery development

Background

The modelling of a Fischer-Tropsch refinery is somewhat different to the modelling of a crude oil refinery, since the physical property correlations and distillation profile based separations are not directly applicable to syncrude. This situation is exacerbated by the need to consider the modified conversion technologies to make it suitable for Fischer-Tropsch syncrude, which is one of the aims of the present study. It was therefore necessary to provide all the data, ranging from the characterisation of the different syncrude fractions and syncrude specific conversion profiles for the different technology blocks, up to the fuel properties of the synthetic fuels. Needless to say, the decision on the platform to use for the refinery design and modelling was crucial to the success of this study, since one could easily miss the wood for the trees.

Modelling platform

Three different modelling platforms were considered for the study, namely a process simulation package, spreadsheet and custom designed software. The decision was based on the following train of thought:

a) *Process simulation package*. The process simulation packages currently available on the market, such as those from AspenTech™ and SimSci™, are very powerful. Complex flow sheets with numerous recycles and detailed compound-based calculations can easily be developed. Conversion calculations can be coded and linked into the simulation package as custom function blocks, enabling proper Fischer-Tropsch specific calculations. These packages are geared for the calculation of mass and energy balances with realistic separation steps, rather than for the calculation of fuel properties, although it is possible to do so. However, the emphasis of the software is to provide an accurate simulation or representation of a process and much effort has to be spent on selecting appropriate thermodynamic models, compound or pseudo-compound based feed compositions and separation steps. This was not the aim of the investigation, which is focussed on syncrude specific conversion and fuels refining. Furthermore, the information that is necessary to build custom conversion steps for syncrude is not always available in the format required by the process simulation package. The level of detail necessary for conceptual refinery development, and that required and provided by a process simulation package, is clearly ill matched.

b) *Spreadsheet*. In a spreadsheet all the information and calculations necessary to build a refinery model has to be provided. It is not possible to calculate any of the separation steps with the level of detail that is possible in a process simulation package, nor is it possible to incorporate such detailed physical and thermodynamic property calculations. However, the complexity of the refining blocks can easily be adapted to the information available and the compound based description can be varied between blocks. It is also possible to have more information on the assumptions available "at a glance" in a spreadsheet than in a process simulation package, making the model far more accessible. No special coding is necessary, although Visual Basic routines can be incorporated if such complexity is needed. As a tool for focussing on refining concepts, rather than slogging out the finer details of separation steps and heat integration, a spreadsheet can be an excellent tool.

c) *Custom software*.[u] With custom software it is possible to achieve some compromise between the detail (and restrictions of such detail) found in process simulation packages and the much lower level of detail inherent in spreadsheet based modelling. Unfortunately it may also result in having the worst of both worlds, since the user-interface can easily be the programming interface and much time can be wasted on coding aspects of the model that are already provided by process simulators and spreadsheets.

It was decided to make use of a spreadsheet for modelling the refinery designs. This decision was made mainly on the ability to match conversion blocks with different levels of detail and the ease of reviewing assumptions at a glance. In this way the focus remained on the conversion technologies and their interaction, with the tacit assumption that the separation steps implied by the product routings can be achieved in practise. To mitigate this shortcoming, the implied separations were kept simple and conceptual designs were steered clear of configurations implying fancy tricks of separation. The plausibility of the implied separation steps was qualitatively checked for all designs and in most cases separation involved only carbon number cuts. Where more involved separations were needed, such as in hydroisomerisation, the availability of the required technology has been confirmed from literature.

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[u] Software for estimating physical properties was developed (ChemDB Ver.2.00).

Syncrude feed definition

The composition of the HTFT syncrude has been based on Sasol Synfuels (Secunda, South Africa) production data, using the averaged values over the period 1 January 1998 to 30 April 1998. The source data[v] included detail at compound level (representative compounds); this level of detail was not used. Compound specific detail was only retained for the C_1-C_3 hydrocarbons and aqueous chemicals. For the C_4-C_8 carbon range, the flows were lumped as *n*-paraffins, iso-paraffins, *n*-olefins, iso-olefins, aromatics and oxygenates. For higher carbon numbers, compounds were classified only as paraffins, olefins, aromatics or oxygenates. The C_9-C_{10}, C_{11}-C_{14}, C_{15}-C_{22} and C_{22}+ compounds were lumped.

The composition of the LTFT syncrude has been based on the data for the Sasol China CTL LTFT base case.(42) The source data, which implies an Fe-based LTFT process, such the commercial SSBP at Sasol 1 (Sasolburg, South Africa), was simplified in a similar way to the HTFT syncrude data. It should nevertheless be noted that the source data was of a lower level of detail compared to the HTFT source data.

Due to reasons of confidentiality,[w] this data may unfortunately not be provided. It can nevertheless be noted that it similar to the syncrude compositions previously given (HTFT in Chapter VI, Table 12 and LTFT in Chapter VI, Table 10).

Capacity

To ensure that all the conceptual refinery designs are on the same feed basis, the Fischer-Tropsch syncrude production has been scaled to a flow rate of 500 $t{\cdot}h^{-1}$ of C_2 and heavier material. This is roughly equivalent to a 100 000 bpd crude oil equivalent refinery.[x] Reference to refinery yield is always expressed on a mass basis relative to the C_2 and heavier syncrude feed to the refinery. Is allows refinery comparisons, but implies that the total Fischer-Tropsch syncrude production may be different, depending on the methane-make.

It should also be noted that the impact of the refinery hydrogen requirement has not been taken into consideration. This is not an omission. Translation of the hydrogen surplus or deficiency into increased or decreased syncrude production requires detailed Fischer-

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[v] Sasol Synfuels PI data historian that logs the field instrument values and compound based analyses from the quality control laboratories.

[w] The Sasol Technology Intellectual Property group requested that this data be removed from the thesis.

[x] The conversion of barrels per day (bpd) crude oil equivalent = 0.1589873 m^3 per day syncrude. Since these numbers are on a volumetric basis, they are density dependent.

Tropsch gas loop modelling, which falls outside the scope of the present work. The actual refinery yield values can therefore not be directly compared if the refinery hydrogen requirements are widely differing.

Fuel specifications and property assumptions

The Euro-4 standards (Chapter II) have been used as benchmark to determine whether the motor-gasoline and diesel fuel meet fuel specifications. For jet fuel the international Jet A-1 specifications (Chapter II) were used. However, not all fuel properties can be calculated accurately, which is reflected by the limited property values reported in this chapter. For example, there is no accurate estimation method for freezing point, a key property for jet fuel. It was consequently necessary to manually check that the compounds included in the jet fuel were likely to result in a fuel that met the freezing point specification (Table 19).

The fuel properties reported for the refinery designs have been calculated by linear blending of the fuel components on a volumetric basis (Equation A1), where V_j is the volume of component j and X_j is the fuel property of the component. The estimated fuel properties are therefore only indicative, since this is an approximation of the non-linear blending nature of fuel properties found in practice.

$$X = \frac{\sum X_j V_j}{\sum V_j} \qquad \ldots \text{(A1)}$$

The ASTM DS 4B tables$^{(21)}$ were used for all compound specific property values except cetane numbers, which were taken from the paper by Santana and co-workers.$^{(28)}$ In cases where the product was similar to that for which syncrude specific property data is known, the property data for the specific conversion process was used.$^{(10)(23)(24)}$ The fuel property values for oligomerisation products, which played an important role in all refinery designs, were feed composition dependent in some instances and had to calculated. The assumptions made for modelling are listed in Table A1.

The octane values of hydrogenated motor-gasoline from SPA oligomerisation are very sensitive to the feed composition, unlike the octane values of unhydrogenated motor-gasoline, which are feed insensitive. The feed significantly affects the degree of branching and carbon number distribution of the product. The hydrogenated motor-gasoline RON

(Equation A2) and MON (Equation A3) were calculated based on a correlation developed from literature data,(14) showing the dependence on the fraction of propylene (f_{C3}), iso-butene (f_{iC4}) and pentenes (f_{C5}) in a butene feed:

$$RON = 86 - 37.\left[f_{C3} + \frac{f_{C5}}{2}\right] + 25.\left[\exp\left(f_{iC4} - 0.08\right) - 1\right] \quad \text{... (A2)}$$

$$MON = 86 - 30.\left[f_{C3} + \frac{f_{C5}}{2}\right] + 10.\left[\exp\left(f_{iC4} - 0.08\right) - 1\right] \quad \text{... (A3)}$$

Table A1. Fuel property values of the olefin oligomerisation products that were used for refinery modelling.

Refinery source	Density (kg·m^{-3})	RON	MON	RVP (kPa)	Flash pt. (°C)	Cetane number
Butanes	581.4	94.7	90.6	380	-	-
SPA motor-gasoline (unhydrogenated)	719.6	95.9	82.1	5.5	-	-
SPA motor-gasoline (hydrogenated)	720	Eq. A2	Eq. A3	5.5	-	-
SPA kerosene	750	-	-	1.2	40	-
SPA distillate	760	-	-	-	-	30
ASA motor-gasoline (unhydrogenated)	Eq. A4	Eq. A5	Eq. A6	72	-	-
ASA motor-gasoline (hydrogenated)	700	80	80	72	-	-
ASA C_9-C_{10} kerosene	760	-	-	1.2	40	-
ASA C_{11}-C_{16} kerosene	790	-	-	0.1	73	-
ASA distillate	810	-	-	-	-	29
ZSM-5 motor-gasoline (unhydrogenated)	738	85	75	57	-	-
ZSM-5 motor-gasoline (hydrogenated)	700	55	55	50	-	-
ZSM-5 kerosene	Eq. A7	-	-	1.2	40	-
ZSM-5 distillate	Eq. A8	-	-	-	-	54

A similar situation exists for ASA oligomerisation, but in this instance the octane values of unhydrogenated motor-gasoline is sensitive to the feed composition, while the octane values of hydrogenated motor-gasoline are insensitive enough to assume it to remain constant. The feed does not significantly change the degree of branching of the product, but the paraffin content in the feed lowers the octane value of the unhydrogenated motor-gasoline. Linear correlations for density (Equation A4), RON (Equation A5) and MON

(Equation A6) and were developed from literature data,(43) showing the dependence on the C_3-C_6 olefin fraction ($f_{C3\text{-}C6}$) in the feed:

$$\rho = 707 \cdot f_{C3\text{-}C6} + 711 \cdot (1 - f_{C3\text{-}C6}) \qquad \text{... (A4)}$$

$$RON = 93 \cdot f_{C3\text{-}C6} + 80 \cdot (1 - f_{C3\text{-}C6}) \qquad \text{... (A5)}$$

$$MON = 71.5 \cdot f_{C3\text{-}C6} + 60 \cdot (1 - f_{C3\text{-}C6}) \qquad \text{... (A6)}$$

The base octane values for ZSM-5 oligomerisation are listed in table A2. Similarly to the ASA derived oligomers, the octane numbers of the motor-gasoline were dependent on the feed paraffin content and had to be calculated on a compound basis.

More general correlations were derived from literature data(31) to calculate the density of the kerosene (Equation A7) and the distillate (Equation A8) from an H-ZSM-5 oligomerisation process. The density was related to the kerosene fraction of the distillate (f_{kero}) before fractionation:

$$\rho_{kero} = 748.5 + 40 \cdot f_{kero} \text{ , valid for } f_{kero} = \{0 \,..\, 0.5\} \qquad \text{... (A7)}$$

$$\rho_{distillate} = 800 - 40 \cdot (0.5 - f_{kero}) \text{ , valid for } f_{kero} = \{0 \,..\, 0.5\} \qquad \text{... (A8)}$$

Although not explicitly stated, the property values for all conversion processes were adjusted if the feed contained inert compounds that would significantly affect the fuel properties.

Conversion technologies

The conversion data reported in literature, as discussed in Chapter VII, were used for the modelling of the conversion units.

Mass balance closure

Proper mass balance closure was ensured for every conversion unit, as well as for the refinery as a whole. In some tables it may seem as if mass balance closure was not obtained, but this is only due to rounding. In instances where it is known that some material had to be purged, such material was reported as “Unrecovered organics”. Material not recovered, such as carboxylic acids dissolved in the Fischer-Tropsch aqueous product, was similarly reported as "Unrecovered organics".

Due to the importance of hydrogen in a refinery, as well as the importance of water as by-product from hydroprocessing of Fischer-Tropsch materials, these compounds were listed separately in the mass balance. Hydrogen was recovered only from product streams with a significant hydrogen content. It was assumed that 85% hydrogen recovery is possible, based on Sasol experience, although Chauvel and Lefebvre(44) reported a lower average value (75%). The remainder of the hydrogen was reported as fuel gas. No restrictions were placed on the composition of the fuel gas, which generally consisted of a mixture of hydrogen, methane, ethane and ethylene.

Separation of Fischer-Tropsch primary products

An advantage of Fischer-Tropsch syncrude refining over crude oil refining that has been pointed out,(6) is that the stepwise condensation of the Fischer-Tropsch primary products act as a pre-separation step. This advantage has not been fully exploited in current commercial designs, but a significant energy saving is possible if the designs of the Fischer-Tropsch synthesis block with its stepwise condensation is integrated with the primary separation in the refinery. In the model realistic assumptions were made for product separation,[y] without modelling each separation step as a unit operation. Proper separation design is implied, with inefficiencies in product separation affecting only one carbon number from the cut point.

One assumption that may be considered unrealistic, is the implied separation between methane and C_2 hydrocarbons in the LTFT refinery designs. On account of the high light hydrocarbon production during HTFT synthesis, the inclusion of cryogenic separation in the design is almost implied, but this is not necessarily true for LTFT. The C_2 hydrocarbons from LTFT synthesis are reported as part of the fuel gas, but in practise the C_2 hydrocarbons can be recycled in the Fischer-Tropsch gas loop. The reason for this "unrealistic" assumption during LTFT modelling is purely to enable reporting of all refinery yields in terms of C_2 and heavier syncrude feed. In instances where ethylene conversion technology is specifically used for an LTFT refinery design, the necessary separation will of course be required.

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[y] For example, the separation efficiency for the carbon number separation between C_3 and C_4 took cognisance of the Linde detailed separation efficiency values, namely 0.8% C_3's in C_4 and 1.4% C_4's in C_3.

CHAPTER X

Conclusion

The thesis set out to improve the understanding of Fischer-Tropsch syncrude refining. By first studying current refining practise, crude oil and syncrude could be compared to identify fundamental differences in refining focus and conversion behaviour. This study was followed by a critical evaluation of the compatibility of HTFT and LTFT syncrudes with the chemistry and catalysis of various conversion processes. The recommendations from the technology evaluation provided the foundation for the development of Fischer-Tropsch syncrude based refinery designs to maximise motor-gasoline, jet fuel and diesel fuel production. These designs showed that Fischer-Tropsch refineries could be less complex than 4th generation crude oil refineries for the production of on-specification transportation fuels. It also illustrated the advantage of considering syncrude fundamentals in developing syncrude specific refineries, rather than imposing crude oil design practises on syncrude refinery designs.

1. Introduction

Refining technology is continuously evolving, driven by the changing legislative pressures associated with transportation fuels. The development, commercialisation and licensing of refining technology gave rise to a whole industry. The focus of this industry is on the conversion of crude oil to transportation fuels. Although the production and refining of Fischer-Tropsch syncrude has been around for a long time, very little effort has been devoted to the development and customisation of refining technologies to specifically upgrade syncrude. The designs of commercial facilities for the conversion of Fischer-Tropsch syncrudes to transportation fuels have likewise been based on crude oil refining technologies and know-how. This is not surprising considering the small market share that syncrude refining has; about 250 000 bpd of more than 85 000 000 bpd refining capacity worldwide. However, this does not explain the lack of understanding that permeated the technology selection and the refining technology application for syncrude refining. The premise explored in this thesis, namely that refining of Fischer-Tropsch syncrude requires significantly different technologies and refinery designs, is a departure from the mainstream practice in the South African synthetic fuels industry.

In the past three decades two distinctly different approaches to syncrude refining emerged. The one approach was to make use of crude oil refining technology for Fischer-Tropsch syncrude refining to transportation fuels, which resulted in complex refineries, such Sasol Synfuels (Secunda, South Africa) and PetroSA Mossgas (Mossel Bay, South Africa). The other approach was to convert the Fischer-Tropsch syncrude to naphtha and distillate, which could be sold as blending components for transportation fuels or as intermediates for chemical production. This approach was used for the Shell Bintulu (Bintulu, Malaysia) and Oryx GTL (Ras Laffan, Qatar) facilities and resulted in much simpler refineries.

The need to improve our *understanding of refining technology selection and refinery design for processing Fischer-Tropsch syncrude*, proved to be an academically fertile and industrially relevant topic for research.

2. What has been achieved?

2.1. Thesis part 1: Background

In order to develop a better understanding of Fischer-Tropsch syncrude refining, a thorough grasp of crude oil refining was required. This was achieved by studying the feed material, conversion steps and fuel specifications that define the transformation process called fuels refining. The results of this background study have been provided in Chapter II (fuel specifications), Chapter III (crude oil description) and Chapter IV (crude oil refineries). Although these chapters dealt mainly with a review of current literature, the information thus gleaned was interpreted in context to *identify trends for future fuel specifications* (Chapter II, section 5) and *future oil refineries* (Chapter IV, section 4). This is an interpretative contribution, albeit speculative, since it deals with the future that is inherently uncertain.

Literature on Fischer-Tropsch technology is available in two recent books[a] on this subject. Rather than rehash information from literature, care was taken to highlight aspects relevant to the present study. Considering that the syncrude composition is dependent on the type of Fischer-Tropsch technology being used and that there are presently six different types

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[a] Steynberg, A. P.; Dry, M. E. Eds. *Fischer-Tropsch Technology*; Elsevier: Amsterdam, 2004. Davis, B. H.; Occelli, M. L. Eds. *Fischer-Tropsch synthesis, catalysts and catalysis*; Elsevier: Amsterdam, 2007.

in commercial operation, *syncrude composition was related to Fischer-Tropsch fundamentals* (Chapter V, section 2) to explain differences in the carbon number distribution and compound classes being present. Some of the refining issues related to syncrude composition were anticipated by *comparing crude oil with syncrude and noting fundamental differences in refining focus and conversion behaviour* (Chapter V, section 5).

This set the scene for a detailed discussion of Fischer-Tropsch refineries (Chapter VI), a topic not previously dealt with in a single reference work. The discussion of the refinery designs pointed out syncrude refining peculiarities by *interpreting the design intent*, which is not specified in the literature. The literature review is also valuable in its own right, since it collated the snippets of information on Fischer-Tropsch refining that have not previously been presented together in a single text.

2.2. Thesis part 2: Refining technology and refinery design

The second part of the thesis deals with Fischer-Tropsch refining. It contributes new insights in two fields that until now received scant coverage in literature, namely *refinery technology evaluation in Fischer-Tropsch context* (Chapter VII) and *conceptual Fischer-Tropsch refinery design* (Chapter IX). In both instances the focus was on conversion technology, with limited reference to separation science.

The approached followed in Chapter VII was to evaluate the *compatibility of Fisher-Tropsch syncrude with the chemistry and catalysis* of different conversion processes. The analysis was based on a fundamental understanding of the conversion involved and how it will be affected by the compound classes present in syncrude that are not present in crude oil. The nature and concentration of the olefins and the oxygenates in syncrude were often the differentiating features. Cognisance was also taken of the environmental impact of the conversion technologies, by assessing the waste production, chemicals needed and energy use. The list of technologies that were evaluated transcended the list of refining technologies found in crude oil refining texts, with conversion processes such as double bond isomerisation, aromatic alkylation, metathesis and alcohol dehydration being included in the study. Recommendations were made within each conversion class to indicate preferred technologies. This information is summarised in a compatibility table for Fischer-Tropsch refining technologies (Chapter VII, Table 8).

The chapter on refinery design (Chapter VIII) was necessary to discuss the design process and is not only limited to Fischer-Tropsch refineries. The approach taken is qualitative and somewhat philosophical, with a clear distinction being made between "real-world" refinery designs and the conceptual design process. Of especial significance was to *highlight the importance of secondary design objectives* in determining the outcome of refinery development. This is not a well-known aspect of refinery design, which is a bit like the law of unintended consequences, and has been illustrated with a "real-world" example (Chapter VIII, Appendix A).

The chapter on conceptual Fischer-Tropsch refinery design (Chapter IX) is the culmination of this study. After the subject matter has been taken apart in Chapters II to VIII, it is put back together again. The insights gained in technology selection and syncrude properties are used to *develop refinery designs for maximum motor-gasoline, jet fuel and diesel fuel* production. Designs were developed for both HTFT and LTFT syncrudes and despite significant differences in these syncrudes, it is shown that neither requires overly complex refinery designs to produce fuels. A total of 16 different fuels refineries were developed and the designs demonstrated that syncrude refineries are often less complex than 4th generation crude oil refineries for the production of on-specification transportation fuels.

A surprising exception was found in the conversion of syncrude to diesel fuel. The refining of on-specification diesel fuel presented a problem on account of a *cetane-density-yield triangle* (Chapter IX, section 5). It could be shown that on a molecular level syncrude is unsuitable for diesel fuel production as defining by current international fuel specifications. This is quite contrary to the expectations created in the media by projects such as Sasol's Oryx GTL and Shell's Pearl GTL.

In essence Chapters VII to IX defined a technology roadmap for the refining of Fischer-Tropsch syncrude. The recommendations on technology selection are based on fundamental scientific principles and are therefore logically auditable. The refinery designs that were developed, provide a framework for future project specific refinery designs, as well as an indication to what extent motor-gasoline, jet fuel and diesel fuel production can be maximised. Such an evaluation has not previously been published.

3. Prospects for future study

Refining is a very broad field and the scope of the present investigation leaves much work undone. During the course of this study, some topics were touched on that deserves treatment in their own right. It is hoped that future researchers may take up these suggestions for further study:

a) *Oxygenate refining*. The significant levels of oxygenates (alcohols, aldehydes, carboxylic acids and ketones) present in Fischer-Tropsch syncrude differentiates it from crude oil. Most refining technologies have been developed without paying any attention to the effect of oxygenates on account of their minor role in crude oil refining. A systematic investigation into the effect of oxygenates on different refining technologies will benefit the syncrude refining industry tremendously. Reference to some of the technologies investigated by myself and my co-workers can be found in the thesis, but it still leaves much to be accomplished.

b) *Separation technology*. Separation presents its own set of challenges to the syncrude refiner. The phase behaviour of the hydrocarbon-oxygenate and oxygenate-water mixtures encountered in a Fischer-Tropsch refinery is non-ideal and finding appropriate thermodynamic models to describe it, is challenging. This is made even more difficult by the lack of equilibrium data for such systems.

c) *Syncrude analysis*. The analytical methodologies adopted by the fuels industry are mostly based on crude oil derived petroleum products. Blindly applying these techniques to syncrude is fraught with error. Deficiencies in the characterisation of syncrude have briefly been mentioned in Chapter V and there is much scope for the development of appropriate analytical methodologies for syncrude.

d) *Catalysis of linear α-olefins and 1-alcohols*. Renewed interest in solid phosphoric acid catalysis for syncrude refining was sparked when it was shown that there is a low temperature isomerisation pathway from 1-butene to isobutene during oligomerisation that produced alkylate equivalent products. A different mode of reaction for 1-butene has also been identified for oligomerisation over amorphous silica-alumina catalysts. There are bound to be more reactions and catalysts that have beneficial reaction pathways for linear α-olefins and 1-alcohols. Probing this field may lead to the discovery of more efficient refining technologies for Fischer-Tropsch syncrude.

e) *Metal carboxylates*. The metal containing species in syncrude are mainly metal carboxylates. These species are fundamentally different from the phorphyrin-type species in crude oil. The metal carboxylates present in syncrude are usually stable enough to survive low to medium severity conversion processes in the refinery and they are not converted by hydrodemetallisation (HDM) catalysts. Thermal decomposition under more severe operating conditions can potentially cause pressure drop problems. Unfortunately the thermal behaviour of many metal carboxylates of interest to syncrude refining are poorly described.

f) *Catalyst evaluation protocol*. The catalyst testing protocols that have been developed for scale-up and scale-down, are mainly concerned with the influence of hydrodynamics. Hydrodynamics is important, but isothermal catalyst evaluation becomes a dangerous practise when dealing with very exothermic conversion processes, such as is often encountered with syncrude (Chapter V, section 5). The need for adiabatic testing in such situations has been discussed in literature. However, this topic is scantily covered, despite its importance for the selection and evaluation of refining catalysts with syncrude feed materials. Such an investigation should preferably also be extended to the design of appropriate laboratory and pilot-scale reactor systems for such evaluations.

g) *Non-energy refineries*. In Chapter IX reference was made to some literature dealing with the refining of Fischer-Tropsch syncrude to chemicals and the study of non-energy refineries was excluded from the scope of this thesis. It is nevertheless a logical next step in extending the technology roadmap for Fischer-Tropsch refining and should move well beyond the obvious chemicals obtainable by separation from syncrude. Chemicals refining potentially require a different set of conversion technologies that have to be evaluated for their compatibility with syncrude. Furthermore, a proper evaluation of chemicals refining presupposes a thorough understanding of the chemicals market, which is quite different to the transportation fuel market. In this respect it will be especially beneficial to investigate the possibility of producing lubricating oils, fuel additives and other speciality products that have synergy with transportation fuels.

h) *Feedstock integration*. The co-refining of syncrude with feedstocks derived from other sources may prove a fertile ground for improving the efficiency of Fischer-Tropsch technology as basis for fuels and chemicals production. Presently, commercial Fischer-Tropsch facilities are already co-refining coal pyrolysis products and natural gas condensates, while some of the downstream products are blended with crude oil derived materials. The integration of these feedstocks and intermediate products may be achieved in many ways, some of which may be more beneficial than current practice. There are also opportunities for the co-refining of other feed materials, such as crude oil and biomass. Some of these opportunities have been mentioned and many more will undoubtedly become apparent as this field is explored.

Research often unearths more questions than it sets out to answer. The suggested topics for future research are just a fraction of the topics in the field of Fischer-Tropsch refining that deserve attention. In energy research, Fischer-Tropsch refining is still comparatively virgin territory. The scope for process intensification is huge, with very little having been done in this respect for the integration of syncrude production and refining. Refining catalysis similarly abounds with opportunities. It is hoped that future researchers may derive the same joy from the exploration of the complexity being offered by this topic.