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

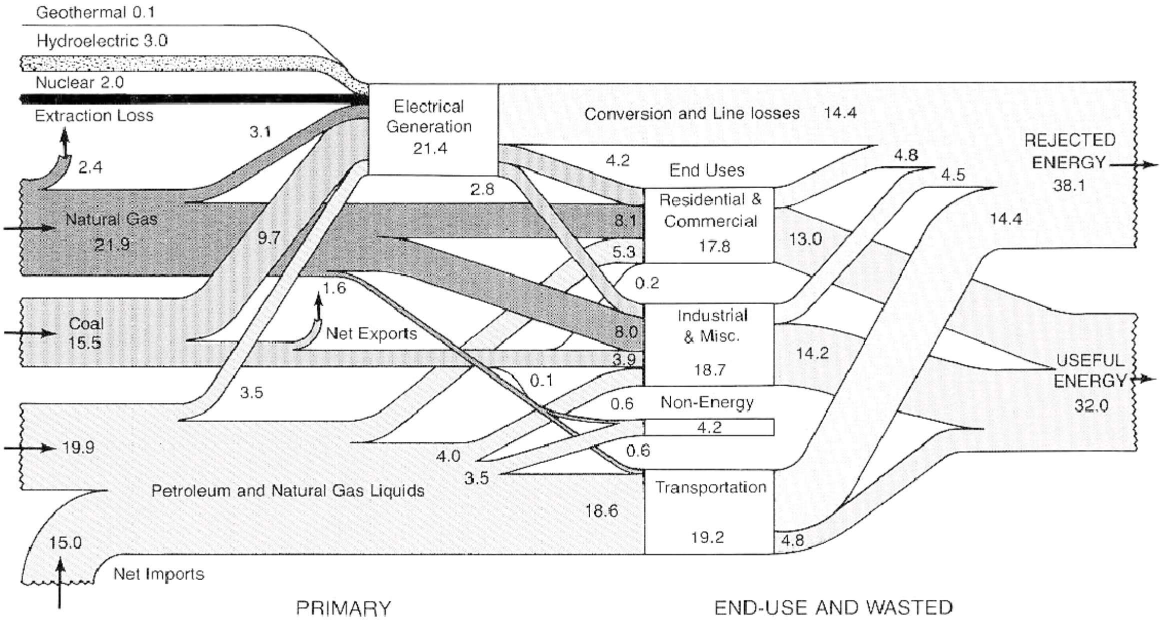

Figure 1. Primary energy inputs in the USA in 1976, shortly after USA peak oil production was reached in 1970. (This figure has been reproduced directly from Ref.(2) and is copyright protected).

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.

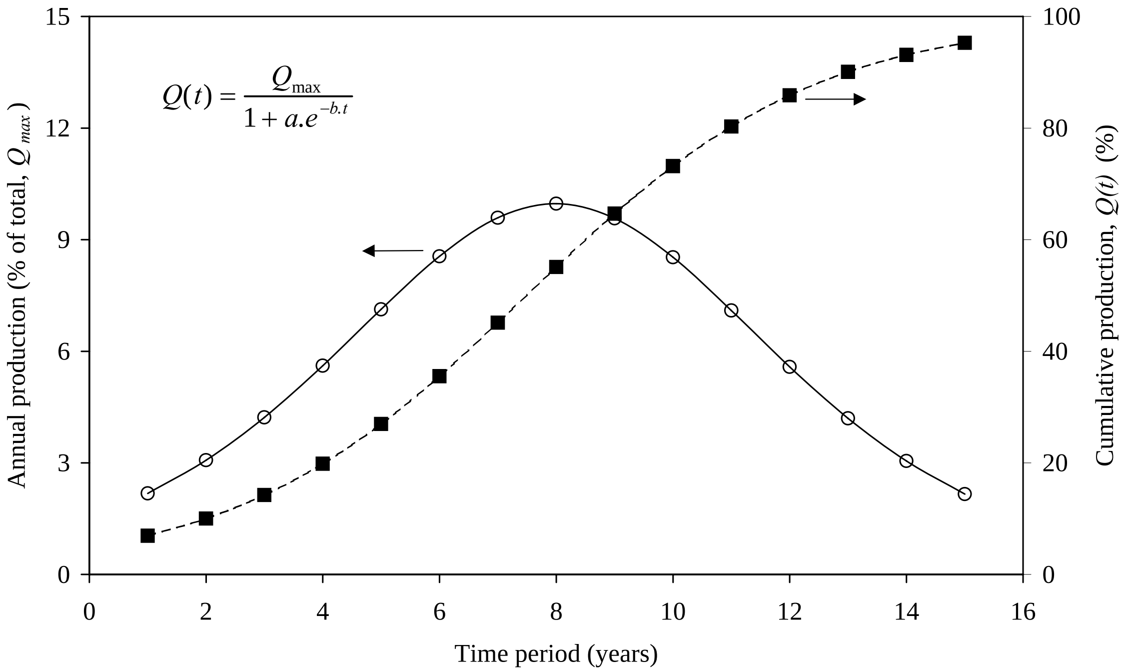

Figure 2. The Hubbert-model description of the production of a non-renewable resource, using arbitrary values for the model parameters a *and* b. *The annual production (○) of the total resource that is available, as well as the cumulative production (■) is shown.*

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.

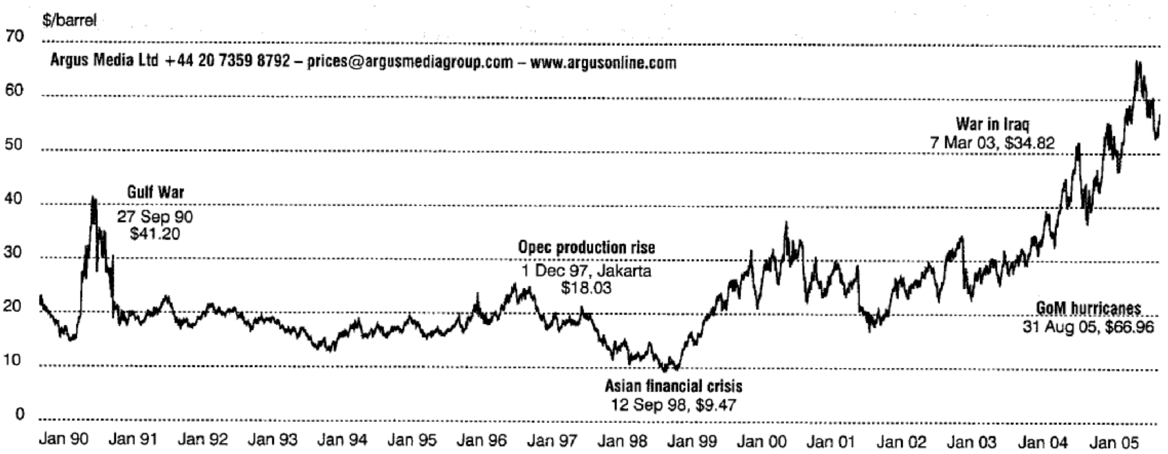

Figure 3. Brent crude oil price fluctuations during the period 1990-2005 (US$/barrel). (This figure has been reproduced directly from Ref.(7) and is copyright protected).

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

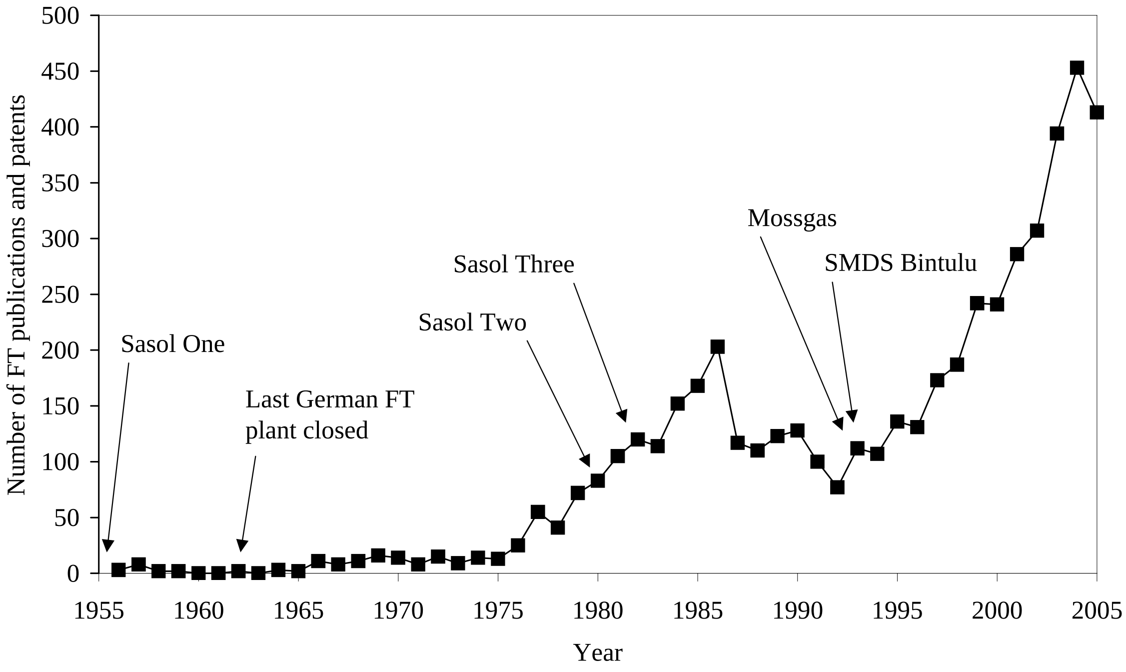

Figure 4. Number of publications in the past 50 years (1955-2005) having "Fischer" and "Tropsch" in the title, keywords or abstract, based on a Chemical Abstract Services SciFinder™ search of abstracted documents in English, German and French.

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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 (≤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·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·kg^{-1}), maximum	500	150	50 / 10
Lead (g·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)

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

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·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 ($kg \cdot m^{-3}$)	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 ($mg \cdot kg^{-1}$), max.	5000	300	30	5-10
Water ($mg \cdot kg^{-1}$), 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.

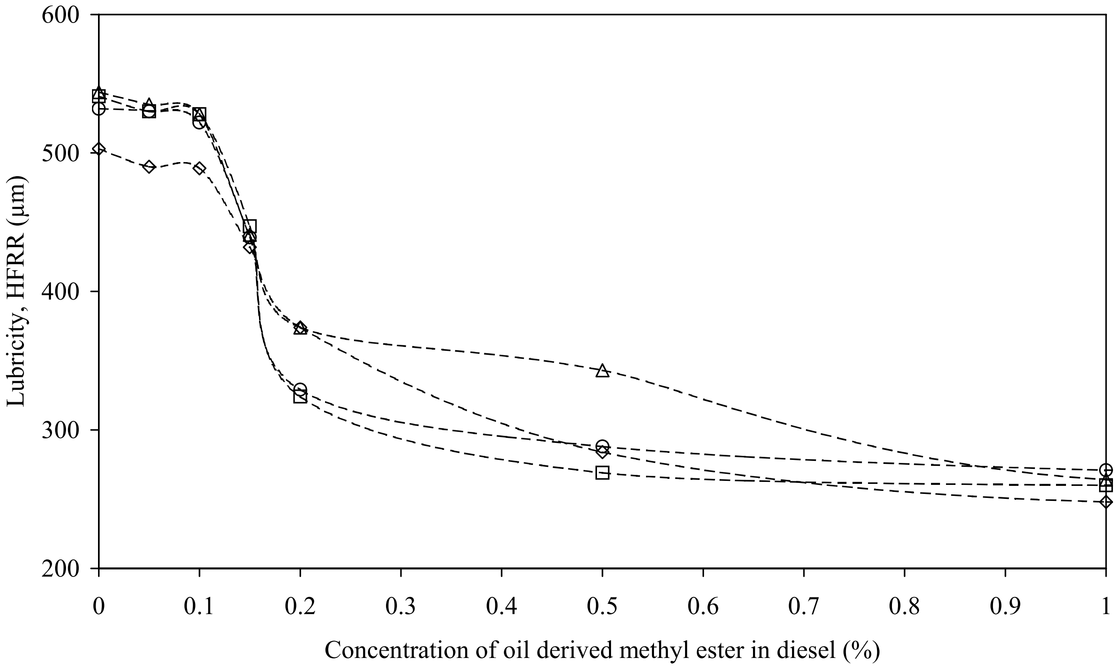

Figure 1. Non-linear lubricity response of low sulphur diesels to the addition of methyl esters of fatty acids from sunflower oil (□), olive oil (◊), corn oil (○) and used frying oil (Δ).

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)

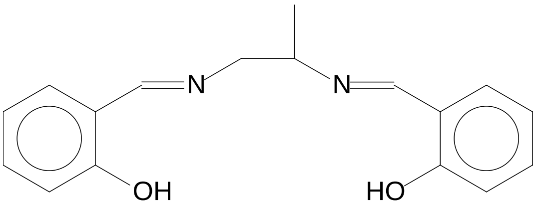

Figure 2. N,N'-disalicylidene-1,2-propane diamine.

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·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·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·m^{-3})	(MJ·kg^{-1})	(MJ·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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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 ($\mu g \cdot g^{-1}$)	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 ($kg \cdot m^{-3}$)	845	837	825	845	845	845	825	845	845
PAH (%) ‡	11	6	1	11	11	11	1	11	11
Sulphur ($\mu g \cdot g^{-1}$)	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.