CHAPTER IX

Conceptual Fischer-Tropsch refinery designs

Refinery designs were developed for maximum motor-gasoline, jet fuel and diesel fuel production from syncrude. Both high temperature Fischer-Tropsch (HTFT) and low temperature Fischer-Tropsch (LTFT) are considered. In all instances it was possible to present at least one design where the targeted fuel could be produced with a 50% or better yield, without resorting to a very complex design. In most designs seven or less conversion units were required in the oil refinery to refine the syncrude to fuels meeting Euro-4 specifications. When aqueous product refining was added, two additional conversion units were needed. Only diesel fuel refining presented a problem, since it was limited by a cetane-density-yield triangle. The naphthenic compounds required to produce diesel fuel in high yield that meets both cetane and density requirements, are not abundant in syncrude. Significant synthetic effort would be required to produce such compounds from a Fischer-Tropsch feedstock and no technologies are commercially available to do so. It was concluded that syncrude (HTFT and LTFT) is on a molecular level unsuited for maximising Euro-4 type diesel fuel production, which is best achieved by blending the syncrude derived distillate with material from other sources, such as coal pyrolysis products or crude oil.

1. Introduction

The aim of this investigation is to determine the suitability of HTFT and LTFT synthesis for the production of maximum motor-gasoline, jet fuel and diesel fuel. Such an investigation, to explore the possibilities within the field of Fischer-Tropsch refining, rather than developing a refinery for a specific project, has never before been undertaken. Limiting variables will be highlighted in an attempt to better understand the possibilities and the constraints within Fischer-Tropsch refineries. In instances where integration opportunities with other feed sources become apparent, such as crude oil, gas condensates and tars, it will only be noted, but not explored. The development of non-energy chemicals refineries has been covered in literature(1)(2)(3)(4) and will not be considered.

2. Modelling details

2.1. Conceptual design

In the previous chapter (Chapter VIII) it has been pointed out that conceptual refinery design requires three important pieces of information: feed description, product description and a list of the refining processes to be considered. These variables have already been discussed:

a) The feed description has been discussed in Chapter V. Since Fischer-Tropsch based coal-to-liquids (CTL), gas-to-liquids (GTL) and biomass-to-liquids (BTL) processes all imply conversion via synthesis gas to Fischer-Tropsch syncrude, a Fischer-Tropsch refinery design is more dependent on the Fischer-Tropsch technology that has been selected than the type of raw material used as feed.[a] There are two main Fischer-Tropsch technology types, namely high temperature Fischer-Tropsch (HTFT) technology and low temperature Fischer-Tropsch (LTFT) technology. Within each Fischer-Tropsch technology type a multitude of variations are possible. For practical reasons the conceptual refinery designs developed in this chapter are limited to only one HTFT syncrude and one LTFT syncrude composition (Appendix A).

b) The product description for a fuels refinery has been discussed in Chapter II. Fuels are classified based on boiling range and properties. Only the three main transportation fuel types were discussed in detail, namely motor-gasoline, jet fuel and diesel fuel. Other fuel types that can be produced and that were not discussed include synthetic natural gas (SNG), heating fuels, liquefied petroleum gas (LPG) and marine fuels. In addition to these, there are various products that can be produced in non-fuels refineries, such as lubricating oils, greases, hydraulic fluids, heat transfer fluids, waxes and chemicals.(5) In this chapter conceptual refinery designs will be developed to maximise only motor-gasoline, jet fuel and diesel fuel.

c) Refining processes have been discussed and evaluated in Fischer-Tropsch refining context in Chapter VII. The conversion technologies considered during the development of conceptual refinery designs will be limited to those already discussed. Justification for the selection of a specific type of technology will be limited to the specific refinery design being considered.

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[a] This is an over-simplification, since CTL gasification technology and the associated production of coal pyrolysis products, or the recovery of associated gas condensates in the feed to GTL facilities, will influence the feed description.

2.2. Refinery economics

Thus far, little attention has been devoted to refinery economics, although some of the drivers determining refinery economics have been discussed (Chapter VIII). The same principles governing crude oil refinery economics apply to Fischer-Tropsch refineries, with the difference that the syncrude composition is fixed in the design phase by the selection of the Fischer-Tropsch technology. The refinery economics can therefore not be improved by judicious selection of crude oils based on day-to-day spot prices in the market. The Fischer-Tropsch syncrude cost is less volatile and based mainly on raw feed material cost, cost of capital and operating cost.

One could arbitrarily divorce syncrude production from syncrude refining[b] and calculate an effective syncrude cost, analogous to crude oil cost. This is bound to yield a high dollar equivalent crude oil price at which syncrude production becomes economical (about US$ 50),(6) because most of the capital cost involved in constructing a Fischer-Tropsch facility is due to syncrude production (Figure 1).(7) The refinery cost is typically less than 15% of the total capital cost (10% in the case of Figure 1). Yet, the refinery makes the

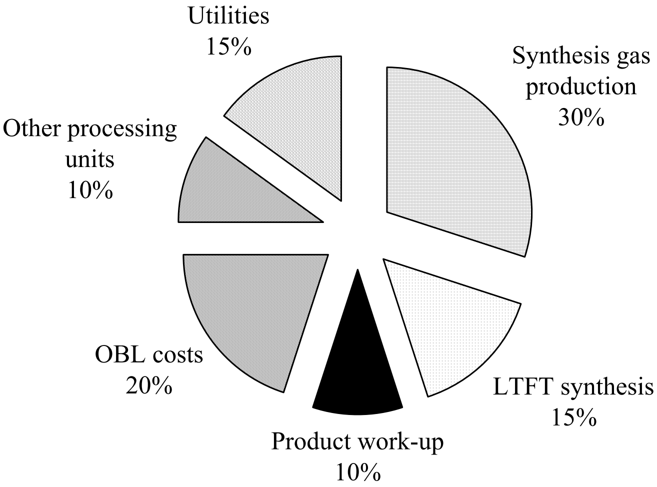

Figure 1. Distribution of capital cost for a gas-to-liquids project in the Middle East.

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[b] In practice divorcing syncrude production and refining negates the synergies between these processes, especially in terms of primary product separation.

difference between selling syncrude as crude oil (like Athabascan tar sand derived syncrude), or final products and is consequently the main value addition step in a Fischer-Tropsch plant.

The key learning point from this is that the yield of final products in a Fischer-Tropsch refinery is pivotal to the economics of the venture. Spending more money in the refinery is less of an issue than in a crude oil refinery, due to its small impact on the overall capital cost of the project. Furthermore, the decision to build a Fischer-Tropsch facility is often driven by a political agenda. In order to realise such a political agenda, economic incentives are provided to investors to offset the high capital cost associated with Fischer-Tropsch facilities for the production of transportation fuels by alternative means. These incentives are generally linked to specific politically desirable final products, not to syncrude production. For this reason, the role of refinery economics will be downplayed during the refinery designs. Nevertheless, the three main refinery types that will be studied are all linked to specific plausible scenarios driven by specific political pressure groups, for example: maximum motor-gasoline (United States Congress); maximum jet fuel (United States Department of Defence); maximum diesel fuel (European Parliament).

3. Motor-gasoline refineries

There are two aspects to consider when aiming for maximum motor-gasoline production from syncrude, namely a) to change the carbon number distribution to maximise the motor-gasoline fraction; and b) to ensure that the molecular composition of this fraction meets motor-gasoline specifications.

The first aspect focuses on the quantity of the syncrude that can be refined in the motor-gasoline boiling range. The maximum amount of motor-gasoline will be determined partly by the amount of straight run syncrude and partly by the amount of syncrude that can be converted to motor-gasoline by conversion processes. The straight run syncrude, which is material already in the correct boiling range, is a function of the Fischer-Tropsch synthesis (Figure 2). From this figure it can be seen that a chain growth probability (α-value) of 0.68-0.72 gives the highest yield of straight run naphtha. This overlaps with the commercial operating window of fused iron-based HTFT synthesis as practised commercially by Sasol and PetroSA. Purely based on straight run yield, it can be said that HTFT syncrude requires less refining effort than LTFT syncrude to produce maximum motor-gasoline. It can also be said the commercial HTFT syncrude is an optimal feed based on straight run motor-gasoline yield. However, this is only part of the picture, since conversion processes resulting in either

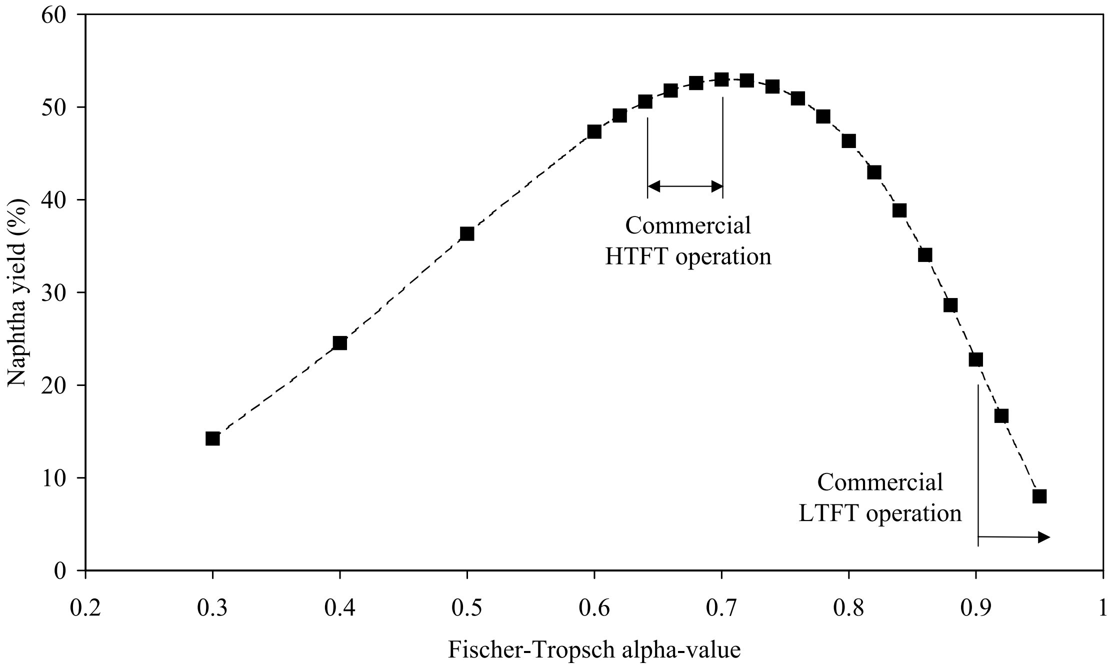

Figure 2. Yield of straight run naphtha (C_5-C_{10}) in the C_3 and heavier hydrocarbon fraction from Fischer-Tropsch as function of the chain growth probability (α-value).

carbon number growth, or in carbon number reduction, can be used to convert lower boiling or higher boiling material to the motor-gasoline range. If this conversion can be done in such a way that it not only increases the quantity of motor-gasoline, but also its quality, it can more than offset any seeming disadvantage based on straight run yield only.

The second aspect focuses on the quality of the refined syncrude. Quality is very important and most refining effort is required for the production of motor-gasoline, a point already made previously (Chapter IV). It is worthwhile to recap the essential qualities needed in motor-gasoline. Octane number is the key refining specification and a minimum RON of 95 and MON of 85 is typically required. The octane requirement must be met within the limitations imposed on composition (35% aromatics, 18% olefins, 15% oxygenates, 10 $\mu g \cdot g^{-1}$ S) and physical properties, such as vapour pressure. Apart from hydrocarbons, oxygenates are the only compound class allowed in significant quantities in fuel. Aromatics and oxygenates can be considered high-octane compounds, with octane numbers generally exceeding that required by fuel specifications. Olefins can be considered as octane "neutral" compounds, with octane numbers generally close to that required by fuel specifications. However, olefins with a low degree of branching and especially linear α-olefins, are low-octane compounds. The octane number of paraffins is very structure sensitive and ranges from less than 0 to more than 100. Since paraffins are the only compound class not limited by fuel specifications, it stands to reason that the crux of motor-gasoline refining is to produce high-octane paraffins.[c] When we compare these quality requirements with the properties of straight run syncrude(8) (Table 1) it is clear that syncrude naphtha refining to motor-gasoline requires:

a) Synthesis of aromatics.
b) Reduction of the olefin content.
c) Improvement of olefin fuel quality.
d) Purification and/or synthesis of appropriate oxygenates.
e) Improvement of paraffin fuel quality.

Table 1. Comparison of straight run iron-based HTFT and LTFT naphtha to specifications and quality requirements for motor-gasoline.

Compound class	HTFT naphtha	LTFT naphtha	Euro-4	Comments
Aromatics	5	0	35% max	Most aromatics are desirable (high RON), but benzene is limited to less than 1% in fuel.
Olefins	70	64	18% max	Branched internal olefins are octane neutral, the linear α-olefins are low in octane.
Oxygenates	12	7	5-15% max	Alcohols or ethers required, FT oxygenates are mainly alcohols, carbonyls and acids.
Paraffins	13	29	unlimited	Highly branched paraffins needed for good octane, but FT paraffins are very linear.

A more detailed analysis of these requirements reveals that the quality issues can be grouped into three categories, although such a grouping may not be immediately obvious.

This first category is the production of *aromatics*. It is possible to aromatise olefins, oxygenates and paraffins by judicious selection of an appropriate aromatisation technology. Since aromatisation needn't be feed dependent, it provides a degree of freedom in the refinery design. Any undesirable material that does not have another natural refining pathway, may be upgraded in this way.

The second category is the production of *oxygenates*. It has previously been pointed out that the nature of the oxygenates that may be included in the fuel is subject to political

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[c] This is somewhat of an over-simplification, but it is much easier to increase the octane number of motor-gasoline by adding appropriate aromatics, olefins and oxygenates than it is by adding paraffins.

pressures. Despite syncrude being rich in oxygenates, only some of these oxygenates are acceptable as fuel oxygenates. Such oxygenates may be separated from the syncrude, for example the production of fuel ethanol by purification of the Fischer-Tropsch aqueous product fraction. Oxygenates may also be obtained from other sources, for example, importing oxygenates from an external source to meet a bio-fuels requirement. Optionally oxygenates may also be synthesised in the refinery, for example the production of fuel ethers, which are compounds not normally found in syncrude. In all instances it is prudent to avoid a tight integration of oxygenate production within the refinery design, since legislation governing oxygenate inclusion has to be considered ever changing.

The third category is the production of *aliphatics*. This is governed by the production of high-octane paraffins. The first guiding principle is that skeletal isomerisation can only be used to upgrade paraffins in the C_4-C_6 range. The C_7 and heavier paraffins are readily cracked(9) before the tri- and tetra-branched species needed for high octane are formed. The second guiding principle is that the production of C_7 and heavier high-octane paraffins can only be accomplished by the addition reaction of two shorter chain aliphatic molecules, either as practised in aliphatic alkylation or as practised in olefin oligomerisation. The third guiding principle is that hydrogenation of excess olefins in the fuel should target those molecules with the smallest octane number difference between the olefin and iso-structural paraffin. The fourth guiding principle is that it is hardly ever worthwhile to upgrade olefins by isomerisation only in order to retain them as olefins in the motor-gasoline.

A last aspect to consider, which has not been touched on, is the preferred way of dealing with material that cannot be accommodated in the motor-gasoline. This may be due to quality issues, or because it does not always make refining (an economic) sense to convert material that is already a transportation fuel into a different transportation fuel. The latter is an important consideration, since the aim is to produce final products. In general it can be said that any product that meets final product specifications, either as chemical, or as fuel, can in principle be retained as such.

3.1. HTFT motor-gasoline refinery development

In order to develop a conceptual design for an HTFT refinery producing maximum motor-gasoline, each boiling fraction will be considered separately. The idea is not to repeat the technology screening (Chapter VII), nor to duplicate literature.(10) This approach just seems to work well for the development of a motor-gasoline refinery.

a) *Residue* (C_{22}+). HTFT syncrude contains about 3% material boiling above 360°C.[d] Using the residue as a fuel oil is tempting from a design perspective, since it avoids the inclusion of any residue upgrading units. However, the aim is to maximise motor-gasoline and some form of cracking is required to reduce the average carbon number of the residue.

b) C_{15}-C_{22} *distillate*. Since HTFT material is sulphur free and low in polynuclear aromatics, the traditional refining approach would be to hydrogenate this material and incorporate it into diesel fuel. The hydrogenated product has a good cetane number, typically >51, and meets all diesel fuel specifications except density. The density of this material is typically around 810 $kg \cdot m^{-3}$, which is lower than the 820 $kg \cdot m^{-3}$ minimum density requirement for diesel. This shortcoming may be overcome by either blending from an external source, or exploiting synergies with tar refining or crude refining. Optionally it may be considered to use a carbon number reduction technology to crack this material into lower boiling material and increase the motor-gasoline production.

c) C_{11}-C_{14} *kerosene*. The straight run kerosene fraction from HTFT can be hydrogenated and used as a Jet A-1 component.(11) Optionally this fraction can be cracked to produce more lower boiling material to increase motor-gasoline production.

d) C_9-C_{10} *naphtha*. Traditionally this naphtha fraction is refined by catalytic reforming to produce aromatics. Despite the low $N+2A$ value, the Sasol and PetroSA HTFT refineries make use of this approach. The main drawback of this approach is that aromatics production is limited, since this fraction constitutes only 5% of the HTFT syncrude. The inclusion of more than one aromatics producing technology can be considered, but such an approach would be costly. However, as straight run motor-gasoline, the C_9-C_{10} naphtha has a low octane value, which becomes worse on hydrogenation. It is not amenable to upgrading by skeletal isomerisation, due to its cracking propensity and oligomerisation would result in a distillate range product, thereby reducing the motor-gasoline product and still leaving the low octane C_9-C_{10} paraffins to be dealt with. After hydrogenation it can be used as jet fuel component, but this also reduces the motor-gasoline production. It can therefore be said that there are numerous upgrading pathways for C_9-C_{10} naphtha, but it is a problematic cut to deal within the context of a motor-gasoline refinery of least complexity.

e) C_8 *naphtha*. This fraction is also traditionally upgraded by catalytic reforming and possibilities for its upgrading can be discussed along similar lines as that for the C_9-C_{10} naphtha. The ability to include C_8 naphtha in jet fuel, however, is limited by its flash point.

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[d] All references to refinery yield are expressed as a mass percentage of C_2 and heavier material in the syncrude.

f) *C_7 naphtha*. In syncrude, like in crude oil refining, this is the most difficult naphtha cut to upgrade.(10) Unlike C_8-C_{10} naphtha, it is poorly converted by catalytic reforming, unless non-acidic Pt/L-zeolite based technology is considered. It cannot be skeletally isomerised efficiently, due to cracking and its hydrogenated straight run octane number (RON<50) makes it a poor motor-gasoline component. High temperature processes, such as aromatisation and catalytic cracking (the latter route having been recently selected by Sasol),[e] can be used as effective refining pathways for C_7 naphtha. These technologies are expensive and considering that the C_7 naphtha constitutes only 7% of HTFT syncrude, it may be difficult to justify from an economic and complexity perspective just for refining the C_7 naphtha.

g) *C_6 naphtha*. Although this cut has a low straight run octane number, there are many ways to refine it to good quality motor-gasoline. The most obvious refining pathway is skeletal isomerisation. Another option is to refine it to aromatics.

h) *C_5 naphtha*. The straight run C_5 naphtha has an octane number of around 90-95 on account of its high olefin content (85%) and can be blended directly into motor-gasoline. The pentenes can also be skeletally isomerised and used as feed for etherification, as is the case at the Sasol Synfuels refineries where it is used for TAME production. More importantly, there is little octane penalty when the C_5 naphtha is hydroisomerised before it is blended into motor-gasoline, which has the advantage of not limiting the inclusion of other olefins into the fuel.

i) *C_4 hydrocarbons*. The C_4 hydrocarbon fraction of HTFT syncrude contains about 85% olefins. Olefin oligomerisation by a motor-gasoline selective technology, such as solid phosphoric acid based oligomerisation, is a natural choice. The remaining butanes can be directly blended into the motor-gasoline and their inclusion is only limited by the vapour pressure constraints placed on the final fuel. Other upgrading pathways that can be considered are aliphatic alkylation and etherification. However, these pathways are less attractive for HTFT syncrude due to the olefin to paraffin (85:15) imbalance, high degree of linearity (n-C_4:iso-$C_4 \approx 9:1$) and large volume (13% of HTFT syncrude).

j) *C_3 hydrocarbons*. The HTFT derived C_3 hydrocarbons have a propylene to propane ratio of 87:13 and constitutes about 15% of the syncrude. This makes it the most abundant carbon number in HTFT syncrude. In order to maximise motor-gasoline, the olefin-based transformations would typically be motor-gasoline selective olefin oligomerisation (SPA), or

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[e] Superflex™ Catalytic Cracker (SCC) technology of KBR, commissioned at Sasol Synfuels in 2007.

alkylation to produce mainly motor-gasoline range products. Propane is normally used for liquid petroleum gas (LPG), but may also be upgraded by an appropriate aromatisation technology to boost motor-gasoline production.

k) *C_2 hydrocarbons*. HTFT syncrude contains about 11% C_2 hydrocarbons and even more if the oxygenates (ethanol, acetaldehyde and acetic acid) are included. The ethylene to ethane ratio is 55:45. Ethylene is not generally considered for motor-gasoline production, but depending on the refinery location, it may not be possible to sell the ethylene as chemical. Some technologies are available for the conversion of ethylene into liquid products, although these technologies are not generally associated with fuels refining, for example hydration, olefin oligomerisation and aromatic alkylation. The ethane can be upgraded by thermal cracking, but this is an expensive technology. Alternatively it can be considered a fuel gas at the expense of reducing the yield of final products from the refinery.

l) *Aqueous phase oxygenates*. About 11% of the HTFT syncrude is on condensation dissolved in the water that was co-produced during HTFT synthesis. These oxygenates can partly be recovered by distillation and sold as chemicals, or it can be refined to fuels. One way of simplifying the aqueous product refining to motor-gasoline is to partially hydrogenate the carbonyls to alcohols and then dehydrating the alcohol-water mixture to olefins.(12) The olefins thus produced can then be refined with the other olefins in the refinery.

3.1.1. HTFT paraffinic motor-gasoline

It has been pointed out that the crux of meeting motor-gasoline specifications is ensuring that the paraffins in the motor-gasoline have a sufficiently high octane number, since the other compound classes are either octane neutral or high-octane compounds. Since the volume of paraffins is not limited, but determines the volume of other compounds that can be included, it is a logical place to start refinery design for maximum motor-gasoline. The easiest high-octane paraffin producing technologies are those that upgrade the C_4-C_6 naphtha.

The first design decision is to evaluate the value of installing a butane isomerisation unit. This may be considered for two reasons, namely a) to boost the octane of the straight run butanes that can be blended into the fuel up to its vapour pressure limit; and b) to produce iso-butane for aliphatic alkylation.

Although iso-butane (RON = 101.3; MON = 97.6) has a 7-8 point higher octane number than *n*-butane (RON = 93.8 ; MON = 89.6), the vapour pressure of iso-butane (RVP = 500 kPa) is also much higher than that of *n*-butane (RVP = 357 kPa). Since the volumetric inclusion of the C_4's are limited by the vapour pressure specification and vapour pressure of the base fuel, the volume of iso-butane to *n*-butane that can be included can be calculated (Equation 1).

$$\frac{V_{iso-C4}}{V_{n-C4}} = \frac{\left(RVP_{n-C4} - RVP_{fuel}\right)}{\left(RVP_{iso-C4} - RVP_{fuel}\right)} \qquad \text{... (1)}$$

Based on equation 1, it is possible to blend 40% less iso-butane than *n*-butane into the fuel. It is consequently not worthwhile to hydroisomerise the butanes for direct inclusion into the fuel.

The next design decision is to evaluate the value of installing an aliphatic alkylation unit in conjunction with butane hydroisomerisation. Aliphatic alkylation is not considered environmentally friendly, but is an effective way to improve the paraffinic octane. In general HF-based alkylation processes yield higher octane products(13) (RON=90-91 with propene and RON=94-95 with FT butenes), although H_2SO_4-based alkylation has a better technology fit with syncrude.

Alkylate production is limited by the butane availability in HTFT syncrude and different scenarios have been considered to maximise alkylate production (Table 2). The alkylate production can be considerably increased if some of the butenes are hydrogenated, especially if alkylation is performed with propylene, which is not a limiting feedstock. Additionally, even more C_4 hydrocarbons can be made available by selective hydrogenation and dehydration of the oxygenates in the aqueous product. In this way, up to 23% of the HTFT syncrude can be converted into alkylate.

Table 2. Maximum production of alkylate as mass percentage of the C_2 and heavier straight run HTFT syncrude by an HF-based aliphathic alkylation process in conjunction with butene hydrogenation and butane hydroisomerisation.

Conversion unit	Using only straight run butanes		Butene hydrogenation optimised		Aqueous product C_4's included	
	C_3-alky	C_4-alky	C_3-alky	C_4-alky	C_3-alky	C_4-alky
Butene hydrogenation	0	0	11.1	4.9	12	5.3
Butane isomerisation	1.6	1.6	12.7	6.5	13.6	6.9
Aliphatic alkylation	2.8	3.2	21.9	12.7	23.4	13.6

Another possibility that can be considered is the production of an alkylate equivalent product by butene oligomerisation. This can be accomplished in more than one way. The easiest method is to make use of the unique low temperature butene skeletal isomerisation pathway on solid phosphoric acid, which yields a product with a hydrogenated octane number of 86-88 from straight run HTFT butenes.(14) Another possibility is to include a butene skeletal isomerisation unit before the olefin oligomerisation process. This would enable the production of an alkylate equivalent with a hydrogenated octane number of around 96. These options are limited to the butene availability. In this way, when the C_4 oxygenates in the reaction water are also converted to olefins, up to 12% of the HTFT syncrude can be converted into alkylate.

Table 3. Hydroisomerisation of hydrogenated C_5-C_6 HTFT naphtha by different processing pathways showing typical composition and fuel quality values. (Cyclo-paraffin composition is not shown due to the low cyclo-paraffin content of Fischer-Tropsch syncrude).

Description	Syncrude		Once-through operation				Recycle operation	
	C_5-only	C_5-C_6	C_5-only	C_5-only	C_5-C_6	C_5-C_6	C_5-only	C_5-C_6
			Pt/Al_2O_3	Pt-MOR	Pt/Al_2O_3	Pt-MOR	Pt-MOR	Pt-MOR
% of HTFT syncrude	10.6	19.2	10.6	10.6	19.2	19.2	10.6	19.2
Typical C_5 composition								
n-pentane	79	79	29	37	29	37	3	3
2-methylbutane	21	21	71	63	71	63	97	97
Typical C_6 composition								
n-hexane		76			11	15		0
2-methylpentane		11			31	34		39
3-methylpentane		11			17	22		26
2,2-dimethylbutane		0			30	20		23
2,3-dimethylbutane		1			10	8		11
Typical fuel properties								
RON	68	54	84	81	81	77	91	87
MON	68	55	82	80	80	77	90	86
Density ($kg\cdot m^{-3}$)	630	645	627	627	641	642	625	640
RVP (kPa)	114	83	131	129	99	96	140	104

In crude oil refineries the mixed C_5-C_6 naphtha cut from the atmospheric distillation unit is known as light straight run (LSR) naphtha. These carbon fractions are often not separated and hydroisomerisation of the C_5-C_6 naphtha is performed in a single conversion unit. This needn't be the case. As discussed previously (Chapter VII) there are a variety of processes and process configurations available, with recycling of the unconverted material that can be considered. When C_5 naphtha is processed separately, recycling of the *n*-pentane is easy and can be accomplished by distillation. This separation becomes more involved when mixed C_5-C_6 naphtha is hydroisomerised, requiring multiple distillation columns or selective adsorption. On account of the slower rate of hydroisomerisation of hexanes compared to pentanes, units processing C_5-C_6 naphtha operate at the thermodynamic equilibrium of the C_5's, but not the C_6's.(15) Different scenarios have been considered for HTFT refining (Table 3). When C_5 hydroisomerisation is considered, the octane number of hydrogenated C_5 syncrude can be improved by more than 20 points using recycle operation, yielding an isomerate with octane numbers above 90. Although the isomerate quality that can be achieved with recycle operation using C_5-C_6 naphtha has a lower octane value (86-87), the octane gain exceeds 30 points and 19% of the HTFT syncrude can be converted to isomerate.

Based on the data presented in Tables 2 and 3, it can be said that there scope to convert up to 42% of the total C_2 and heavier HTFT syncrude to paraffinic motor-gasoline with octane numbers in the range of 85-95. This excludes additional conversion that may be possible from C_4-C_6 material generated by other conversion processes in the refinery.

3.1.2. HTFT aromatic motor-gasoline

The main source of high octane compounds in motor-gasoline is aromatics. In choosing an aromatics production technology, apart from the technology issues already covered (Chapter VII), there are three important aspects to consider from a motor-gasoline refinery development perspective:

a) *Feed*. Aromatics production has three functions in a refinery, namely to provide high-octane motor-gasoline, hydrogen production and as a sink for low octane or otherwise unwanted material. The latter aspect is quite important, since the technology can be selected in such a way that a refining pathway is created for the upgrading of material to improve motor-gasoline yield, or for the upgrading of material that could be detrimental to the quality of the motor-gasoline. In this respect metal promoted H-ZSM-5 based aromatisation technology is the best, since it is capable of converting material in the C_3-C_{10} range. Conversely, platinum promoted non-acidic L-zeolite based aromatisation is by far the most efficient aromatisation process, having a high yield of liquid products and hydrogen, but it is restricted to processing feed in the C_6-C_{10} range (preferably C_6-C_8 naphtha). Ironically, one of the key crude oil refining units, namely catalytic reforming (chlorided Pt/alumina), is the least flexible in terms of feed, being efficient only at converting C_8-C_{10} naphtha, although low conversion of C_6-C_7 naphtha is possible.[f]

b) *Yield structure*. The yield structure of the different aromatisation technologies has been discussed previously (Chapter VII). Of special importance is the co-production of paraffins in the same boiling range as the aromatics, typically C_7 and heavier aliphatics. These hydrocarbons have low octane numbers and are difficult to separate from the aromatics. The octane number of the aromatic motor-gasoline is adversely affected by the presence of these paraffins and such co-production should be minimised. This is a drawback associated mainly with chlorided Pt/alumina based catalytic reforming, which produces the lowest octane aromatic motor-gasoline (RON = 95-100).[g] The octane number of the reformate is controlled by temperature and can be increased by increasing the temperature, but this results in a lower liquid yield.

A low liquid yield is the main drawback of ZSM-5 based aromatisation, which necessitates recycling of the C_3-C_4 paraffins to reduce the overall motor-gasoline yield loss. The octane number that can be obtained from such a process is nevertheless higher (RON = 100-105). An even higher octane number can be achieved with L-zeolite based aromatisation (RON = 105-110), but this brings us to another important selectivity issue, the co-production of benzene.

c) *Benzene*. The benzene content of motor-gasoline is limited to less than 1% by volume in most countries, because it is a known human carcinogen. Although benzene selectivity is low in chlorided Pt/alumina catalytic reforming and ZSM-5 based technologies, it is co-produced, especially if benzene precursors are present in the feed. Conversely, in platinum promoted non-acid L-zeolite based technology, benzene selectivity from C_6 naphtha is very high (>90%). In any event, benzene co-production may exceed the maximum allowable limit in motor-gasoline, in which case something must be done to reduce the

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[f] Conversion of heavier than C_{10} hydrocarbons is possible with all three aromatisation technologies, but falls outside the design intent of such technologies.

[g] Due to the low *N*+2*A* content of Fischer-Tropsch syncrude, it requires quite severe operation to maintain a RON 95 product. Although it has been shown that with heavier feed materials higher octane numbers can be obtained, such figures cannot be used for conceptual design purposes.

benzene content.(16) In a Fischer-Tropsch refinery, where olefins are abundant, the alkylation of benzene with olefins is an obvious possibility.

It is therefore possible to convert any material in the C_3-C_{10} range to aromatic motor-gasoline with an octane number above RON 95 by an appropriate selection of aromatisation technology.

3.1.3. HTFT olefinic motor-gasoline

Olefinic motor-gasoline is a blending component that is considered mainly due to the inherently high olefin content of straight run HTFT naphtha (Table 1). All olefin oligomerisation technologies are able to produce an olefinic motor-gasoline, but not all of these technologies produce a good olefinic motor-gasoline. Only in exceptional cases can the olefinic motor-gasoline be hydrogenated without much octane loss. Nevertheless, olefin oligomerisation is a convenient way to increase the average carbon number of a feed material and it enables the conversion of C_2-C_4 olefins to motor-gasoline. In this respect SPA based oligomerisation is by far the best oligomerisation technology for motor-gasoline production from straight run syncrude.

3.1.4. HTFT oxygenated motor-gasoline

There are three natural ways in which the oxygenate content of the motor-gasoline can be increased, apart from importing oxygenates:

a) *Alcohol recovery from syncrude*. The aqueous product from HTFT synthesis contains dissolved ethanol and iso-propanol that can be recovered for use as fuel alcohols. These alcohols constitute 3-4% of the C_2 and heavier syncrude fraction. It should be noted though, that iso-propanol is less commonly used as fuel alcohol. Production of fuel alcohols can be increased by selective hydrogenation of acetaldehyde and acetone to their corresponding alcohols. This increases the overall yield of ethanol and iso-propanol to 6% of the C_2 and heavier syncrude fraction.

b) *Hydration of syncrude olefins*. The oxygenate content of the motor-gasoline can be further increased by hydration of ethylene to ethanol or even propylene to iso-propanol. These technologies are not found in fuels refineries. Ethylene hydration is especially interesting for fuel refineries far from markets where ethylene can be sold as a chemical. It is also a convenient way of moving a normally gaseous olefin into motor-gasoline.

c) *Etherification.* Etherification of branched olefins with an alcohol, or even etherification of alcohols, are two ways in which fuel ethers can be prepared. The alcohols may be imported, recovered from the HTFT aqueous product or produced by hydration. Some branched olefins are present in the syncrude, but not all are active for etherification, since the C=C double bond is not always on the tertiary carbon atom. Furthermore, not all alcohols produce high-octane ethers and care should be taken in the selection of etherification products. For example, di-*sec*-butylether (1-methyl-propoxy-2-butane) has blending octane number below 100.(17)

It is possible to produce the necessary oxygenated motor-gasoline components by separation and/or synthesis from HTFT syncrude. The preferred oxygenates will depend on legislation and currently ethanol is favoured as fuel oxygenate.

3.2. HTFT motor-gasoline refinery flowschemes

3.2.1. Flowscheme 1

The first refinery flowscheme that was developed, focused on the upgrading of C_4-C_6 naphtha to high-octane paraffinic motor-gasoline (Figure 3). Based on environmental considerations,

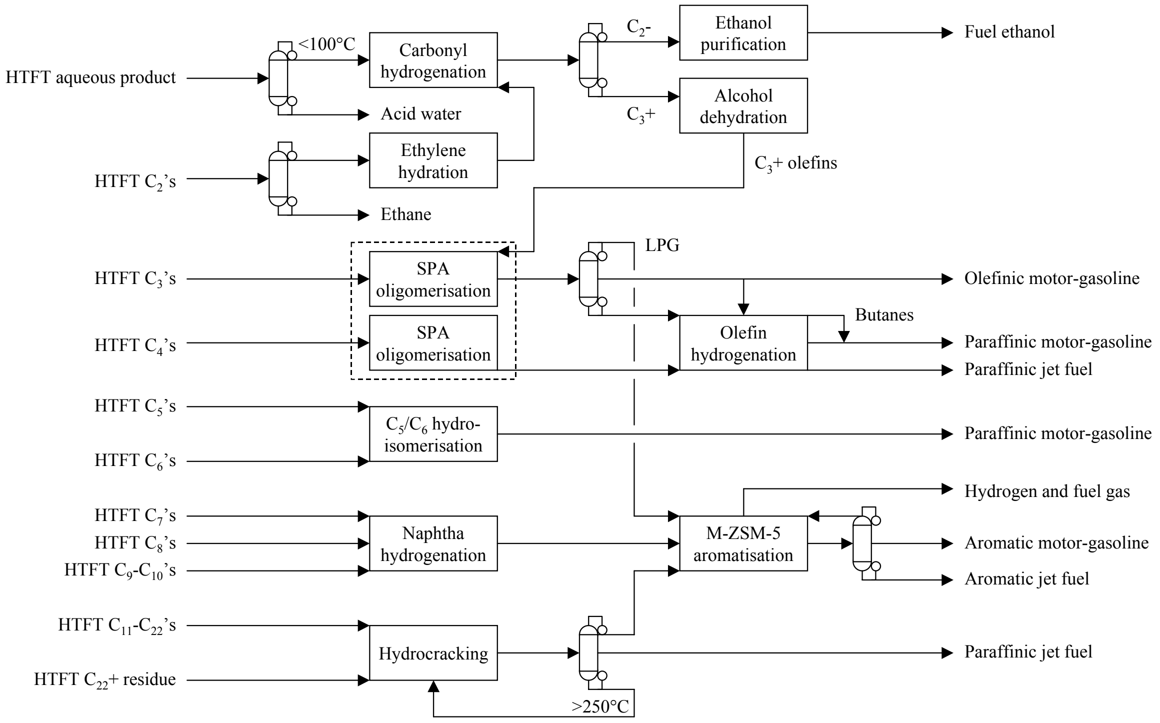

Figure 3. HTFT motor-gasoline refinery, flowscheme 1.

aliphatic alkylation was not considered and the C_4 naphtha was converted to paraffinic motor-gasoline by direct blending of the butanes, while the butenes were oligomerised in a process based on a SPA catalyst and the product was hydrogenated. The C_5-C_6 naphtha was hydroisomerised with full recycle, in a typical commercial total isomerisation process (TIP) configuration. These conversion processes converted 30% of the refinery feed to an 86 octane paraffinic motor-gasoline.

The refining of the Fischer-Tropsch aqueous product was integrated with the refining of the lighter than C_4 compounds. Ethanol was recovered from the aqueous product and combined with the ethanol produced by hydration of ethylene. The combined ethanol-water mixture was then further refined to produce fuel ethanol. Ethanol was blended as oxygenated motor-gasoline component. The C_3 and heavier oxygenates in the aqueous product were selectively hydrogenated to alcohols and dehydrated to olefins.(12) These olefins were combined with the C_3 hydrocarbons and oligomerised in a SPA-based process. The product was mainly retained as an olefinic motor-gasoline component.

The aromatic motor-gasoline was produced by ZSM-5 based aromatisation of a mixture of the residual light paraffins and C_7-C_{10} naphtha. Some of this material originated from hydrocracking, since the heavier syncrude fraction was hydroisomerised and hydrocracked at high severity to produce mainly a C_{16} and lighter product. A ZSM-5 based aromatisation process was selected specifically to reduce the yield loss associated with high severity hydrocracking, since such a process is able to convert the LPG fraction to aromatics. The aromatic product from aromatisation was fractionated in such a way that the kerosene range material could be blended to produce jet A-1, with the rest of the aromatics being used as high-octane motor-gasoline.

The yield structure of the refinery is given in Table 4.[h] The refinery yield of liquid fuels was 92%, while the motor-gasoline yield was 62%. The design was successful in terms of the yield structure, but the motor-gasoline did not meet Euro-4 specifications (Table 5). The RON was too low (93 versus 95 required), benzene exceeded the specification (1.5% versus 1% required) and the motor-gasoline density was too low (718 $kg\cdot m^{-3}$ versus 720-775 $kg\cdot m^{-3}$ required). The low density is understandable, since more than a third of the motor-gasoline was C_4-C_6 material (35% of the motor-gasoline by mass and 40% by volume), which also helped to boost the volumetric yield of the refinery. Liquid fuels production was about 94 000 bpd.

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[h] Unrecovered organics are mainly carboxylic acids that are present in the aqueous effluent (acid water).

Table 4. Yield structure of the HTFT motor-gasoline refinery shown in Figure 3 having a liquid fuel yield of 92% (mass) and a motor-gasoline yield of 60% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	309090	430	64951	69.0
Excess fuel ethanol	49391	62	9390	10.0
Jet fuel	100817	130	19639	20.9
Diesel fuel	0	0	0	0.0
LPG	647	1	177	0.2
Other products				
Fuel gas	38027			
Unrecovered organics	15801			
Hydrogen	-3461			
Water	-10313			
Σ	500000	624	94157	100

Looking at Table 5, it is immediately apparent that there is scope for aromatic and oxygenated gasoline addition to boost the octane number.

Table 5. Motor-gasoline quality from the HTFT motor-gasoline refinery shown in Figure 3.

Fuel properties	Refinery	Euro-4	
RON	93	95	Min
MON	87	85	Min
Vapour pressure (kPa)	59	60	Max
Density ($kg \cdot m^{-3}$)	718	720-775	Range
Olefins (vol %)	18.0	18	Max
Aromatics (vol %)	18.4	35	Max
Oxygenates (vol %)	5.0	15	Max
Benzene (vol %)	1.5	1	Max
Ethanol (vol %)	5.0	5	Max

Further aromatics production from syncrude is limited to re-routing some of the C_5-C_6 naphtha to the aromatisation unit, or aromatising some of the already refined product, such as olefin oligomers and/or jet A-1. The latter would not only result in an overall yield loss, but also make little sense from an economic perspective. Furthermore, the benzene content of the motor-gasoline is already an issue and increasing the aromatics production would make this worse, since the flowscheme (Figure 3) does not make provision for benzene mitigation. However, a decrease in the benzene content of the motor-gasoline can be accomplished by modifying the flowscheme to extract the benzene as chemical, hydrogenate the benzene to cyclohexane or to alkylate the benzene with an olefin.

Additional fuel ethanol is available to increase the octane number, but adding it as oxygenated fuel component can only be considered in countries that have higher vapour pressure and ethanol specifications than Euro-4. Some of the ethanol may be used for etherification to produce ETBE or TAEE, which would overcome these shortcomings, but this would require a modification to the flowscheme.

3.2.2. Flowscheme 2

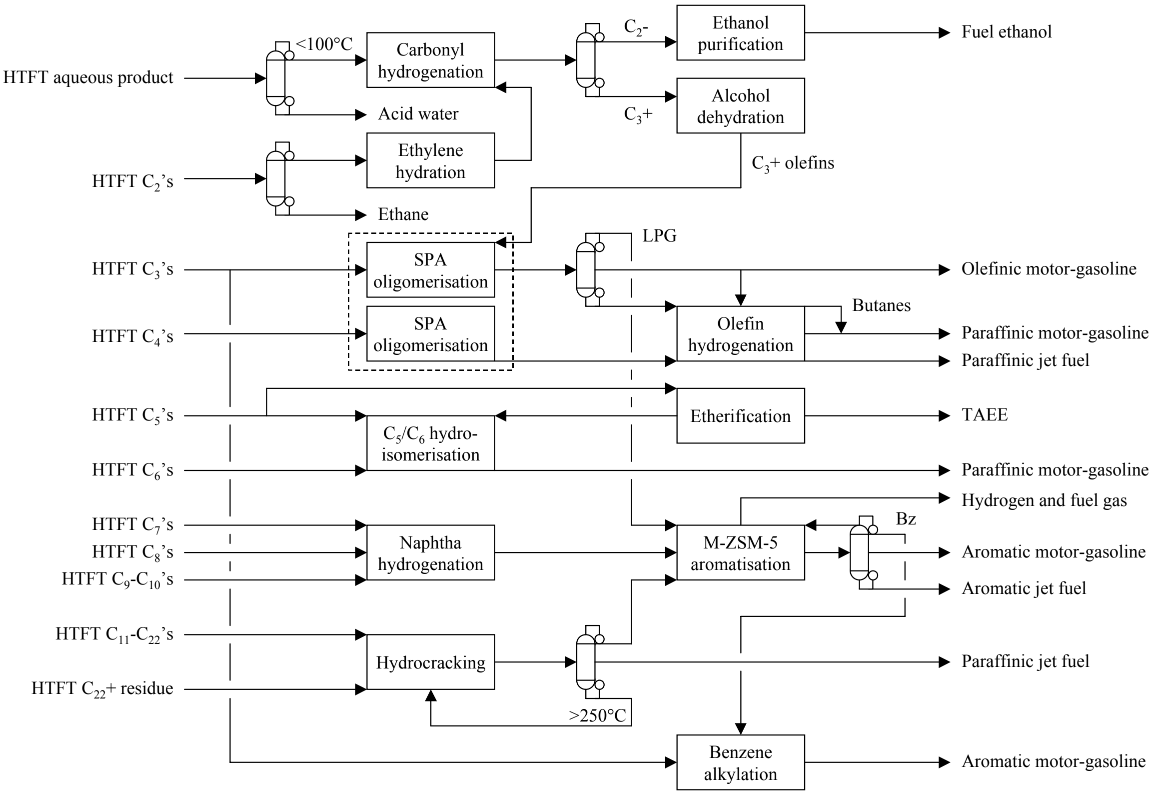

Figure 4. HTFT motor-gasoline refinery, flowscheme 2.

Incremental improvements to the previous flowscheme (Figure 3) in order to meet the Euro-4 specifications, can result in a rapid proliferation of units. It is possible to address the deficient motor-gasoline octane, benzene and density specifications by adding an etherification unit and an aromatic alkylation unit as previously suggested (Figure 4). These changes increase the refinery complexity and reduce the yields, but ensure that the motor-gasoline and jet fuel meet specifications. Although a benzene alkylation unit has been added to the flowscheme as a separate unit, there is a more efficient way of doing this alkylation. It has been shown that it is possible to alkylate the benzene in the SPA based oligomerisation process by directly co-feeding the benzene with the propylene rich feed.(18)

Different scenarios have been investigated to understand the trade-offs involved in meeting the motor-gasoline specifications:

a) The aromatics production was increased by routing 20% of the C_6 naphtha to the ZSM-5 based aromatisation unit. Oxygenated gasoline production was increased by routing the olefinic C_5 naphtha to the etherification unit, where it was converted to tertiary amyl ethyl ether (TAEE). This reduced the light naphtha inclusion, thereby solving the density issue and lowering the RVP, while the additional aromatics and fuel ethers boosted the octane of the motor-gasoline. The benzene specification was addressed by alkylation with propylene to produce cumene, which is also a high-octane aromatic that could be blended into the motor-gasoline. The yield structure (Table 6) did not change much, although the overall refinery yield decreased to 93 000 bpd, which is a little less compared to the 94 000 bpd of the previous design (Table 4).

b) It was found that the C_6 naphtha could be substituted by 6% of the motor-gasoline from C_3 oligomerisation. This fraction would otherwise have to be hydrogenated to meet the olefin specification. Re-routing this material removed RON 50 paraffins from the fuel pool and converted them to high-octane aromatics. The other aspects of the refinery design being the same as in scenario (a). The yield structure (Table 7) changed only marginally compared to the previous scenario, with the refinery yield increasing to 93 500 bpd.

c) Surprisingly it was found that when 60% of the C_6 naphtha is routed to the ZSM-5 based aromatisation unit, sufficient octane was generated by the aromatic motor-gasoline to meet the octane requirements. This has the advantage of eliminating the etherification unit. This implies that if the benzene alkylation is performed in the C_3 SPA-based oligomerisation unit, the present flowscheme (Figure 4) can again be simplified to flowscheme 1 (Figure 3)! The effect of this on the yield structure (Table 8) was to reduce the overall yield to 92 000 bpd on account of the higher density of the increased aromatic motor-gasoline.

Table 6. Yield structure of the HTFT motor-gasoline refinery shown in Figure 4 with 20% C_6 *naphtha routed to aromatisation. It has a liquid fuel yield of 92% (mass) and a motor-gasoline yield of 62% (mass).*

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	311895	428	64649	69.5
Excess fuel ethanol	43806	55	8328	8.9
Jet fuel	101505	131	19779	21.3
Diesel fuel	0	0	0	0.0
LPG	1169	2	319	0.3
Other products				
Fuel gas	38809			
Unrecovered organics	15991			
Hydrogen	-2862			
Water	-10313			
Σ	500000	617	93075	100

Table 7. Yield structure of the HTFT motor-gasoline refinery shown in Figure 4 with 6% of the motor-gasoline from C_3 *oligomerisation routed to aromatisation. It has a liquid fuel yield of 92% (mass) and a motor-gasoline yield of 63% (mass).*

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	312927	432	65179	69.7
Excess fuel ethanol	43806	55	8328	8.9
Jet fuel	101199	131	19718	21.1
Diesel fuel	0	0	0	0.0
LPG	1169	2	319	0.3
Other products				
Fuel gas	38300			
Unrecovered organics	15983			
Hydrogen	-3072			
Water	-10313			
Σ	500000	620	93544	100

Table 8. Yield structure of the HTFT motor-gasoline refinery shown in Figure 4 with 60% C_6 *naphtha routed to aromatisation and no etherification (TAEE) unit. It has a liquid fuel yield of 91% (mass) and a motor-gasoline yield of 60% (mass).*

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	301553	412	62141	67.4
Excess fuel ethanol	50100	63	9525	10.3
Jet fuel	103435	133	20148	21.9
Diesel fuel	0	0	0	0.0
LPG	1274	2	348	0.4
Other products				
Fuel gas	40455			
Unrecovered organics	16017			
Hydrogen	-2522			
Water	-10313			
Σ	500000	611	92162	100

Table 9. Motor-gasoline quality from scenarios (a) to (c) of the HTFT motor-gasoline refinery shown in Figure 4.

Fuel properties	Different refinery configurations			Euro-4	
	(a)	(b)	(c)		
RON	95	95	95	95	Min
MON	88	88	88	85	Min
Vapour pressure (kPa)	51	52	56	60	Max
Density ($kg \cdot m^{-3}$)	728	725	733	720-775	Range
Olefins (vol %)	18.0	17.7	17.9	18	Max
Aromatics (vol %)	20.6	19.3	24.8	35	Max
Oxygenates (vol %)	9.2	9.1	5.0	15	Max
Benzene (vol %)	0.0	0.0	0.0	1	Max
Ethanol (vol %)	5.0	5.0	5.0	5	Max
TAEE (vol %)	4.2	4.1	0.0	15	Max

Although these are all workable designs, they have two important shortcomings, namely a significant hydrogen deficit and a close approach to the fuel specifications on more than one account (Table 9). The hydrogen deficit implies that hydrogen has to be taken from the Fischer-Tropsch gas loop, which will effectively reduce the production of syncrude. This is less of a concern than a similar situation in a crude oil refinery, but nevertheless a shortcoming. When fuel specifications are just being met after considerable tweaking of the refinery design, the refinery is very inflexible in dealing with upsets. This is not a conceptual design problem, but will become an issue if such a design is to be built. With RON, olefin content and ethanol content being close to specification, there is little room to solve problems in the blending operation.[i]

3.2.3. Flowscheme 3

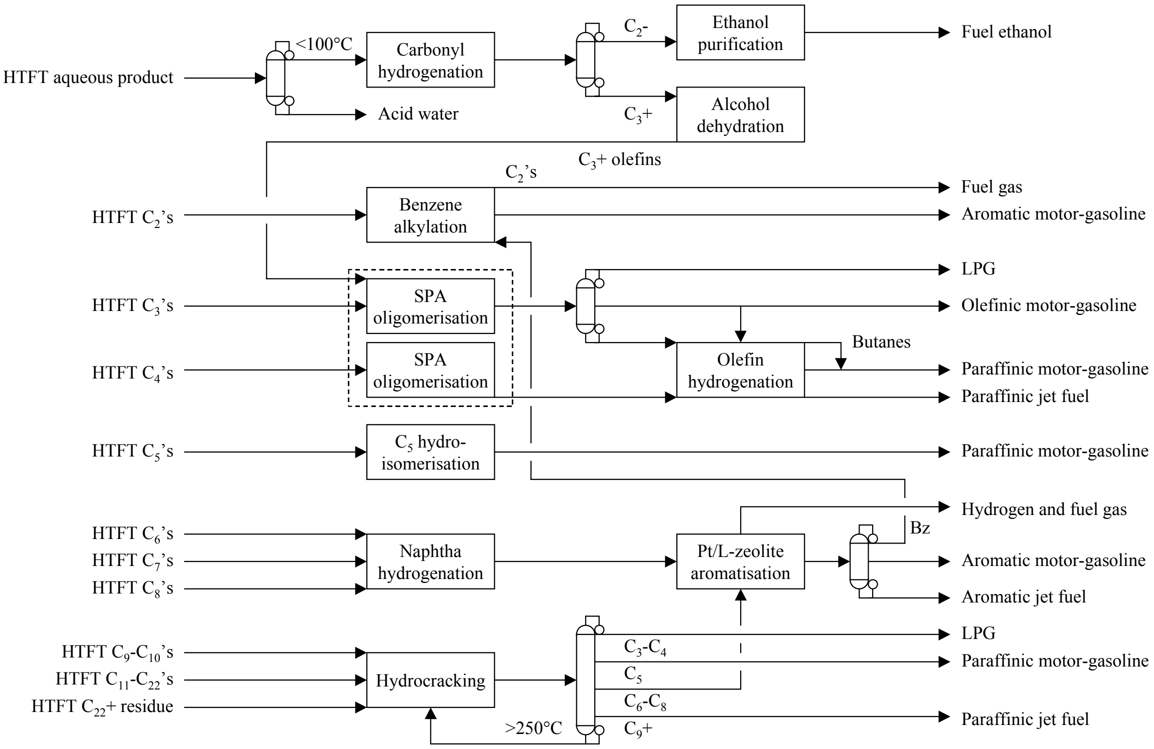

Figure 5. HTFT motor-gasoline refinery, flowscheme 3.

To address the issue of hydrogen availability and tightness in meeting motor-gasoline specifications, the refinery design should be approached differently. Hydrogen availability and octane limitations can be resolved simultaneously by producing more aromatics.[j] By changing the aromatisation technology to an L-zeolite based process, maximum aromatics

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[i] A close approach to fuel specifications can be viewed in a positive light too, since it implies that there is little refinery give-away. However, since this is a conceptual refinery design, it will be viewed in a negative light.

[j] It is for exactly this reason that a catalytic reformer is the central conversion unit (and often the limiting conversion unit) in a crude oil refinery.

and hydrogen selectivity can be achieved (Figure 5). Since the need for aromatic alkylation has already been shown, the high benzene selectivity of the L-zeolite based process is not a new concern. As a matter of fact, this can be put to good advantage to eliminate the ethylene-splitter and ethylene hydration unit, by selecting ethylene as alkylating olefin for benzene alkylation. The feed to the L-zeolite based aromatisation has been limited to C_6-C_8 naphtha. One implication of restricting the feed to C_6-C_8 naphtha is that there is flexibility left to route heavier naphtha to this unit, should it be needed.[k] Another implication is that the C_5/C_6 hydroisomerisation unit in the previous flowschemes (Figures 3 and 4) becomes just a C_5 hydroisomerisation unit. This simplifies the hydroisomerisation unit design and efficiency, because recycle operation is made easier. The rest of the conversion units are similar to that in flowschemes 1 and 2, although the feed routing to the hydrocracker now includes C_9-C_{10} naphtha.

Table 10. Yield structure of the HTFT motor-gasoline refinery shown in Figure 5 having a liquid fuel yield of 89% (mass) and a motor-gasoline yield of 53% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	267078	364	54957	60.4
Excess fuel ethanol	17624	22	3351	3.7
Jet fuel	140447	181	27363	30.1
Diesel fuel	0	0	0	0.0
LPG	18592	35	5256	5.8
Other products				
Fuel gas	32466			
Unrecovered organics	14894			
Hydrogen	-379			
Water	9277			
Σ	500000	602	90927	100

The yield structure (Table 10) shows liquid fuel production of 91 000 bpd, which is equivalent to an overall refinery yield of 89%. Compared to the previous motor-gasoline

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[k] In practise this would imply that the necessary transfer lines and spare capacity on the unit should be included in the design. Conceptually it implies that there is a degree of freedom in the design that is not being used.

flowschemes there is a significant increase in LPG and jet fuel production. The increase in LPG production was expected, since more feed material is hydrocracked and the L-zeolite based aromatisation technology is not capable of converting the LPG into aromatics. The increase in jet fuel production was also expected, since the hydrocraker, which doubles as a kerosene hydroisomerisation unit, is also one an important source of jet fuel. By routing the C_9-C_{10} naphtha to the hydrocracker, production of both kerosene and LPG range material is increased at the expense of naphtha production. Although this is contrary to the aim of maximising motor-gasoline, the refinery complexity was reduced and some flexibility was gained. The fuel quality has been improved to such an extent that the motor-gasoline meets Euro-4 specifications before ethanol addition (Table 11). It indicated that the basic refinery design was decoupled from the politically sensitive oxygenate mandate. The ability to use blending to vary the relationship between octane number, oxygenate content and olefin content, is a measure of the flexibility of the design. The design is also flexible with respect to the jet fuel and the motor-gasoline blending operation, which can be further be deconstrained by blending more of the C_3 SPA derived motor-gasoline into jet fuel (not shown).

Table 11. Motor-gasoline quality from the HTFT motor-gasoline refinery shown in Figure 5 showing (a) the blend without oxygenates, (b) the blend with the addition of ethanol and less C_4's, and (c) the blend with addition of ethanol and maximum olefins.

Fuel properties	Refinery operating scenarios			Euro-4	
	(a)	(b)	(c)		
RON	95	96	98	95	Min
MON	89	89	90	85	Min
Vapour pressure (kPa)	60	60	60	60	Max
Density ($kg \cdot m^{-3}$)	734	738	738	720-775	Range
Olefins (vol %)	16.3	15.6	18.0	18	Max
Aromatics (vol %)	27.2	26.1	26.0	35	Max
Oxygenates (vol %)	0.0	5.0	5.0	15	Max
Benzene (vol %)	0.3	0.3	0.3	1	Max
Ethanol (vol %)	0.0	5.0	5.0	5	Max

Despite the lower refinery yield, the refinery is less reliant on imported hydrogen and the basic refinery design is robust.

3.3. LTFT motor-gasoline refinery development

The carbon number distribution of LTFT syncrude (Figure 2) is far from optimal for motor-gasoline production. Most of the syncrude is heavier boiling than naphtha, which implies that residue upgrading will be an important aspect of the refinery design. Although the main aim of residue upgrading will be to change the carbon number distribution to increase the quantity of naphtha, the technology selection may be driven by quality considerations. From the preceding discussion on HTFT motor-gasoline refinery development, the production of high-octane paraffinic motor-gasoline components and aromatic motor-gasoline emerged as key aspects of a successful refinery design. The refining of the various carbon number fractions will be discussed, as was discussed for HTFT syncrude:

a) *Residue* C_{22}+. The residue (>360°C boiling) fraction contains 52% of the LTFT syncrude, making it the largest fraction to refine. Although hydrocracking and thermal cracking have a better technology fit with LTFT syncrude (Chapter VII), catalytic cracking is quite efficient at cracking Fischer-Tropsch waxes. The reason for considering catalytic cracking in this specific instance, is related to the nature of its products in relation to the aim of the refinery, namely motor-gasoline production. Catalytic cracking produces a product that is rich in iso-olefinic material, which has significant synthetic value for motor-gasoline production. Furthermore, the product from catalytic cracking of wax consists mostly of products in the C_3-C_{11} range.(19) Although thermal cracking can also be used to produce olefins, the product from thermal cracking is rich in linear α-olefins, which are less desirable for motor-gasoline production than the iso-olefins produced by catalytic cracking. Hydrocracking yields the least desirable product for further refining to motor-gasoline, since it is mainly paraffinic.

b) C_{15}-C_{22} *distillate*. The density of the distillate range material from LTFT syncrude is around 780 $kg \cdot m^{-3}$, which is well below the minimum diesel fuel density specification. The low density of LTFT distillate is due to its low aromatics content (<1%). Although this makes it suitable for special uses, such as indoor heating and lighting, refining it to meet diesel fuel specifications presents a challenge. Since the aim of the refinery design is to maximise motor-gasoline production and not to produce diesel fuel, this cut can rather be converted to naphtha range material by catalytic cracking.

c) C_{11}-C_{14} *kerosene*. The straight run LTFT kerosene will not meet the freezing point specification of jet fuel on account of its significant *n*-paraffin content. This shortcoming can be addressed by mild hydroisomerisation. Alternatively this material can also be converted by catalytic cracking to lighter material for refining to motor-gasoline. When pushing for maximum motor-gasoline production, the latter course of action is probably the best, although it may be less efficient than refining it to jet fuel.

d) *C_9-C_{10} naphtha*. The discussion on the refining of this HTFT syncrude cut is equally applicable to LTFT syncrude. Although it is already in the motor-gasoline boiling range, it has a low octane value and in the absence of a catalytic reformer, its refining pathway is less clear. It can be used as a jet fuel component, at the loss of motor-gasoline, or it can be co-processed with the heavier fractions in a catalytic cracker to make it more amenable to motor-gasoline refining.

e) *C_2-C_8 material*. Less than 20% of the LTFT syncrude is contained in this fraction, which is very olefinic (>60% olefins), unlike the heavier material. It can be upgraded to motor-gasoline in a similar fashion as discussed for HTFT, but ethylene refining is less of a problem, since ethylene constitutes only 1% of the LTFT syncrude.

f) *Aqueous phase oxygenates*. About 4-5% of the LTFT syncrude is dissolved in the water produced during Fischer-Tropsch synthesis. Methanol and ethanol are the main products and can be recovered by the appropriate separation processes. However, it should be noted that no aqueous phase oxygenates are recovered in the current commercial LTFT refinery designs, since it is considered uneconomical.

3.3.1. Catalytic cracking of LTFT wax

The selection of the cracking technology for the upgrading the LTFT residue fraction is central to the success of the refinery design when motor-gasoline has to be maximised. By selecting a catalytic cracker for the conversion of the bulk of the syncrude, the feedstock that has to be refined to motor-gasoline loses much of its Fischer-Tropsch character. However, it would be wrong to say that the yield structure from fluid catalytic cracking of wax is similar to that from crude oil FCC. The yield of motor-gasoline and gas is substantial (Table 12)(19)(20) and the motor-gasoline contains less aromatics than the product from the FCC of crude oil. As a matter of fact, the FCC derived naphtha from LTFT syncrude resembles HTFT syncrude, although there are no oxygenates and the hydrocarbons are more branched. One would therefore expect that a similar refining strategy could be followed as was devised for the development of an HTFT motor-gasoline refinery.

Table 12. Yield structure of fluid catalytic cracking (FCC) of wax as determined at 90% conversion on a commercial equilibrium catalyst (Ecat) at 525°C and 4 s residence time in a microriser reactor. This is compared to a typical yield structure from FCC of crude oil.

Products	Selectivity to cracking products (mass %)			
	FCC of wax. Ref.(19)		FCC of crude oil. Ref.(20)	
Dry gas (H_2, CH_4, C_2's)	0.9		3.42	
propylene	6.0		3.9	
propane	0.6		1.1	
n-butenes	3.5		4.38	
iso-butene	4.2		1.82	
butanes	0.5		2.48	
C_5-C_{11} naphtha	83.9		47.6	
- *n*-olefins		19.3		23.2
- iso-olefins		42.8		
- *n*-paraffins		0.4		7.7
- iso-paraffins		14.3		
- cyclo-olefins		4.2		1.1
- cyclo-paraffins		0.4		
- aromatics		2.5		15.6
Distillate (LCO)	0.0		16.3	
Residue (HCO)	0.0		14.6	
Coke	0.4 ‡		4.4	

‡ Reported as 2.6%, but for mass balance closure it must be 0.4%. The latter number makes more sense, since it is known that FT feed is non-coking.

3.3.2. Hydrocracking of LTFT wax

When hydrocracking technology is used to upgrade the residue, as is being done commercially, the distillate production is maximised, not the naphtha production. By increasing the severity, more naphtha and gas can be produced, but it is paraffinic. The C_4-C_6 naphtha can be upgraded as naphtha, but to counteract the high vapour pressure of this high-octane motor-gasoline, some heavier material is also needed. This presents a problem, because the LTFT syncrude contains less than 1% butenes, which are an important feed material for heavier high-octane motor-gasoline production.

Aromatic motor-gasoline can be produced to counteract the high vapour pressure of the C_4-C_6 motor-gasoline, but the inclusion of aromatics is limited by the fuel specifications. The type of aromatisation technology that can be used is also somewhat dependent on the selection of hydrocracking for residue upgrading. When a platinum promoted non-acidic L-zeolite based technology is selected, the feed is limited to the C_6 and heavier naphtha. However, inclusion of the C_6 naphtha in the feed not only removes material from the C_4-C_6 motor-gasoline, but also results in a high benzene production. In an HTFT refinery benzene production is not a problem, since it can be alkylated with short chain olefins, but in a hydrocracker based LTFT refinery the availability of such olefins is limited. The volume of benzene that can be alkylated is consequently also limited. Selection of a ZSM-5 based aromatisation technology is better suited to a hydrocracker based LTFT refinery, since the LPG fraction can be converted to aromatics. Nevertheless, the volume of on-specification motor-gasoline that can be produced in this way is rather limited and such a design is better suited to jet fuel production.

3.4. LTFT motor-gasoline refinery flowschemes

3.4.1. Flowscheme 4

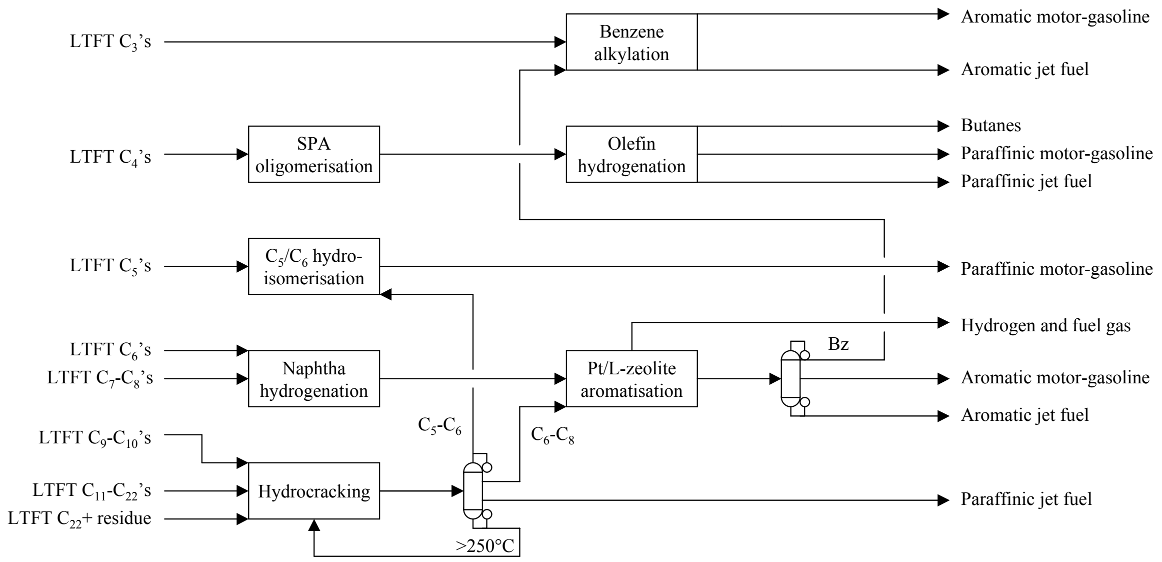

Figure 6. LTFT motor-gasoline refinery, flowscheme 4.

The aim with this refinery design was to explore to what extent hydrocracking can be used as residue upgrading technology for an LTFT motor-gasoline refinery. The selection is based on the good technology fit with syncrude, despite the arguments already raised against its applicability to motor-gasoline production. This train of thought, namely to select the technology with the best fit to Fischer-Tropsch syncrude, was continued with the selection of the aromatisation technology. A platinum promoted non-acidic L-zeolite based process is employed. The resulting refinery design is shown in Figure 6. The flowscheme does not include recovery of the C_2 hydrocarbons and the oxygenates dissolved in the aqueous product. This is in line with the practise at current commercial LTFT facilities such as Shell's Bintulu plant in Malaysia and Sasol's Oryx facility in Qatar.

All C_9 and heavier material is hydrocracked to material lighter boiling than 250°C by operating the hydrocracker in kerosene-mode. The C_6-C_8 product from hydrocracking is combined with the hydrotreated C_6-C_8 LTFT syncrude fraction and aromatised. The C_5-C_6 product from hydrocracking is combined with the C_5 LTFT syncrude fraction and hydroisomerised. It will be noted that C_6 hydrocarbons from the hydrocracker are only partly routed to the aromatisation unit. The split of C_6 material between aromatisation and hydroisomerisation is determined by the benzene processing capability of the refinery. The benzene is alkylated with propylene to produce cumene, typically on a SPA catalyst. Since the amount of propylene in the LTFT syncrude is limited, benzene alkylation capacity is constrained by olefin availability. Although it is in principle possible to use butene as alkylating olefin too, it is not only less efficient, but the butenes are also needed for the production of heavier high-octane non-aromatic motor-gasoline.

The refinery design (Figure 6) resulted in a low motor-gasoline yield (Table 13) and significant production of LPG and jet fuel. The quality of the motor-gasoline was borderline with respect to some fuel specifications (Table 14), while the jet fuel failed to meet the density specification for Jet A-1. However, the jet fuel could easily be upgraded to either Jet A-1 or even BUFF (flash point specification of 60°C) by routing more heavy aromatics to the jet fuel. Some benefits of L-zeolite aromatisation could be seen, such as the high octane number of the motor-gasoline and the small refinery hydrogen requirement. Surprisingly, the design showed that an L-zeolite based aromatisation process could be combined with hydrocracking in an LTFT refinery, despite expectations to the contrary.

Table 13. Yield structure of the LTFT motor-gasoline refinery shown in Figure 6 using L-zeolite based aromatisation. It has a liquid fuel yield of 92% (mass), a motor-gasoline yield of 28% (mass) and a jet fuel yield of 52% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	140157	189	28585	29.7
Jet fuel	261121	340	51290	53.2
Diesel fuel	0	0	0	0.0
LPG	59403	109	16484	17.1
Other products				
Fuel gas	16006			
Unrecovered organics	22396			
Hydrogen	-573			
Water	1490			
Σ	500000	638	96359	100

Table 14. Motor-gasoline and jet fuel quality from the LTFT motor-gasoline refinery shown in Figure 6.

Fuel properties	Refinery	Fuel specification	
Motor-gasoline		*Euro-4*	
RON	98	95	Min
MON	92	85	Min
Vapour pressure (kPa)	61	60	Max
Density ($kg \cdot m^{-3}$)	740	720-775	Range
Olefins (vol %)	0.5	18	Max
Aromatics (vol %)	35.0	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.7	1	Max
Jet fuel		*Jet A-1*	
Density ($kg \cdot m^{-3}$)	768	775-840	Range
Aromatics (vol %)	12.1	8-25	Range
Flash point (°C)	57	38	Min
Vapour pressure (kPa)	0.5	-	

3.4.2. Flowscheme 5

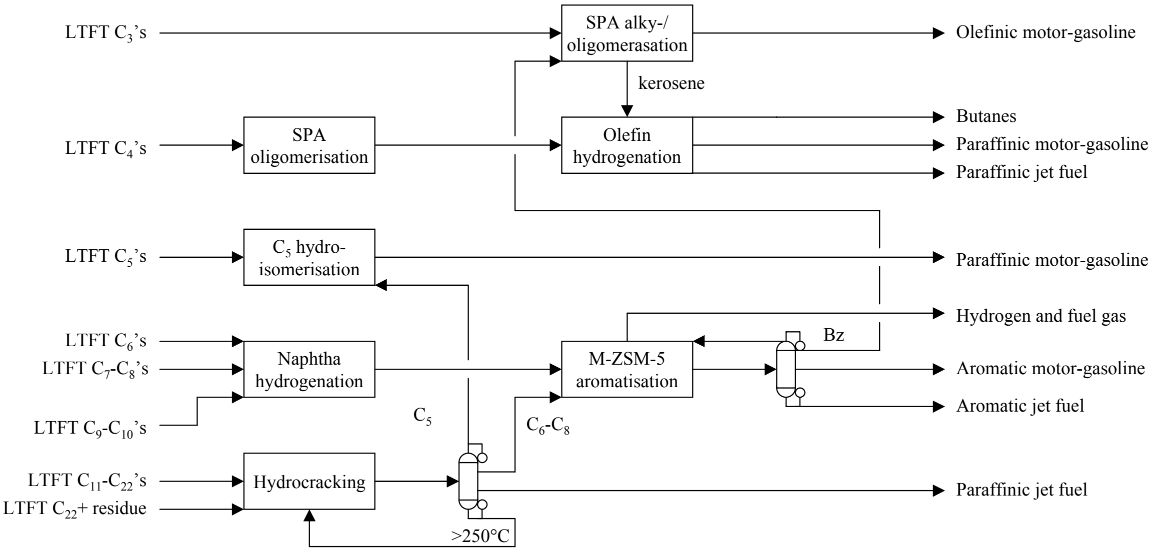

Figure 7. LTFT motor-gasoline refinery, flowscheme 5.

The same design principles as in flowscheme 4 was used to develop a hydrocracker based refinery design employing a metal promoted H-ZSM-5 based aromatisation technology (Figure 7). It was hoped that the ZSM-5 based aromatisation unit could reduce the LPG production, as well as offer a more direct upgrading pathway for the C_9-C_{10} naphtha. In general the design is very similar to flowscheme 4, apart from the aromatisation technology and the operation of the benzene alkylation unit. The latter unit was operated as a C_3 SPA based oligomerisation unit, with benzene being co-fed to enable alkylation.(18) Unlike conventional aromatic alkylation units, this mode of operation entails a low aromatics to olefin ratio in the feed. Oligomerisation is therefore not suppressed and may even be the main reaction.

The C_5's from the hydrocracker serve as feed for hydroisomerisation and aromatisation and the vapour pressure of the motor-gasoline determines the split being used. The design of the hydroisomerisation unit is thereby simplified, since it takes only C_5 hydrocarbons as feed and *n*-pentane recycle can be achieved by distillation.

The yield structure (Table 15) changed and the yield of motor-gasoline decreased to 22% compared to the 28% of the previous design! Although the LPG production was reduced by the use of ZSM-5 based aromatisation, most of the gain was reflected in jet fuel production. Nevertheless, the design was less quality constrained, with both motor-gasoline and jet fuel meeting specifications (Table 16).

Table 15. Yield structure of the LTFT motor-gasoline refinery shown in Figure 7 using ZSM-5 based aromatisation. It has a liquid fuel yield of 91% (mass), a motor-gasoline yield of 22% (mass) and a jet fuel yield of 59% (mass).

Product	Refinery production			
	(kg·h^{-1})	(m^3·h^{-1})	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	108308	148	22309	23.7
Jet fuel	293867	377	56979	60.5
Diesel fuel	0	0	0	0.0
LPG	53744	98	14835	15.8
Other products				
Fuel gas	23957			
Unrecovered organics	22614			
Hydrogen	-3805			
Water	1315			
Σ	500000	624	94122	100

Table 16. Motor-gasoline and jet fuel quality from the LTFT motor-gasoline refinery shown in Figure 7.

Fuel properties	Refinery	Fuel specification	
Motor-gasoline		*Euro-4*	
RON	96	95	Min
MON	89	85	Min
Vapour pressure (kPa)	60	60	Max
Density (kg·m^{-3})	733	720-775	Range
Olefins (vol %)	5.1	18	Max
Aromatics (vol %)	34.7	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.1	1	Max
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	779	775-840	Range
Aromatics (vol %)	20.3	8-25	Range
Flash point (°C)	54	38	Min
Vapour pressure (kPa)	0.7	-	

The vapour pressure of the motor-gasoline was a limiting specification in flowscheme 4 (Figure 6) and flowscheme 5 (Figure 7). This excluded the butanes from being blended into the motor-gasoline and even resulted in some C_5 naphtha not being hydroisomerised to keep the RVP within specification limits. The vapour pressure of the fuel could not be lowered by further aromatics blending, since the aromatic content was already close to its limit. A lack of short chain olefins precluded production of heavier olefinic motor-gasoline, which left oxygenated motor-gasoline as the only lever remaining in order to introduce more flexibility in the fuel pool. Since vapour pressure was limiting, only fuel ethers such as TAME and TAEE could be considered as oxygenate motor-gasoline additives. Unfortunately the C_5 olefin fraction in LTFT syncrude that is amenable to etherification (2-methyl-1-butene and 2-methyl-2-butene) is too small for meaningful syncrude based etherification. A significant modification of the refinery flowscheme was therefore required to enable syncrude based ether production. Alcohols would have to be recovered from the aqueous product, a pentene skeletal isomerisation unit would have to be added to increase the yield of reactive isoamylenes and an etherification unit would have to be included. These additions would increase the refinery complexity and cost considerably, yet, it would be able to convert only 2% of the syncrude to fuel ethers. This avenue of refinery development was consequently not explored any further.

From the designs (flowschemes 4 and 5) it was clear that a hydrocracker based LTFT refinery is not good for maximum motor-gasoline production.

3.4.3. Flowscheme 6

When catalytic cracking is used as residue conversion unit in the refinery design (Figure 8), the refinery contains the same conversion units as in the previous two LTFT refinery designs (Figures 6 and 7), but the motor-gasoline yield is significantly increased (Table 17). The almost doubling of motor-gasoline yield comes at the expense of some overall liquid fuel yield loss. This is to be expected from a carbon rejection technology such as FCC.

Without repeating the discussion on feed and product routing, some of the differences in this design will be highlighted.

The C_4 product from the FCC contains about 50% iso-butene. This allows the SPA based oligomerisation process to be operated at a lower temperature to produce a product rich in trimethylpentenes. The negative impact of the excess propylene (11% of olefins) that is co-fed to this unit is more than offset by the positive impact of the iso-butene. The calculated

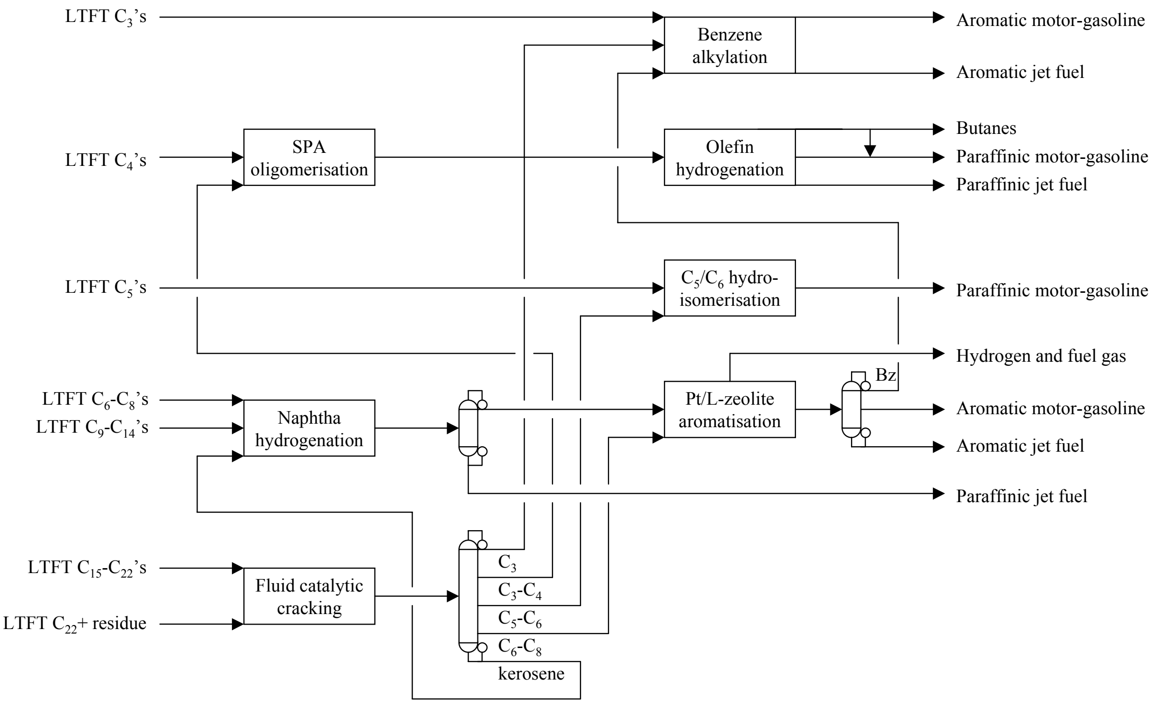

Figure 8. LTFT motor-gasoline refinery, flowscheme 6.

hydrogenated motor-gasoline properties are RON 91 and MON 86, which are better than can be achieved with C_4-only HTFT feed.(14) The short chain olefin shortage that limited benzene alkylation capacity (as noted in the discussion of flowscheme 4) has been addressed by the FCC. Some propylene could therefore be routed to the olefin oligomerisation unit.

Platinum promoted non-acidic L-zeolite based aromatisation technology has been selected to convert the C_6-C_8 LTFT naphtha and most of the C_6-C_8 FCC derived naphtha to aromatics. Since FCC increased the naphtha volume and is not a hydrogen consumer like hydrocracking, the refinery has a significant surplus of hydrogen (Table 17).

The motor-gasoline and jet fuel produced by this design meet fuel specifications (Table 18). The motor-gasoline production is vapour pressure constrained and only a limited fraction of the butanes could be blended into the motor-gasoline. However, the high iso-olefin content of the FCC naphtha makes it possible to consider etherification without the need for an olefin skeletal isomerisation unit as would be required for flowschemes 4 and 5. This reduces the vapour pressure in the motor-gasoline (Table 18) and opens possibilities to further increase the motor-gasoline yield by blending in butanes, etc. In addition to the beneficial effect on vapour pressure, ether addition also adds further blending flexibility with respect to octane and aromatics content.

Table 17. Yield structure of the LTFT motor-gasoline refinery shown in Figure 8. It has a liquid fuel yield of 90% (mass) and a motor-gasoline yield of 51% (mass).

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	254329	344	51936	56.4
Jet fuel	177030	228	34462	37.4
Diesel fuel	0	0	0	0.0
LPG	20228	37	5659	6.1
Other products				
Fuel gas	20488			
Unrecovered organics	23710			
Hydrogen	2746			
Water	1471			
Σ	500000	610	92058	100

Table 18. Motor-gasoline quality from the LTFT motor-gasoline refinery shown in Figure 8 showing (a) the blend without oxygenates, and (b) the blend with the addition of TAME from an additional etherification unit (not shown in Figure 8).

Fuel properties	Refinery scenarios		Euro-4	
	(a)	(b)		
RON	98	102	95	Min
MON	92	93	85	Min
Vapour pressure (kPa)	60	52	60	Max
Density ($kg\cdot m^{-3}$)	739	750	720-775	Range
Olefins (vol %)	0.8	0.8	18	Max
Aromatics (vol %)	33.9	32.2	35	Max
Oxygenates (vol %)	0.0	14.9	15	Max
Benzene (vol %)	0.2	0.0	1	Max
Ethanol (vol %)	0.0	0.0	5	Max
TAME (vol %)	0.0	14.6	15	Max

From this refinery design it should be clear that residue upgrading by FCC is much better than hydrocracking for maximising motor-gasoline production from LTFT syncrude.

However, the improvement is not only limited to motor-gasoline yield, but also in terms of motor-gasoline quality and refinery flexibility.

4. Jet fuel refineries

When maximum jet fuel production is considered, it is important to adjust the carbon number distribution, as well as the properties of the material. In this respect it is not different from maximum motor-gasoline refining. The carbon number distribution determines the yield, while the properties determine whether jet fuel specifications will be met.

Kerosene range material is typically in the carbon number range C_9-C_{14},[1] which overlaps with motor-gasoline and diesel fuel. Using this range, it can be shown that the maximum straight run kerosene from syncrude is produced when the Fischer-Tropsch catalyst has chain growth probability (α-value) of 0.80-0.84 (Figure 9). In practise, the distillation range of straight run Fischer-Tropsch syncrude that can be included in jet fuel is determined by the flash point (minimum 38°C) and freezing point (maximum –47°C) specifications on account of its high linear hydrocarbon content (Table 19).(21)

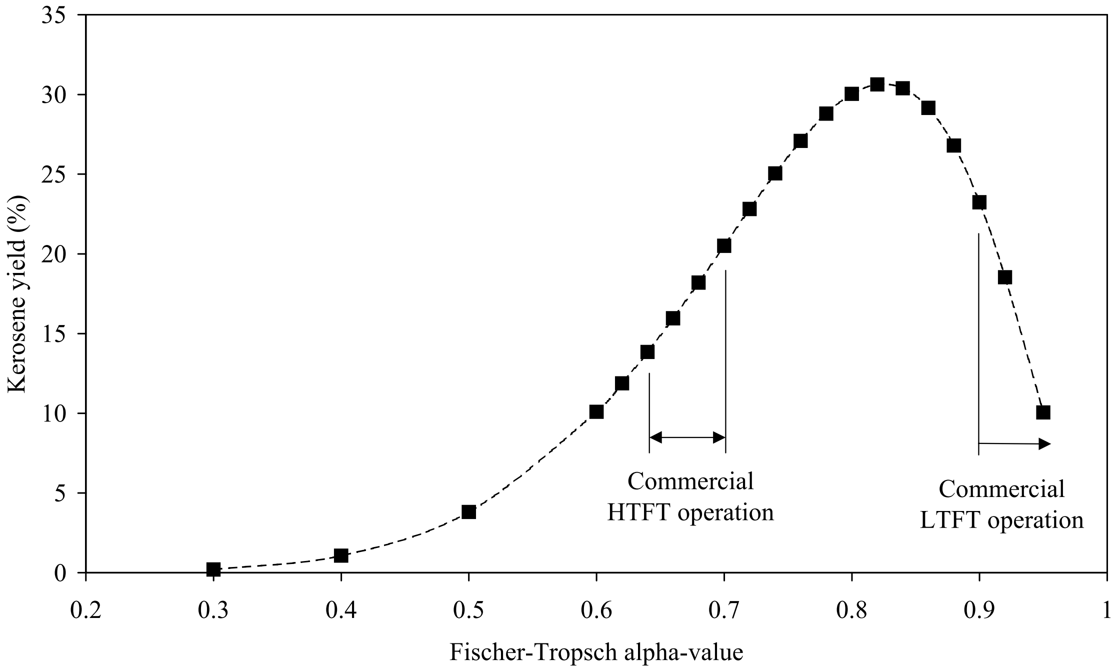

Figure 9. Yield of straight run kerosene (C_9-C_{14}) in the C_3 and heavier hydrocarbon fraction from Fischer-Tropsch as function of the chain growth probability (α-value).

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[1] The Jet A-1 specification limits the maximum final boiling point temperature to 300°C, but it does not prescribe a minimum initial boiling point temperature. The initial boiling point temperature is indirectly regulated by specifying a minimum flash point of 38°C and maximum T10 temperature of 205°C.

Table 19. Physical properties relevant to jet fuel of some hydrocarbons, namely freezing point (T_m), normal boiling point (T_b), flash point (T_{fp}) and vapour pressure at 15.6°C (RVP).

Compound	T_m (°C)	T_b (°C)	T_{fp} (°C)	RVP (kPa)
Linear paraffins				
n-nonane	-53.5	150.8	31.1	1.2
n-decane	-29.6	174.2	46.1	0.4
n-undecane	-25.6	195.9	65.0	0.1
n-dodecane	-9.6	216.3	73.9	<0.1
n-tridecane	-5.4	235.2	-	<0.1
n-tetradecane	5.9	253.8	100.0	<0.1
n-pentadecane	9.9	270.7	-	<0.1
n-hexadecane	18.2	286.9	-	<0.1
Branched paraffins				
2-methyloctane	-80.4	143.3	-	1.7
2,2,5-trimethylhexane	-105.8	124.1	12.8	4.3
2-methylnonane	-74.7	167.0	-	0.6
Aromatics				
benzene	5.5	80.1	-11.1	22.1
toluene	-95.0	110.6	4.4	7.1
ethylbenzene	-95.0	136.2	15.0	2.6
o-xylene	-25.2	144.4	17.2	1.8
m-xylene	-47.8	139.1	25.0	2.3
p-xylene	13.3	138.4	25.0	2.4
cumene	-96.0	152.4	43.9	1.3
sec-butylbenzene	-75.5	173.3	52.2	0.5
tert-butylbenzene	-57.9	169.1	60.0	0.6
o-cymene	-71.5	178.2	-	0.4
m-cymene	-63.7	175.1	-	0.5
p-cymene	-67.9	177.1	47.2	0.4
o-diethylbenzene	-31.2	183.4	57.2	0.3
m-diethylbenzene	-83.9	181.1	56.1	0.3
p-diethylbenzene	-42.8	183.8	56.7	0.3
n-hexylbenzene	-61.0	226.1	71.7	<0.1

Quality-wise jet fuel requires neither a high octane number, nor a high cetane number. Since Fischer-Tropsch syncrude is naturally low in sulphur and dinuclear aromatics, it requires only some hydroisomerisation to meet the freezing point specification and the inclusion of aromatics to meet the aromatic content (8-25%) and density (775-840 $kg \cdot m^{-3}$) specifications.[m] Jet fuel therefore does not require much refining to achieve specification. The basic steps involved in producing maximum jet fuel from syncrude are:

a) Adjust the carbon number distribution to maximise kerosene.

b) Synthesise appropriate kerosene range aromatics.

c) Skeletally isomerise the linear hydrocarbons to lower their freezing point.

d) Hydrogenate the syncrude to reduce the olefin and oxygenate content.

The development of a syncrude refinery that produces just jet fuel is not practical and it is expected that some material will end up as LPG, naphtha and heavy distillate. An important aspect of the refinery design, which is less obvious, is to ensure that these non-kerosene range fractions are of sufficient quality that the naphtha can be sold as motor-gasoline and that the heavy distillate can be sold as diesel fuel. This was also tacitly done in the flowschemes for maximum motor-gasoline production.

4.1. HTFT jet fuel refinery development

The synergy between motor-gasoline refining and jet fuel refining has indirectly been explored with flowschemes 1-3, where jet fuel was the main secondary product. If we compare the requirements for motor-gasoline and jet fuel, two aspects of commonality are obvious, namely the need for alkyl aromatics and the undesirability of linear paraffins. The requirements for upgrading of the different fractions are discussed on a carbon number basis:

a) *Residue* (C_{22}+). Despite the HTFT residue fraction being small, the need to hydroisomerise the kerosene range material and the possibility to convert heavy distillate to kerosene, strongly argues for the inclusion of a hydrocracker. The hydrocracker should be operated in kerosene mode to maximise the kerosene range products and avoid over-cracking to naphtha and gas.

b) C_{15}-C_{22} *distillate*. Considering that the inclusion of a hydrocracking unit is likely, the distillate can be partly converted into a branched paraffinic kerosene component that should have good cold flow properties. In doing so, the main shortcoming of using HTFT

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[m] Full syn-jet has not yet been approved, but in anticipation, maximum aromatics has been set at 25%, not 22%.

distillate as diesel fuel, namely its low density, is overcome by moving the material out of the diesel boiling range.

c) *C_{11}-C_{14} kerosene*. The straight run HTFT kerosene does not meet jet fuel specifications, but can easily be converted to a fully synthetic jet fuel. Hydrogenation of the oxygenates and hydroisomerisation of the hydrocarbons render a product that meets all the jet A-1 specifications, including aromatics content and density.[n] This is best achieved by operating a hydrocracking unit in such a way that the kerosene range material is only hydroisomerised, although some material will inevitably be lost due to hydrocracking.

d) *C_9-C_{10} naphtha*. This heavy naphtha fraction also falls within the kerosene range and can be refined in a similar way to the C_{11}-C_{14} kerosene, namely by hydroisomerisation in a hydrocracking unit. Strictly speaking it is not even necessary to hydroisomerise the C_9-C_{10} naphtha, which only requires hydrotreating, since it will be present in low enough concentration for the freezing point of the *n*-decane not to be a problem. Two benefits can be gained by only hydrotreating, rather than hydroisomerising this fraction. The flash point is not worsened and no material is lost to lighter products. The inclusion of the C_9-C_{10} naphtha in jet fuel effectively rules out catalytic reforming as technology to produce aromatics. This is not of concern, because it has previously been argued that the low $N+2A$ value of HTFT syncrude makes it a poor feed material for chlorided Pt/alumina catalytic reforming.

e) *C_7-C_8 naphtha*. The inclusion of C_7-C_8 naphtha in jet fuel is limited by the flash point specification, while its inclusion in motor-gasoline is limited by its poor octane value. The bulk of this fraction must therefore be converted in some way and aromatisation is the logical refining pathway. Olefin oligomerisation can also be considered as way to move some of this material into the kerosene boiling range.

f) *C_6 naphtha*. The two obvious upgrading pathways for the C_6 naphtha are hydroisomerisasion and aromatisation. The former results in a product destined exclusively for motor-gasoline, while the latter results in the production of aromatics that can potentially be refined to jet fuel. Since the aim is to produce maximum jet fuel, aromatisation is the preferred choice. Nevertheless, some refinery designs may dictate otherwise depending on the motor-gasoline quality requirements. Although olefin oligomerisation is a less obvious way to refine the C_6 olefin fraction, it may be considered as a method to increase the kerosene production.

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[n] It was shown that the preparation of Jet A-1 from a hydrogenated HTFT kerosene fraction and iso-paraffinic kerosene from short chain olefin oligomerisation over SPA meets all the Jet A-1 specifications. Ref.(11). Certification of fully synthetic jet fuel from HTFT is expected in 2007/8.

g) *C_5 naphtha*. The C_5 naphtha is primarily a motor-gasoline component, with hydroisomerisation yielding high-octane C_5 isomerate. Depending on the constraining motor-gasoline specifications, olefin skeletal isomerisation followed by etherification may also be considered. Optionally the pentene fraction can be used as feed for aromatic alkylation or olefin oligomerisation to increase the kerosene production.

h) *C_4 hydrocarbons*. Butene oligomerisation on SPA forms the basis for the production of heavier high-octane hydrogenated motor-gasoline. Some kerosene is co-produced during this process. The butenes can also be oligomerised on other types of acid catalysts to boost kerosene production. Aromatic alkylation is a less preferred refining pathway. However, it is anticipated that the technology selection for C_4 upgrading will be determined by motor-gasoline quality requirements.

i) *C_3 hydrocarbons*. SPA based propylene oligomerisation is an ideal jet fuel technology. The SPA catalyst restricts oligomer formation to the kerosene range (no heavier material is being co-produced) and kerosene is the main product. The resultant iso-paraffinic kerosene (IPK) produced by hydrogenation of the oligomers is known to be an excellent jet fuel component.(11) It is therefore ironic that benzene alkylation with propylene is also an efficient way to produce an aromatic component that is well suited for inclusion in both motor-gasoline and jet fuel. These processes can in principle be combined to produce a fully synthetic jet fuel in a single step.(18)

j) *C_2 hydrocarbons*. In the context of a maximum jet fuel refinery, ethylene should preferably be used for aromatic alkylation. Other refining pathways include hydration and purification for chemical use.

l) *Aqueous phase oxygenates*. The possibilities for the refining of the oxygenates dissolved in the aqueous product from HTFT synthesis has already been discussed. From a fuels refining perspective the easiest and least complex pathway is selective hydrogenation and dehydration to increase the production of mainly C_2-C_5 olefins that can be co-refined with the rest of such material.(12)

4.2. HTFT jet fuel refinery flowschemes

4.2.1. Flowscheme 7

The recommendations made in the previous section were applied to the development of an HTFT refinery to maximise jet fuel (Figure 10). This resulted in a refinery design very similar to that of flowscheme 3. The main differences being the routing of the products from C_3 SPA oligomerisation, which is included *in toto* in the jet fuel, and the hydrogenation of the C_9-C_{10} naphtha that is also included in the jet fuel.

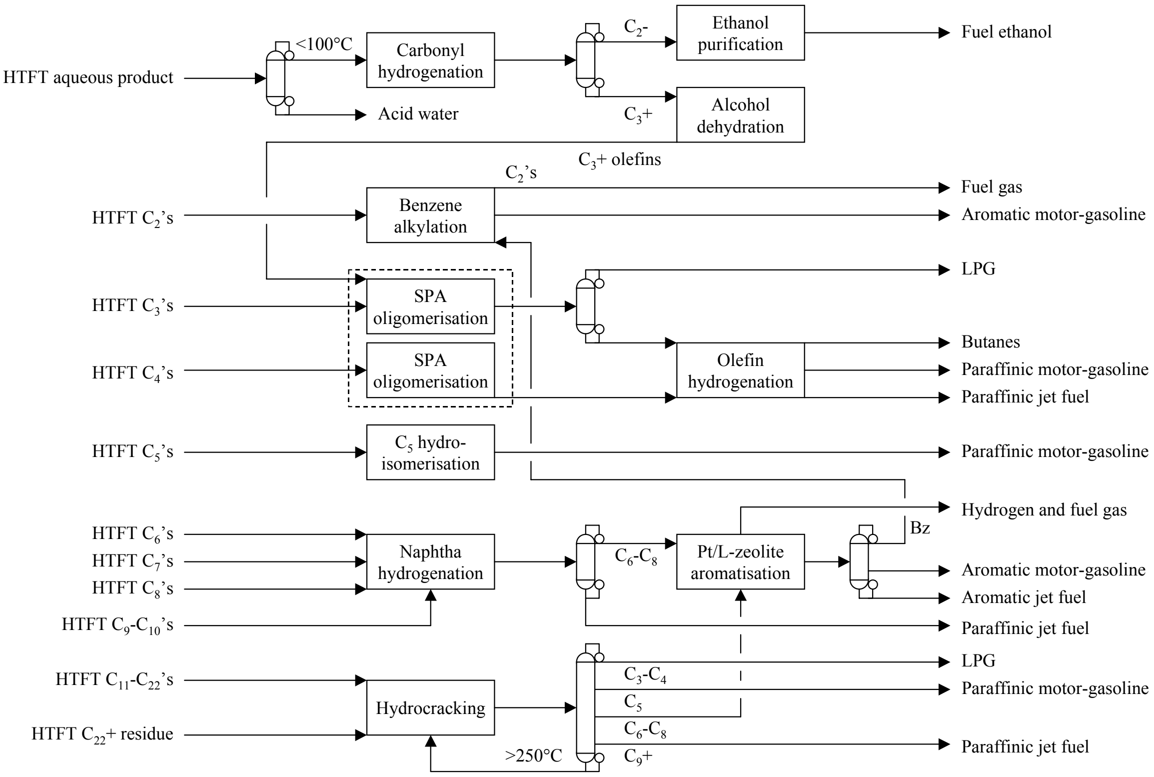

Figure 10. HTFT jet fuel refinery, flowscheme 7.

The yield structure (Table 20) shows a motor-gasoline to jet fuel volume ratio of 47:53, but once the motor-gasoline is blended with either butanes or ethanol to its vapour pressure limit, the ratio is closer to 50:50. The refinery design required no tweaking to meet motor-gasoline and jet fuel specifications (Table 21), indicating that it is a robust design for real-world situations.

The main drawback of flowscheme 7 is its jet fuel yield, which is low considering that the aim was to maximise jet fuel production. The refining pathways for the different syncrude fractions were analysed to determine in what way the jet fuel yield could be improved. It was found that the C_4, C_5, C_7 and C_8 naphtha fractions were refined mainly to motor-gasoline. It was also realised that these fractions were used to produce good quality high-octane motor-gasoline blending components and that care would have to be taken not to make motor-gasoline that does not meet specifications.

Table 20. Yield structure of the HTFT jet fuel refinery shown in Figure 10, which has a liquid fuel yield of 89% (mass) and jet fuel yield of 43% (mass).

Product	Refinery production			
	($kg\cdot h^{-1}$)	($m^3\cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	183049	249	37598	41.5
Excess fuel ethanol	17624	22	3351	3.7
Jet fuel	214417	275	41560	45.9
Diesel fuel	0	0	0	0.0
LPG	29054	54	8122	9.0
Other products				
Fuel gas	32612			
Unrecovered organics	14894			
Hydrogen	-928			
Water	9277			
Σ	500000	600	90631	100

Table 21. Jet fuel and motor-gasoline quality from the HTFT jet fuel refinery in Figure 10.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density ($kg\cdot m^{-3}$)	779	775-840	Range
Aromatics (vol %)	24.2	8-25	Range
Flash point (°C)	52	38	Min
Vapour pressure (kPa)	0.7	-	
Motor-gasoline		*Euro-4*	
RON	96	95	Min
MON	91	85	Min
Vapour pressure (kPa)	56	60	Max
Density ($kg\cdot m^{-3}$)	735	720-775	Range
Olefins (vol %)	1.3	18	Max
Aromatics (vol %)	29.2	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.5	1	Max
Ethanol (vol %)	0.0	5	Max

4.2.2. Flowscheme 8

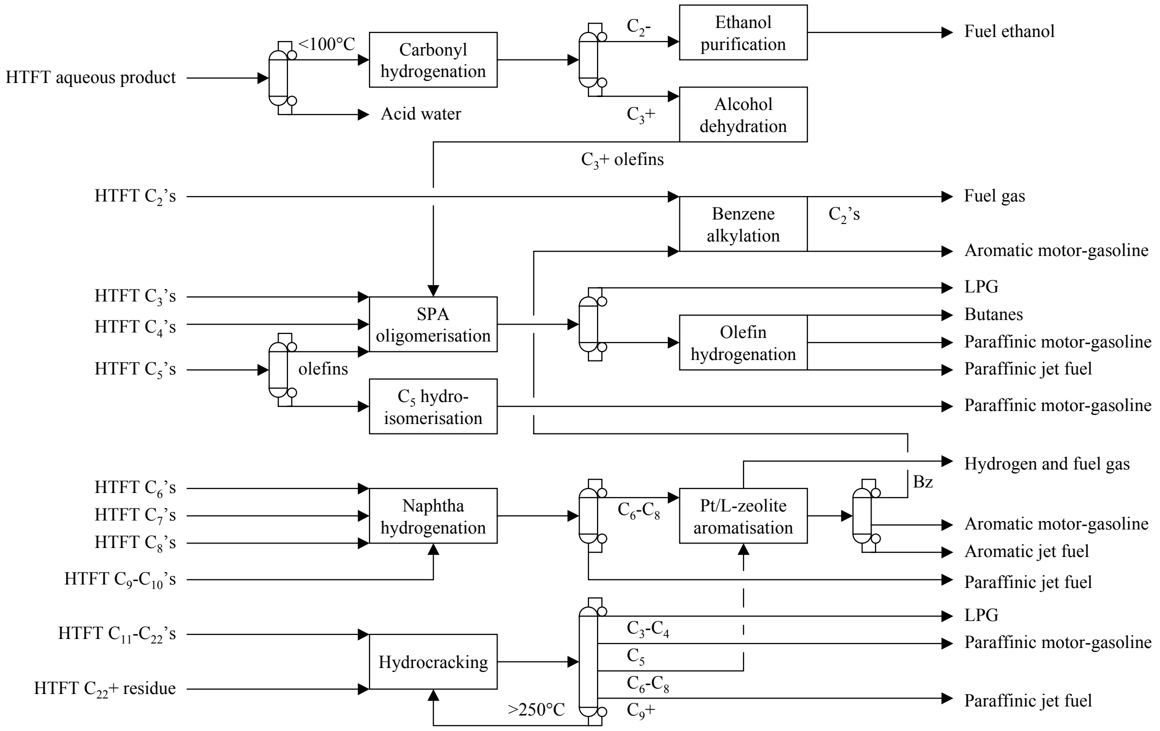

Figure 11. HTFT jet fuel refinery, flowscheme 8.

The objective of this refinery design was to find a way of incorporating more of the syncrude into jet fuel. The development of the refinery design focussed specifically on the routing of the C_4 and C_5 naphtha, since these fractions constitute 23% of the syncrude. The crux of the design (Figure 11) was the selective conversion of these cuts into jet fuel, by exploiting the unique properties of SPA catalysis. The rest of the design is similar to that of flowscheme 7.

When a mixture of propylene, butenes and pentenes are oligomerised, conjunct polymerisation results (the products are not integer multiples of the feed carbon number). On a mechanistic level, propylene dominates reaction initiation due to its ability to form a strong phosphoric acid ester.(22) The C_8-rich product fraction found during C_4-only oligomerisation is thereby greatly reduced, with most of the oligomers being in the C_9-C_{14} range. The SPA catalysed oligomerisation of a mixed C_3-C_5 syncrude naphtha yields a significant kerosene fraction, especially if the distillation cut point is between C_8 and C_9. This allowed the present flowscheme to convert more than 80% of the olefinic C_3-C_5 material into jet fuel, compared to only around 50% in the previous design, flowscheme 7. Since the hydrogenated kerosene fraction from SPA oligomerisation is iso-paraffinic kerosene, aromatics can be blended into the kerosene to further increase the jet fuel volume.

Table 22. Yield structure of the HTFT jet fuel refinery shown in Figure 11, which has a liquid fuel yield of 89% (mass) and jet fuel yield of 61% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	98880	131	19742	22.4
Excess fuel ethanol	17624	22	3351	3.8
Jet fuel	302863	389	58650	66.5
Diesel fuel	0	0	0	0.0
LPG	23568	42	6410	7.3
Other products				
Fuel gas	32612			
Unrecovered organics	14894			
Hydrogen	281			
Water	9277			
Σ	500000	584	88152	100

Table 23. Jet fuel and motor-gasoline quality from the HTFT jet fuel refinery in Figure 11.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density ($kg \cdot m^{-3}$)	780	775-840	Range
Aromatics (vol %)	24.9	8-25	Range
Flash point (°C)	50	38	Min
Vapour pressure (kPa)	0.8	-	
Motor-gasoline		*Euro-4*	
RON	99	95	Min
MON	90	85	Min
Vapour pressure (kPa)	60	60	Max
Density ($kg \cdot m^{-3}$)	756	720-775	Range
Olefins (vol %)	15.6	18	Max
Aromatics (vol %)	32.6	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.9	1	Max
Ethanol (vol %)	0.0	5	Max

Another benefit realised by the conversion of the pentenes to heavier products was that the vapour pressure of the motor-gasoline was reduced. This allowed more butanes to be blended into the fuel, thereby reducing the LPG production. It is also possible to blend in fuel ethanol in exchange for some of the butanes.

The yield structure of the design reflected the significant increase in jet fuel production (Table 22). The design was robust and the quality of the motor-gasoline was not compromised (Table 23) by meeting jet fuel specifications. As a matter of fact, the motor-gasoline quality was sufficient to exclude the C_5 hydroisomerisation unit from the design and still meet the motor-gasoline octane specifications! Another important benefit of this design is that it is hydrogen self-sufficient.

4.2.3. Flowscheme 9

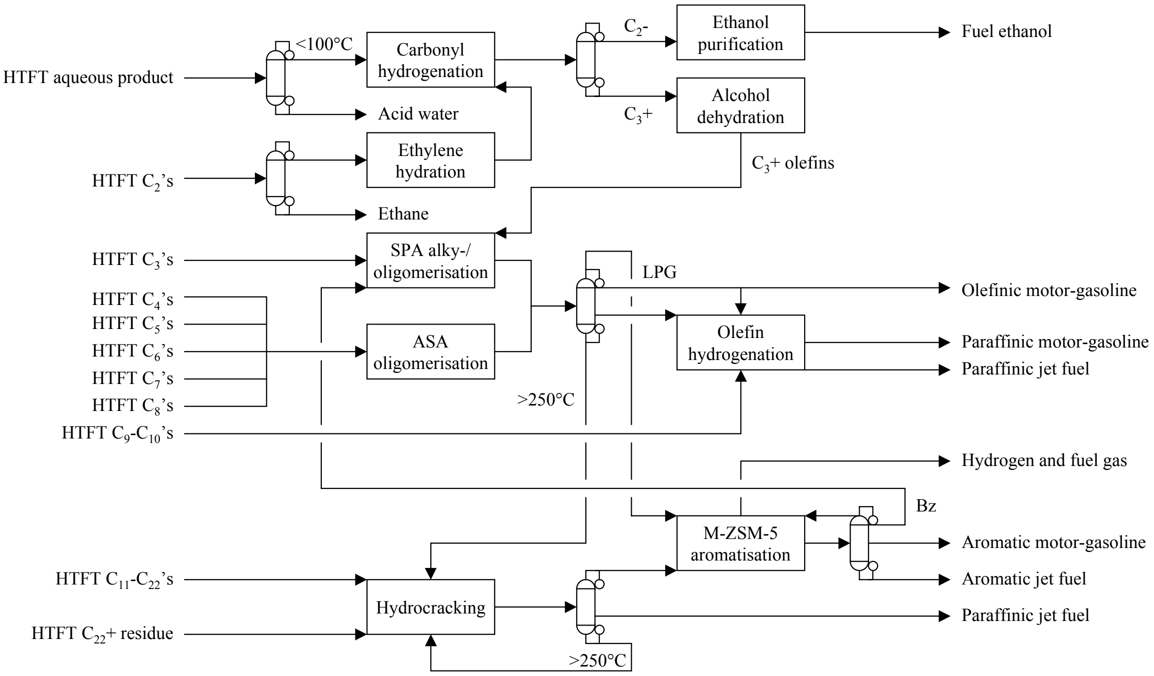

Figure 12. HTFT jet fuel refinery, flowscheme 9.

Despite the robustness and high jet fuel yield of flowscheme 8, the possibility to increase the jet fuel yield even further was explored by changing the oligomerisation and aromatisation technologies. In this design (Figure 12), oligomerisation by amorphous silica-alumina and aromatisation with a metal promoted H-ZSM-5 catalyst were employed, because both technologies are capable of converting material within a wide carbon number range. It was hoped that the combination of the kerosene-mode hydrocracker and ZSM-5 based aromatisation would be able to force most of the material into the kerosene range by cracking the heavier material and aromatising the light material. These changes in technology necessitated a change in alkylation technology too, since ZSM-5 based aromatisation has a low selectivity to benzene. Alkylation of the benzene with ethylene using a zeolite based alkylation technology would have been sub-optimal and combined alkylation/oligomerisation on SPA was better suited to the task. This still left the HTFT ethylene to be refined. Ethylene hydration was used in order to convert the ethylene to fuel ethanol, although by doing so the ethanol production far exceeded motor-gasoline requirements. This flowscheme (Figure 12) is consequently different in many respects from flowscheme 7 (Figure 10) and flowscheme 8 (Figure 11).

Table 24. Yield structure of the HTFT jet fuel refinery shown in Figure 12, which has a liquid fuel yield of 91% (mass) and jet fuel yield of 69% (mass).

Product	Refinery production			
	($kg{\cdot}h^{-1}$)	($m^3{\cdot}h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	46287	59	8914	10.2
Excess fuel ethanol	66405	84	12625	14.4
Jet fuel	343887	437	65979	75.4
Diesel fuel	0	0	0	0.0
LPG	0	0	0	0.0
Other products				
Fuel gas	38772			
Unrecovered organics	17836			
Hydrogen	-2876			
Water	-10311			
Σ	500000	580	87518	100

This approach was a successful refining strategy for increasing jet fuel production (Table 24), with a volumetric motor-gasoline to jet fuel ratio of 13:87 being obtained. However, it was less successful from the point of view of motor-gasoline quality, with only the jet fuel meeting specifications (Table 25). The motor-gasoline resembled a petrochemical feedstock, being high in olefins and aromatics and further refining in a non-energy refinery would make more economic sense.

Table 25. Jet fuel and motor-gasoline quality from the HTFT jet fuel refinery in Figure 12.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	787	775-840	Range
Aromatics (vol %)	25.0	8-25	Range
Flash point (°C)	52	38	Min
Vapour pressure (kPa)	0.8	-	
Motor-gasoline		*Euro-4*	
RON	96	95	Min
MON	84	85	Min
Vapour pressure (kPa)	8	60	Max
Density (kg·m^{-3})	784	720-775	Range
Olefins (vol %)	31.9	18	Max
Aromatics (vol %)	45.3	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.3	1	Max
Ethanol (vol %)	0.0	5	Max

On a conceptual level one could consider recycling most of the motor-gasoline to extinction. One could also consider fluid catalytic cracking as an alternative to hydrocracking for converting the unwanted naphtha range material into olefins and paraffins that can be converted in the oligomerisation and aromatisation units. However, further recycling and processing by energy intensive conversion units were seen as steps in the wrong direction, although it could potentially result in a higher jet fuel yield.

4.3. LTFT jet fuel refinery development

During the development of the LTFT motor-gasoline refineries, some good pointers were obtained on how to develop a jet fuel refinery. As a matter of fact, flowscheme 5 (Figure 7) is a good example of an LTFT jet fuel refinery, meeting both motor-gasoline and jet fuel specifications and having a 59% jet fuel yield.

The lack of olefins for motor-gasoline production is less of an issue when jet fuel is maximised and in general LTFT syncrude is better suited for jet fuel production than for motor-gasoline production. This can be understood in terms of the molecular requirements of jet fuel, with jet fuel consisting mainly of iso-paraffins, naphthenes and alkyl aromatics. Iso-paraffins are easily prepared by the hydroisomerisation and hydrocracking of the linear paraffins present in LTFT syncrude to yield a good quality jet fuel component.(23) Aromatics are also easily produced from paraffins, with the aromatisation technology influencing the feed range that can be converted and the product distribution that can be expected.

The motor-gasoline that is co-produced during jet fuel refining must still meet specifications. Aromatics production is common requirement to both motor-gasoline and jet fuel, while the availability of olefins are important mostly for the production of motor-gasoline. Increasing the jet fuel yield should consequently be beneficial for motor-gasoline production, since it indirectly increases olefin availability for motor-gasoline refining. Details of the refining requirements for motor-gasoline and jet fuel production have already been covered in the previous sections and it serves no purpose rehashing this discussion on a carbon number basis in the present context.

4.4. LTFT jet fuel refinery flowschemes

4.4.1. Flowscheme 10

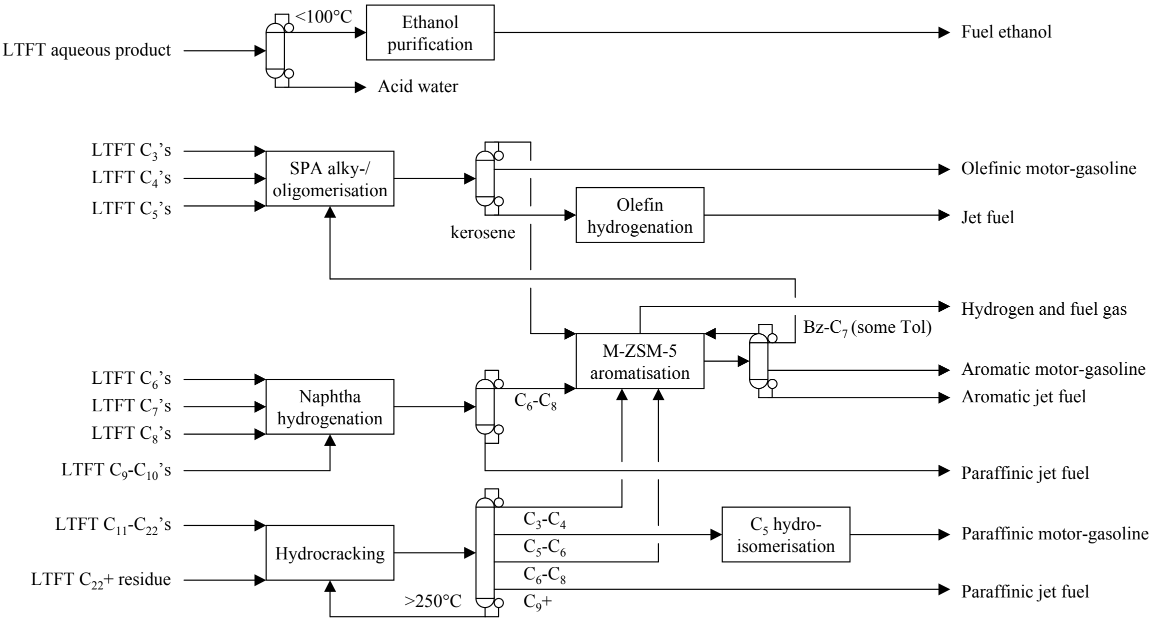

Figure 13. LTFT jet fuel refinery, flowscheme 10.

It has been demonstrated in flowscheme 5 (Figure 7) that the combination of hydrocracking and ZSM-5 based aromatisation is well-suited to jet fuel production. It has further been shown in flowscheme 8 (Figure 11) that SPA catalysed oligomerisation of mixed C_3-C_5 olefins produces good jet fuel and good motor-gasoline if the distillation cutpoint is between C_8 and C_9. Yet, it is also known that when there is not too much benzene in the refinery, that the benzene can be alkylated in a SPA catalysed oligomerisation process without disrupting the olefin oligomerisation. A new LTFT jet fuel refinery was developed by combining these ideas into a single refinery design (Figure 13). The main aim of this design was to maximise jet fuel production, while still meeting the motor-gasoline specifications.

As in the previous LTFT refinery designs, due to economic reasons the C_2 hydrocarbons were not recovered. Contrary to the previous LTFT designs, some aqueous product refining was included in this design (Figure 13), since the motor-gasoline required ethanol addition to meet fuel specifications. The ethanol, or another type of fuel oxygenate can also be obtained from an external source and the inclusion of some aqueous product refining is not central to the design.

The mixed C_3-C_5 hydrocarbons from the LTFT syncrude are used as feed to a SPA based oligomerisation unit, where it is partly oligomerised and partly used to alkylate benzene and some toluene from the aromatisation unit. The kerosene fraction of the product, which contains alkyl aromatics and olefin oligomers, is hydrotreated to produce jet fuel. The naphtha fraction is directly included in the motor-gasoline, while the unconverted C_3-C_5 olefins and paraffins are used as feed for the aromatisation unit.

The LTFT C_6-C_{10} naphtha is hydrotreated before being fractionated into kerosene (C_9-C_{10}) for jet fuel and naphtha (C_6-C_8) for aromatisation.

The heavier LTFT syncrude (C_{11} and heavier) fraction that consists of the straight run distillate and wax, is fed to the hydrocracker. The hydrocracker is operated in kerosene-mode, with the material that is higher boiling than 250°C being recycled to extinction. The product is fractionated into kerosene, C_6-C_8 naphtha, C_5-C_6 naphtha and LPG fractions. The C_5-rich fraction is hydroisomerised in a C_5 hydroisomerisation unit and the C_6 content of this fraction (about 15% of the C_6 hydrocracker product) is determined by the paraffin requirements of the motor-gasoline. The LPG and C_6-C_8 naphtha fractions are employed as feeds to the aromatisation unit.

The aromatisation unit has to make use of metal promoted H-ZSM-5 based technology in order to convert the C_3-C_5 hydrocarbons and keep the benzene production low.

The aromatic-rich product is fractionated, with the toluene rich fraction being used for motor-gasoline and the C_8 and heavier aromatics being blended into the jet fuel.

The refinery design has a volumetric motor-gasoline to jet fuel ratio of 22:78 and yielded 71% jet fuel (Table 26), while meeting both jet fuel and motor-gasoline specifications (Table 27). The motor-gasoline blending is tight, with RON and aromatics being borderline. The refinery as a whole is at its limit with respect to aromatics and it is clear that any additional aromatics production would decrease the yield of jet fuel.[o] There is some leeway for more olefinic motor-gasoline production, but considering the RON of the motor-gasoline, the design is very close to the maximum amount of jet fuel that can be obtained with the conversion unit selection made for this flowscheme. Since this is the highest yield of jet fuel (71%) obtained in any of the HTFT and LTFT flowschemes presented and the blending is very constrained, it may well be close to the maximum yield that can be achieved before significantly increasing the complexity of the refinery.

Table 26. Yield structure of the LTFT jet fuel refinery shown in Figure 13, which has a liquid fuel yield of 92% (mass) and jet fuel yield of 71% (mass).

Product	Refinery production			
	($kg{\cdot}h^{-1}$)	($m^3{\cdot}h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	101328	137	20641	23.0
Excess fuel ethanol	2272	3	432	0.5
Jet fuel	355912	455	68720	76.5
Diesel fuel	0	0	0	0.0
LPG	0	0	0	0.0
Other products				
Fuel gas	26781			
Unrecovered organics	15634			
Hydrogen	-3243			
Water	1315			
Σ	500000	595	89793	100

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[o] The maximum aromatic content in jet fuel is 25%, but in motor-gasoline it is 35%. Since both fuels are blended to their respective aromatics limits, any further aromatics production has to be included in the fuel with the higher aromatics limit. This implies that excess aromatics would have to be diluted with jet fuel and added to the motor-gasoline.

Table 27. Jet fuel and motor-gasoline quality from the LTFT jet fuel refinery in Figure 13.

Fuel properties	Refinery	Fuel specification	
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	782	775-840	Range
Aromatics (vol %)	24.8	8-25	Range
Flash point (°C)	52	38	Min
Vapour pressure (kPa)	0.8	-	
Motor-gasoline		*Euro-4*	
RON	95	95	Min
MON	87	85	Min
Vapour pressure (kPa)	58	60	Max
Density (kg·m^{-3})	741	720-775	Range
Olefins (vol %)	6.5	18	Max
Aromatics (vol %)	34.9	35	Max
Oxygenates (vol %)	4.6	15	Max
Benzene (vol %)	0.2	1	Max
Ethanol (vol %)	4.6	5	Max

5. Diesel fuel refineries

Thus far the production of diesel fuel has been studiously avoided. The aim in the previous designs had been to maximise motor-gasoline and jet fuel production, and convenient refining pathways could be found to refine all distillates to those products. Nevertheless, considering the marketing hype surrounding the GTL ventures of Sasol and Shell, it may have been surprising that no attempt was made to produce diesel fuel in any of the previous flowschemes.

It is true that HTFT and LTFT syncrude have good straight run cetane numbers and being sulphur-free, are high quality distillates. However, there is one diesel fuel specification that is not easily met by syncrude, namely diesel density (820-845 kg·m^{-3}). Acyclic aliphatic hydrocarbons in the distillate boiling range typically have densities in the range 740-800 kg·m^{-3}, which are well below the diesel density specification. One may instinctively think that the density shortfall can be overcome by aromatics addition, just like aromatics had been used to boost the octane number of motor-gasoline and were required to meet jet fuel specifications. Unfortunately this is not the case. For example, if we select a typical mid-range syncrude distillate hydrocarbon such as *n*-hexadecane (777.2 kg·m^{-3}) and co-boiling aromatic such as *n*-nonylbenzene (859.9 kg·m^{-3}), the diesel fuel requires a 52% aromatic content to meet the minimum density specification!

In this respect HTFT syncrude is better suited to diesel fuel production than LTFT syncrude, since the distillate range material contains aromatics and naphthenes, giving it a straight run density close to the diesel specification. When the straight run HTFT distillate is processed in a distillate hydrotreater (such as the Sasol Synfuels U35/235 DHT), the light diesel has a cetane number of 54-58, kinematic viscosity of 2.1-2.4 cSt and density of 804-813 kg·m^{-3}.(24) Unfortunately the HTFT straight run C_{11}-C_{22} distillate is only 8% of the HTFT syncrude and hardly enough to form the base stock for a maximum diesel fuel refinery. More material is needed in the diesel fuel range and this material is not only required to increase the density, but also to increase the overall diesel fuel yield.[p] In order to address some of these shortcomings, the Kölbel-Engelhardt conversion of CO and H_2O into an aromatic-rich Fischer-Tropsch-type of product, may have an advantage over normal Fischer-Tropsch synthesis, since the aromatics fraction includes bicyclic species, such as indanes and naphthalenes.(25)(26)

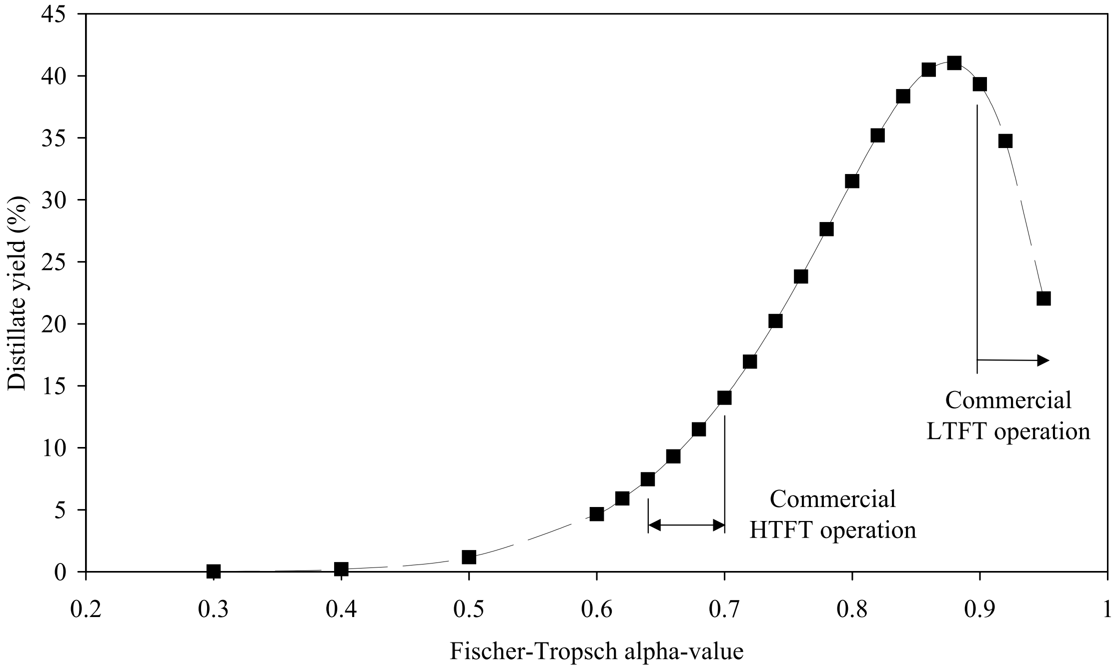

Figure 14. Yield of straight run distillate (C_{11}-C_{22}) in the C_3 and heavier hydrocarbon fraction from Fischer-Tropsch as function of the chain growth probability (α-value).

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[p] It is ironic that in Fischer-Tropsch refineries it is difficult to meet the minimum density requirement for diesel fuel, while the opposite is true in crude oil refineries. There is synergy in combining these two refinery types.

The carbon number distribution of LTFT syncrude is such that it has much more distillate range material than HTFT syncrude (Figure 14), with an α-value of 0.88 being close to the optimum for maximum straight run distillate production. However, the distillate from an LTFT process, such as the Sasol SPD™ process, has a high cetane number, typically >70, but it has a density of less than 780 kg·m^{-3}.(10) Producing a high volume of distillate with a high cetane number is therefore not an issue, but in terms of meeting the density requirement, the situation is precarious.

From the preceding discussion on HTFT and LTFT straight run distillate properties the conundrum of Fischer-Tropsch diesel fuel refining emerges. It seems straightforward to refine syncrude to distillate, but how to refine syncrude to maximise distillate volume, as well as meet the diesel properties required by fuels specifications, is far from obvious.(27)

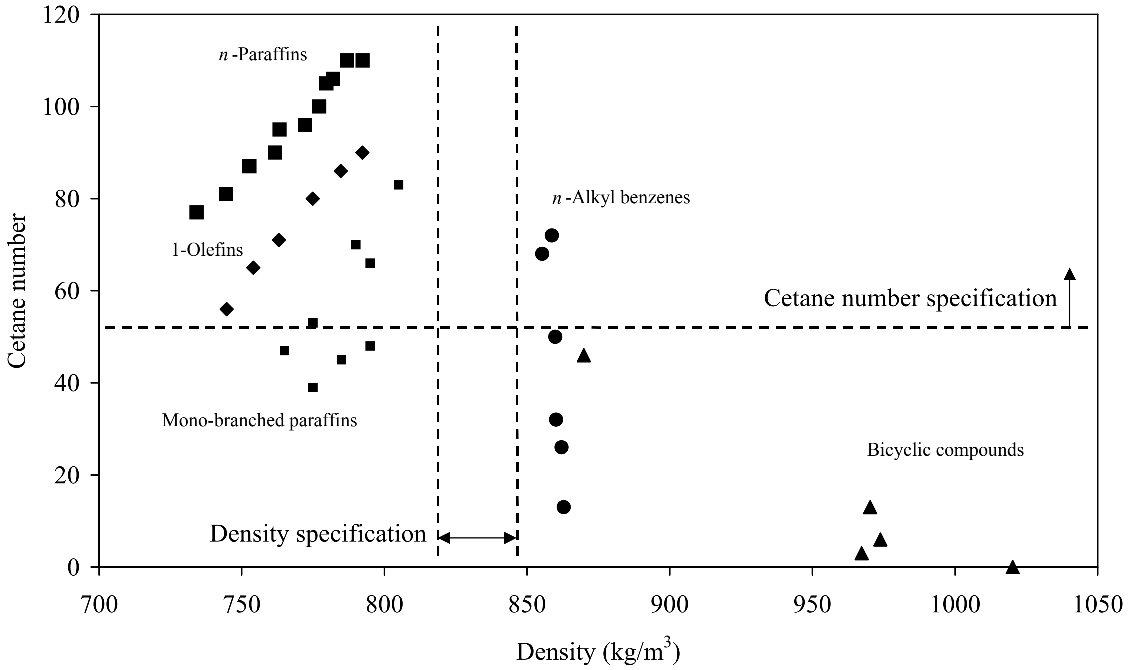
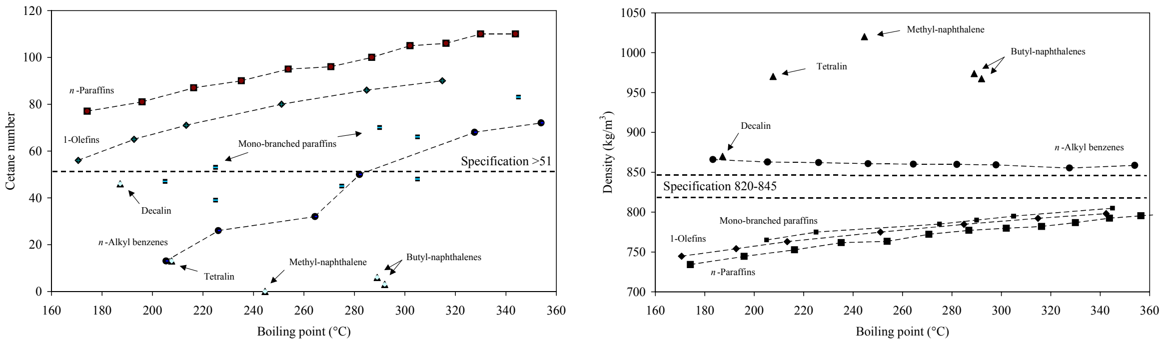


Figure 15. Cetane-density relationship of various compounds in the distillate boiling range from 170 to 360°C.

The key to maximum diesel fuel refining from Fischer-Tropsch syncrude lies in a refining problem that I will call the *density-cetane-yield triangle*. It is possible to meet any two of these three requirements without too much refining effort, but meeting all three is very difficult. This may not be apparent from the discussion thus far, since the cetane number of the distillate has never been an issue. However, if one compares the relationship of cetane number and density of different hydrocarbons in the distillate boiling range, a very disheartening picture emerges (Figure 15).(21)(28) The relationship between cetane number, density and molecular composition is not a new insight - it forms the basis for many predictive equations for cetane number.(29)(30) At this point it is worthwhile mentioning that diesel viscosity may also become a constraint, since a minimum viscosity of 2 cSt is required. However, viscosity is more closely related to the distillation profile than to the nature of the hydrocarbons in the distillate.(31)

There is potential for a cetane number versus density trade-off in order to increase the density of the syncrude derived diesel fuel. Depending on what compound class is used, this may result in a cetane deficient diesel fuel, despite Fischer-Tropsch distillate being known for its high cetane number. With the abundance of olefins in a Fischer-Tropsch refinery, the production of alkylbenzenes (860 kg·m^{-3}) to increase diesel density is a natural choice, but from a cetane number perspective they are the worst compounds to use. Monocycloalkanes in the diesel boiling range have cetane values close to that of acyclic paraffins, but their density (mean density of 815 kg·m^{-3}) is insufficient to densify the diesel. Although benzocycloalkanes and benzodicycloalkanes have slightly lower cetane numbers, they have much higher densities (>950 kg·m^{-3}) and are good compounds to use for densification.(29) Dicycloalkanes can also be considered on account of their high density, but they have worse cetane numbers than the cycloalkanes having one aromatic ring.(29)



(a) (b)

Figure 16. Relationship of cetane number and density to the boiling point temperature of compounds in the distillate boiling range.

The first general trend that is of benefit in increasing diesel quality is realising that with increasing boiling point the cetane number (Figure 16a) and density (Figure 16b) increases within each compound class. A heavier distillate is therefore preferable to a light distillate and the co-production of jet fuel in a Fischer-Tropsch refinery will improve the diesel quality. However, even a very heavy distillate derived from syncrude will require the addition of a significant volume of cyclic compounds to meet the density specification.

Cookson, Lloyd and Smith(32) described the compositional prerequisites for acceptable diesel fuel in an insightful manner. They have not used density as a key constraining variable in their discussion or analyses, but they have successfully modelled most other composition-property relationships by a simple linear correlation (Equation 2).

$$P = \kappa_1 \cdot [\mathrm{n}] + \kappa_2 \cdot [\mathrm{BC}] + \kappa_3 \cdot [\mathrm{Ar}] \qquad \text{... (2)}$$

The property value, P, is expressed as a function of the abundance of *n*-paraffins, [n], branched and cyclic aliphatics, [BC], and aromatics [Ar]. In a simple example it was shown that a diesel fuel consisting mostly of branched and cyclic aliphatics would meet diesel fuel specifications more readily than a fuel in which either *n*-paraffins or aromatics are the dominant compound classes.(32) Some additional pointers for the improvement of diesel fuel quality can be found in the work of industrial research laboratories, like those of ConocoPhillips(28) and ExxonMobil.(33) In these studies the problem is approached from the opposite angle, namely a high density and low cetane number, which is typical of crude oil derived distillates. Although not specifically highlighted by any of these studies, the importance of naphthenes becomes quite clear when read in conjunction with Figures 15 and 16. This supports the previous analysis by showing that distillate base stock that is rich in naphthenes has a reasonable cetane and density. Such a base stock can more easily be blended to on-specification diesel fuel by the addition of heavier *n*-paraffins for cetane number improvement, and some aromatics and partially saturated aromatics for density improvement.

It is possible that in future the fuel specifications may change to mandate a 5% *bio-diesel* addition. This would be beneficial for syncrude derived distillate, since it will increase the synthetic diesel density by 3-4 kg·m^{-3} without any cetane penalty.

Commercial bio-diesel consists of a mixture of fatty acid methyl esters (FAME) in the C_{16}-C_{18} range. Property values reported for bio-diesel from different suppliers seem to be close to each other, with a cetane number of 54,(34) kinematic viscosity of 4.2 cSt(34) and density of 878 kg·m^{-3}.(35) The properties of such bio-diesel mixtures are poorer than that reported for bio-diesel derived from pure oils, which have cetane numbers of 57-65, viscosities of 4.4-4.7 cSt and densities of 880-886 kg·m^{-3}.(36)

Additive packages can be used to increase the cetane number, which allows more leeway for the inclusion of low cetane, but high density compounds in the Fischer-Tropsch derived diesel fuel. This may be a more efficient way of satisfying the density-cetane-yield triangle than just refining syncrude molecules to reach the cetane number specification. Nevertheless, it should be noted that specifications such as Euro-4 also include a cetane index requirement, which in the case of Euro-4 is a minimum of 46. The cetane index is calculated based on the distillation properties of the diesel fuel, which by its definition cannot be improved by a cetane booster.

5.1. HTFT diesel fuel refinery development

The importance of generating a good quality base stock for blending to diesel fuel has already been highlighted. The straight run HTFT distillate range material is a good base stock, but its yield is far too little for a maximum diesel fuel refinery. One or more conversion processes are needed for carbon number growth to push the naphtha and gas into the distillate range.

A comparison of the distillate properties of three olefin industrial oligomerisation processes, solid phosphoric acid (SPA), amorphous silica alumina (ASA) and H-ZSM-5 based, show that from a density perspective, ASA based oligomerisation is the best.(37),[q] It is capable of producing a 60-70% distillate yield with the distillate having a density of 809-816 kg·m^{-3}, kinematic viscosity of 2.8-3.6 cSt and cetane number of 28-30. The product contains distillate range aromatics and naphthenes to provide density. Unfortunately the cetane number is low and the hydrogenated distillate from ASA oligomerisation makes a poorer quality base stock than hydrogenated straight run HTFT distillate. A refinery design based on ASA oligomerisation is therefore expected to be cetane constrained.

Since the crude oil refining industry has never had to increase the density of distillate, no refining technologies have been developed for this purpose. It is speculated that if such a technology was to be developed, that it is likely to exploit the selective ring closing behaviour of supported non-acidic noble metal catalysts,(38) typically using supports with an open pore structure. More conventional alternatives would include refining to aromatics with subsequent hydrotreating and it may well be possible to use standard reforming technology with heavy (C_{10}+) feed to produce compounds of the naphthalene and indene families. These binuclear compounds could provide density. Hydrotreating could restore the cetane loss, without compromising density, for example, *trans*-decalin has a density of 869.9 kg·m^{-3} and a cetane number of 46.

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[q] It is ironic that the one technology recently developed for the conversion of HTFT olefins to distillate, namely the COD-process, is based on H-ZSM-5, which produces a distillate with high cetane number (>51), but low density (787-801 kg·m^{-3}).

Nevertheless, the prognosis for the development of a maximum diesel refinery based on HTFT syncrude to produce diesel fuel that meets specification is not good when only commercial refining technologies are considered. Blending with coal pyrolysis products or crude oil derived distillates provide technically less challenging solutions than the development of a standalone HTFT syncrude based diesel refinery. In this sense Fischer-Tropsch derived diesel fuel is like diesel made from renewables – it is excellent in mixtures with crude derived products, but it is not so good just on its own.

The refining pathways for diesel fuel production will be explored on a carbon number basis:

a) *Residue (C_{22}+)*. The HTFT residue is a good source of heavy material to improve the density of the diesel fuel. This can be achieved by moderate hydrocracking, taking care not to over-crack the material.

b) *C_{11}-C_{22} distillate*. Hydrotreating of this fraction yields a product with good diesel fuel properties. Commercial HTFT distillate hydrogenation is quite severe and the product is completely hydrodeoxygenated. In this respect the advantages of moderate hydrotreating has not yet been realised. Much of the potential lubricity and storage stability characteristics imparted by long chain carboxylic acids and alkylated phenols are destroyed by severe hydrotreating. It may be beneficial from a density and cetane point of view to use the C_{11}-C_{14} fraction of the distillate for jet fuel. If this approach is to be followed, the C_{11}-C_{14} fraction will have to be hydroisomerised. However, the hydrogenated straight run HTFT distillate is good diesel base stock and should be retained as such considering that the aim of the refinery design is to maximise diesel fuel production.

c) *C_9-C_{10} naphtha*. This naphtha fraction yields poor motor-gasoline, but can be hydrotreated with the distillate to give a good quality kerosene component for jet fuel production. It is not necessary to hydroisomerise this cut. Alternatively it can be used as feed for ASA oligomerisation to increase distillate production. The use of such material for the production of linear alkyl benzenes as high density and cetane diesel fuel additives has also been considered, but it is doubtful whether this would be realistic in refining context.

d) *C_3-C_8 hydrocarbons*. The selection of the aromatisation technology determines the way in which the different carbon number fractions will be utilised. If a platinum promoted non-acidic L-zeolite based technology is used, then the C_6-C_8 naphtha cut would be the most appropriate feed for it. There is more feed flexibility if metal promoted H-ZSM-5 based technology is selected. In order to maximise the distillate blend stock, a significant part of the olefins in the C_3-C_8 fraction may be oligomerised on ASA. Whatever routing is selected, there is some trade-off involved, not only in terms of the density-cetane-yield triangle, but also in terms of the aromatics that are needed for motor-gasoline, jet fuel and diesel fuel.

e) *C_2 hydrocarbons*. Ethylene is a convenient aromatic alkylation agent to produce alkyl aromatics for all the transportation fuel types. This should be qualified though, because cetane numbers of such short chain alkyl aromatics are low, which may limit inclusion in diesel fuel. Pathways such as hydration and purification for chemical use can be considered, but in general it can be said that refining of ethylene to diesel fuel is limited. One exception that may be considered, is using ethylene oligomerisation technology for the production of linear α-olefins.(39) These linear α-olefins can the be co-refined with the HTFT syncrude, which is in any case rich in such material.

f) *Aqueous phase oxygenates*. The conversion of oxygenates dissolved in the aqueous phase by selective hydrogenation and dehydration to olefins, has already been noted.(12) The olefins thus produced can be co-refined with the HTFT syncrude. One modification to this idea that may be considered, is the production of heavier ethers from the alcohols. Distillate range ethers are high cetane diesel additives.(40) Unfortunately the production of heavier ethers will be limited due to the small C_5+ fraction being present in the aqueous phase and it is unlikely to be cost effective. Another possibility that may be considered is esterification of the carboxylic acids in the aqueous product with heavier alcohols in the oil product. This would produce shorter chain FAME-equivalents, which may be beneficial from both a cetane number and density perspective.[r]

5.2. HTFT diesel fuel refinery flowschemes

5.2.1. Flowscheme 11

In order to establish a baseline for HTFT refinery designs to maximise diesel fuel production, a design was developed that incorporated aspects of the preceding discussion (Figure 17). The design strategy was to convert most of the olefins in the gas and naphtha range into distillate range oligomers, thereby increasing the distillate yield (albeit not quality). Some incremental distillate yield improvement was gained by cracking the small residue fraction.

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[r] Esterification ($RCOOH + \text{'}ROH \rightleftharpoons RCOO\text{`}R + H_2O$) is an equilibrium limited reaction and using a dilute acid solution may not be economical. On the other hand, the use of an alcohol in a non-polar medium may result in extraction of the ester into the non-polar medium, thereby favouring the equilibrium. In any event, whatever the dominating equilibrium effect, mass transfer will probably be the main limitation.

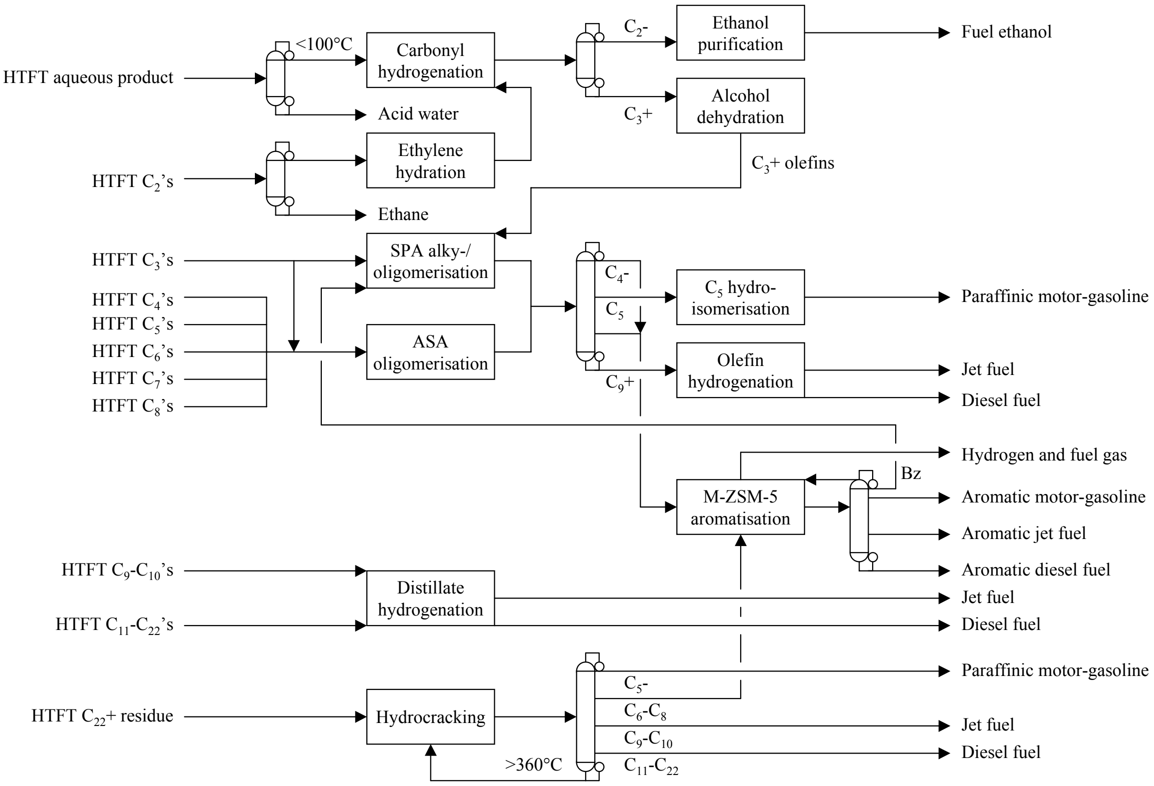

Figure 17. HTFT diesel fuel refinery, flowscheme 11.

Table 28. Yield structure of the HTFT diesel fuel refinery shown in Figure 17, which has a liquid fuel yield of 93% (mass) and diesel fuel yield of 42% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	58491	79	11890	13.4
Excess fuel ethanol	63304	80	12035	13.6
Jet fuel	132975	171	25866	29.1
Diesel fuel	208392	256	38709	43.6
LPG	1100	2	304	0.3
Other products				
Fuel gas	34543			
Unrecovered organics	14369			
Hydrogen	-2863			
Water	-10311			
Σ	500000	588	88804	100

The residue is converted mostly to distillate by hydrocracking, while the kerosene and distillate range material is just hydrotreated and fractionated into jet fuel (C_9-C_{10}) and diesel fuel (C_{11}-C_{22}). Most of the olefins in the C_3-C_8 range are oligomerised in an ASA based process. Some of the C_3 olefins and the olefins that were obtained from the selective hydrogenation and dehydration of the aqueous phase oxygenates, are used to alkylate the benzene in a SPA based combined alkylation and oligomerisation process. The products from the ASA and SPA based processes are combined. The kerosene and distillate fractions are hydrogenated and fractionated into jet fuel and diesel fuel. Most of the C_3-C_8 fraction is used as feed for metal promoted ZSM-5 based aromatisation, with only the C_5 cut being reserved for hydroisomerisation to produce motor-gasoline.

Table 29. Diesel fuel, jet fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 17.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	813	820-845	Range
Cetane number	31	51	Min
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	776	775-840	Range
Aromatics (vol %)	22.2	8-25	Range
Flash point (°C)	42	38	Min
Vapour pressure (kPa)	1.2	-	
Motor-gasoline		*Euro-4*	
RON	97	95	Min
MON	88	85	Min
Vapour pressure (kPa)	55	60	Max
Density (kg·m^{-3})	743	720-775	Range
Olefins (vol %)	14.4	18	Max
Aromatics (vol %)	34.8	35	Max
Oxygenates (vol %)	5.0	15	Max
Benzene (vol %)	0.1	1	Max
Ethanol (vol %)	5.0	5	Max

The refinery yield structure (Table 28) indicates a high overall refinery yield (93%), but expressed on a volumetric basis it is equivalent to only around 89 000 bpd. A significant fraction of the liquid production is due to excess fuel ethanol from ethylene hydration. The distillate yield was more than the combined motor-gasoline and jet fuel yields, but only marginally so. It can nevertheless be seen as a maximum diesel fuel refinery design.

Ironically the motor-gasoline and jet fuel meet specifications, but not the diesel fuel (Table 29). The diesel fuel density is only 813 kg·m^{-3}, while the cetane number is only 31, which is clearly unacceptable! Despite these serious shortcomings, the refinery design is instructive by demonstrating the impact of the inherent low density of syncrude. A suitable synthetic pathway to meet density, cetane and yield is unfortunately not obvious.

5.2.2. Flowscheme 12

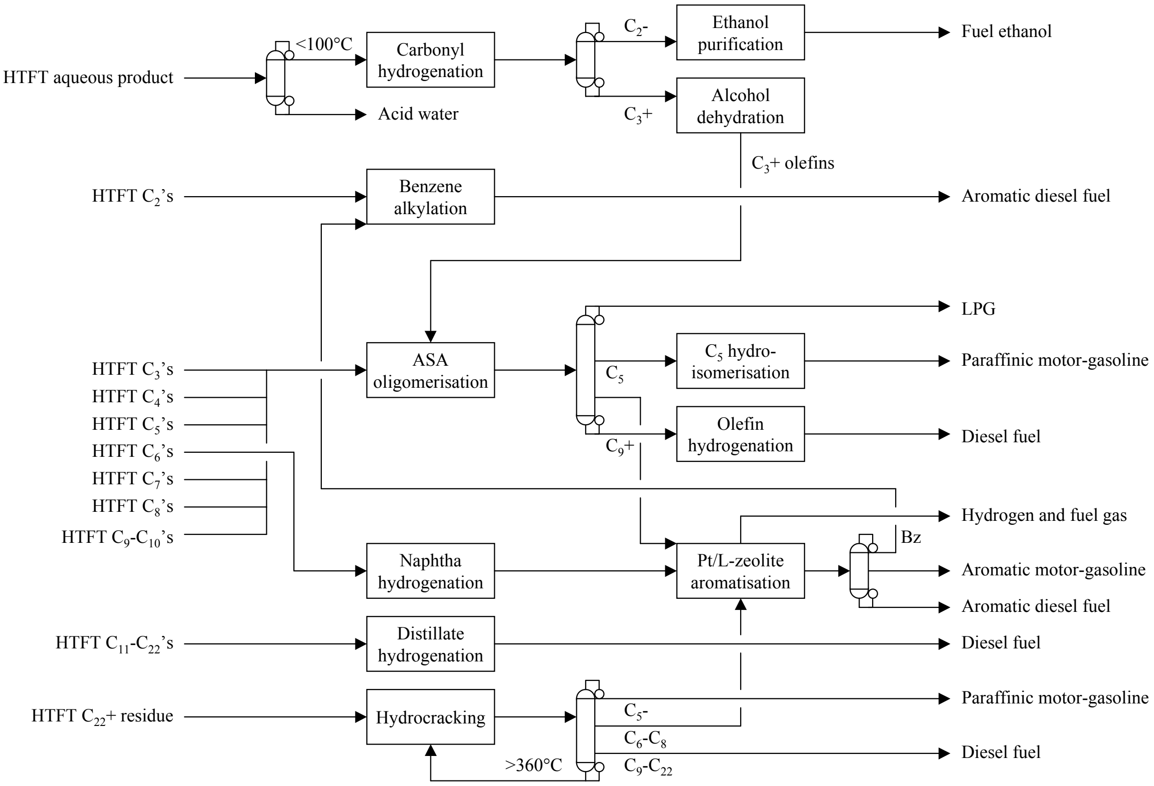

Figure 18. HTFT diesel fuel refinery, flowscheme 12.

It has been shown that HTFT syncrude has considerably less straight run distillate than LTFT syncrude (Figure 14) and the tacit assumption is sometimes made that HTFT technology cannot be used to produce a high yield of distillate. The previous design (flowscheme 11) indicated that it is difficult to produce diesel fuel meeting specification, despite trying to do so and the yield structure was constrained by the deliberate attempt to meet specification for all transportation fuel types. In the present flowscheme (Figure 18) the focus was shifted to the yield structure to explore to what extent diesel fuel yield can be maximised. In order to achieve this objective all kerosene range material has been included in the diesel fuel as a light diesel component.

The aqueous phase oxygenates were selectively hydrogenated to alcohols and dehydrated to olefins. These olefins were combined with the HTFT syncrude and all C_3-C_5 and C_7-C_{10} olefins from the HTFT syncrude and alcohol dehydration were converted in an ASA based oligomerisation unit. The C_6-C_8 naphtha thus produced was combined with the C_6 HTFT syncrude naphtha and used as feed for aromatisation on a platinum promoted non-acidic L-zeolite. Since this technology is very selective for the conversion of C_6 naphtha to benzene, the aromatic product contained more than 50% benzene. The benzene was alkylated with ethylene to produce a mixture of ethylbenzene and diethylbenzenes, thereby utilising most of the ethylene. The C_{11}-C_{22} straight run distillate was hydrotreated and the C_{22}+ material was hydrocracked in a similar way as the previous flowscheme.

Table 30. Yield structure of the HTFT diesel fuel refinery shown in Figure 18, which has a liquid fuel yield of 89% (mass) and diesel fuel yield of 69% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	60895	80	12064	14.1
Excess fuel ethanol	17624	22	3351	3.9
Jet fuel	0	0	0	0.0
Diesel fuel	343358	417	62958	73.8
LPG	25188	46	6944	8.1
Other products				
Fuel gas	29823			
Unrecovered organics	13307			
Hydrogen	824			
Water	8982			
Σ	500000	565	85317	100

Table 31. Diesel fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 18.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density ($kg\cdot m^{-3}$)	823	820-845	Range
Cetane number	27	51	Min
Motor-gasoline		*Euro-4*	
RON	98	95	Min
MON	91	85	Min
Vapour pressure (kPa)	57	60	Max
Density ($kg\cdot m^{-3}$)	762	720-775	Range
Olefins (vol %)	0.0	18	Max
Aromatics (vol %)	38.2	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	1.7	1	Max
Ethanol (vol %)	0.0	5	Max

This refining approach resulted in a distillate yield of 69% from the C_2+ syncrude (Table 30), while the overall refinery yield was 89%. This demonstrated that it is possible to devise a refinery design to convert HTFT syncrude with high yield to distillate. It was also surprising to note that the motor-gasoline almost met the Euro-4 fuel specifications (Table 31), while the diesel fuel met the density, but not the cetane specification. Since the product meets the density specification, some lower density high cetane material can conceivably be blended into the diesel to increase the cetane number and lower the density. This train of thought was explored for the new South African CTL project, which employs a combined HTFT and LTFT refinery design.(27)

One salient point worth highlighting is that flowscheme 12 contains the same conversion units as flowscheme 11. The only difference is in the technology selection of the conversion units and the routing of the various streams. Yet, the way in which the design was developed resulted in a refinery that met the density and yield requirements of the density-cetane-yield triangle.

5.2.3. Flowscheme 13

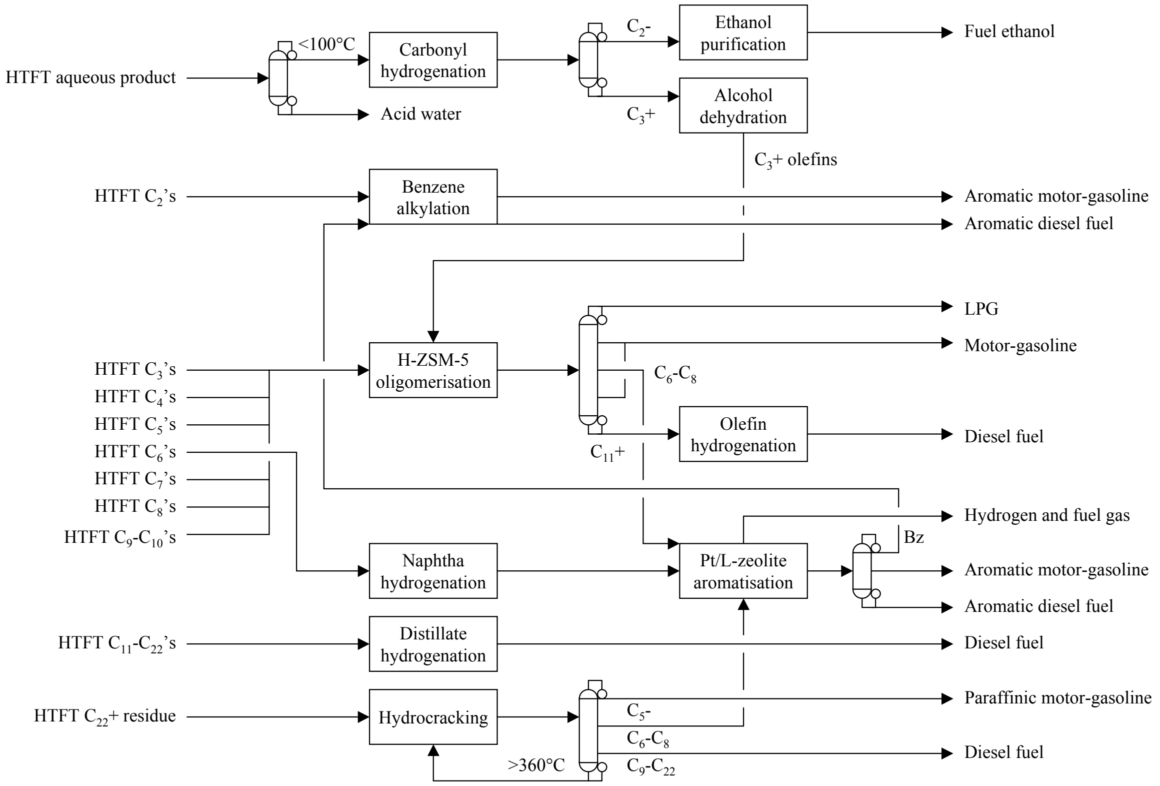

Figure 19. HTFT diesel fuel refinery, flowscheme 13.

Based on the outcome of flowscheme 12, it should also be possible to devise a refinery that would maximise diesel yield and have a high cetane. By exploring this side of the density-cetane-yield triangle, it may be possible to calculate the lever necessary to meet all three requirements simultaneously. The aim of flowscheme 13 was therefore to find a refinery that would maximise diesel yield, but rather have a high cetane than a high density (Figure 19).

In doing so the basic strategy remained the same, but the oligomerisation technology was changed. The pore constrained geometry of the ZSM-5 zeolite is known to limit the degree of branching of the oligomers, thereby increasing the cetane number and decreasing the octane number of the distillate and naphtha respectively.(31)

It was possible to obtain a 24:76 split between naphtha and distillate (Table 32), with a distillate yield of 60% being obtained. The overall liquid yield from the refinery design was 89%, but the contribution of LPG to the yield had been much more than in flowscheme 12 (Figure 18).

Table 32. Yield structure of the HTFT diesel fuel refinery shown in Figure 19, which has a liquid fuel yield of 89% (mass) and diesel fuel yield of 60% (mass).

Product	Refinery production			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	87839	116	17470	19.9
Excess fuel ethanol	17624	22	3351	3.8
Jet fuel	0	0	0	0.0
Diesel fuel	299223	372	56099	64.0
LPG	38754	71	10700	12.2
Other products				
Fuel gas	33100			
Unrecovered organics	13307			
Hydrogen	1171			
Water	8982			
Σ	500000	580	87619	100

The present design (Figure 19) showed that even with a good cetane distillate from H-ZSM-5 oligomerisation, the cetane number of the base stock (cetane around 51-55) was lowered significantly by the inclusion of aromatics in the diesel fuel (Table 33). The diesel fuel made neither cetane nor density specifications. Furthermore, the considerably lower octane number of the motor-gasoline fraction from H-ZSM-5 based oligomerisation caused the motor-gasoline to fail specifications on numerous accounts (Table 33). Even the inclusion of a C_5 hydroisomerisation, as in flowscheme 12 (Figure 18), failed to remedy the situation (Table 33).[s]

This clearly indicated that ASA based oligomerisation is a better technology for distillate production in a Fischer-Tropsch refinery than H-ZSM-5 based oligomerisation, since the distillate yield is better, the motor-gasoline almost meets specification (aromatics content of 38% exceeding 35% limit) and the diesel meets the density specification. It also demonstrated the importance of C_5 hydroisomerisation technology in upgrading octane-constrained motor-gasoline, resulting in a 6 RON gain in this specific instance.

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[s] Further incremental improvements in motor-gasoline quality can be achieved by blending in ethanol (5% maximum) and butanes (vapour pressure 60 kPa maximum) in tandem with increasing the ethyl benzene inclusion (35% aromatics maximum). However, none of the above results in a motor-gasoline that comes close to meeting the octane number specification.

Table 33. Diesel fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 19, as well as a design with a C_5 hydroisomerisation unit added as in Figure 18.

Fuel properties	Refinery as in Figure 19	Refinery with C_5 hydroisomerisation	Fuel specification	
Diesel fuel			*Euro-4*	
Density (kg·m^{-3})	805	805	820-845	Range
Cetane number	42	42	51	Min
Motor-gasoline			*Euro-4*	
RON	81	87	95	Min
MON	77	82	85	Min
Vapour pressure (kPa)	39	46	60	Max
Density (kg·m^{-3})	759	757	720-775	Range
Olefins (vol %)	33.4	13.9	18	Max
Aromatics (vol %)	35.0	34.8	35	Max
Oxygenates (vol %)	0.0	0.0	15	Max
Benzene (vol %)	1.1	1.1	1	Max
Ethanol (vol %)	0.0	0.0	5	Max

5.3. LTFT diesel fuel refinery development

Commercial LTFT based GTL plants that employ hydroprocessing as the only conversion type can achieve a distillate selectivity of around 70% with a cetane number exceeding 70.(4) The base stock is density constrained, with the density being around 780 kg·m^{-3}. The point that was made during the discussion of HTFT syncrude refining to diesel fuel is therefore equally valid for LTFT syncrude, namely, that it is better to use LTFT syncrude in combination with material derived from other sources, such as crude oil(41) and coal pyrolysis products, in order to meet diesel specifications. However, when a standalone LTFT refinery design for maximum diesel fuel production is considered, the main challenge is to increase the density of the diesel fuel.

On a conceptual level it is important to retain the cetane advantage of the linear paraffin rich LTFT syncrude. This can be achieved by focussing on a carbon number reduction strategy to convert most of the waxy material into the heavy diesel fuel range (260-

360°C) by mild hydrocracking. Hydroisomerisation of the linear paraffins that takes place in tandem with hydrocracking is beneficial in two ways, namely, to improve the cold flow properties and to increase the density slightly (Figure 16b). This could create a base stock with good cetane number (60-70) and reasonable density (790-800 kg·m^{-3}), which may just be good enough to upgrade with alkyl aromatics to meet the density specification, while not decreasing the cetane number too much (Figure 20).

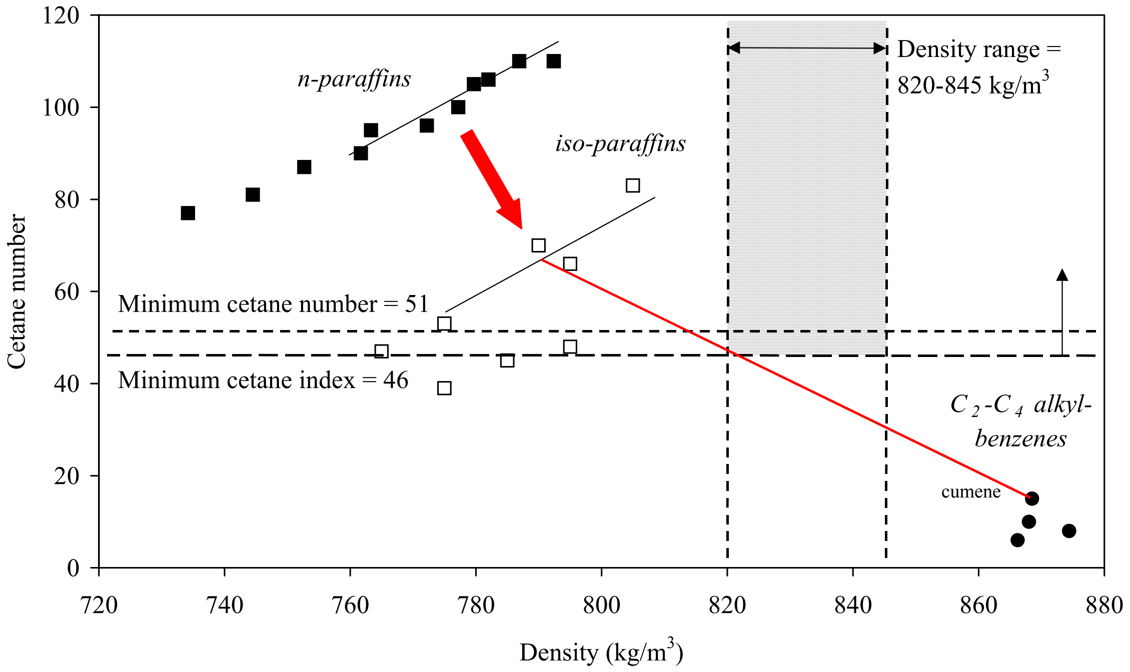

Figure 20. Graphic illustration of a potential refining strategy for the production of diesel fuel from LTFT syncrude that meets fuel specifications.

This is quite important, since a refinery design based on such a concept does not require unconventional refining technologies[t] and may be achievable in practice. Nevertheless, it is clear that alkyl aromatics are not a particularly good compound class to improve density. Furthermore, there will be a yield reduction associated with this approach, since the kerosene range material is not included in the diesel fuel.

The kerosene range material may be used for jet fuel, should enough aromatics be produced to meet the aromatics specification. The product from hydrocracking will be isomerised and is a very good base stock for jet fuel, as was seen in flowscheme 10. The same cannot be said of the motor-gasoline. It is expected that significant refining effort will be required to upgrade the naphtha to motor-gasoline.

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[t] The use of the UOP Pacol process (paraffin conversion to olefin) in combination with LAB (linear alkyl benzene) production can theoretically be considered as means of producing good cetane, high density material, but it would be quite expensive and large volumes would be required.

By discussing the refining pathways for diesel fuel production from LTFT syncrude on a carbon number basis, further constraints emerge:

a) *Residue (C_{22}+).* The key conversion step in the refinery is the hydrocracking of wax to distillate. Since the aim is to maximise the 260-360°C fraction, the hydrocracker design and operation will have to limit material being lost to the kerosene and naphtha range.

b) *C_{15}-C_{22} distillate.* Unlike hydrotreated HTFT distillate, hydrotreating of this LTFT fraction yields a diesel with a very high cetane number, a low density and poor cold flow properties on account of its high linear paraffin content. It has already been shown that some of these shortcomings can be overcome by hydroisomerisation. This can be accomplished by feeding this fraction to a hydrocracker, but limiting its contact time to reduce cracking losses.

c) *C_{11}-C_{14} kerosene.* The most efficient refining pathway for the kerosene is probably hydroisomerisation in a hydrocracking unit operated in such a way that cracking losses are minimised. In this way the freezing point specification of the jet fuel will be met. The main disadvantage of this approach in the context of maximum diesel fuel refining is that it labels material in the kerosene range as a final jet fuel product, with no further conversion of kerosene to diesel fuel. Arguably this material can be included in the diesel fuel, but its inclusion will be detrimental to cetane and density, which are the main reasons for considering this cut separately. One of the options available is to oligomerise the kerosene range olefins (straight run LTFT kerosene contains about 50% olefins) with the naphtha range olefins to produce distillate. Yet, to fully exploit the kerosene range material, both the olefins and the paraffins will have to be targeted. Two possible refining pathways that can be considered are aromatisation (needed for density) and catalytic cracking (to produce olefins for alkylation and oligomerisation).

d) *C_9-C_{10} naphtha.* This fraction can be hydrotreated and used as jet fuel. However, similar arguments as raised for the C_{11}-C_{14} kerosene fraction are applicable to this material. This fraction may be refined in the same way as the C_{11}-C_{14} cut.

e) *C_3-C_8 naphtha.* The naphtha range material is the source of feed for aromatisation, aromatic alkylation and oligomerisation. The allocation of the various cuts will depend on the refinery design. It is suffice to state that balancing this allocation will be an important aspect of a diesel fuel refinery design.

As in most of the previous LTFT refinery designs, the recovery of C_2 hydrocarbons and oxygenates dissolved in the aqueous product are not considered. It is in principle possible to refine these fractions (for example flowscheme 10), but unless the product slate specifically calls for it, it is not considered cost effective.

5.4. LTFT diesel fuel refinery flowschemes

5.4.1. Flowscheme 14

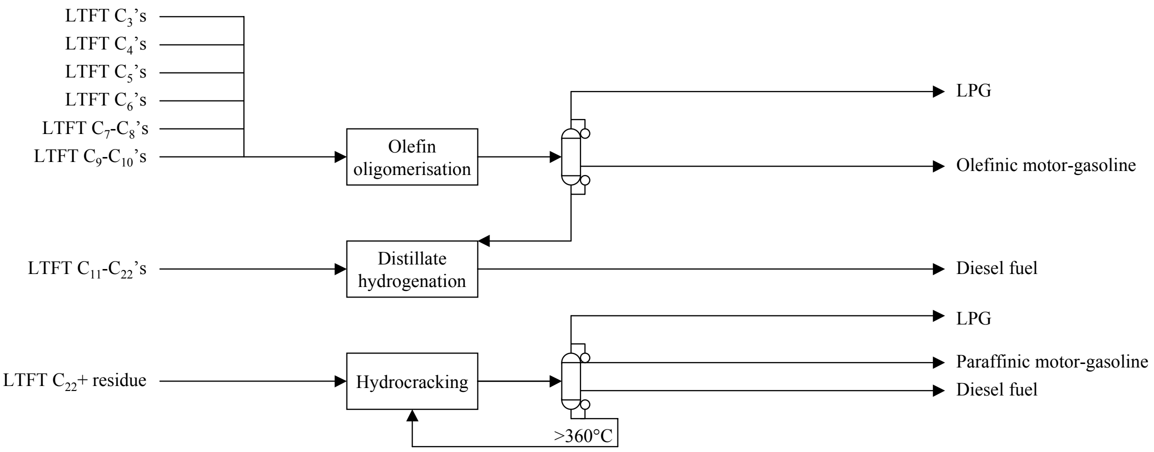

Figure 21. LTFT diesel fuel refinery, flowscheme 14.

The aim of this refinery design (Figure 21) is to establish a base case for LTFT diesel fuel production by maximising the diesel yield when not much attention is paid to the properties of the diesel fuel. Wax hydrocracking, distillate hydrotreating and naphtha oligomerisation are combined to force the carbon number distribution into the distillate boiling range. This is a slightly more complicated refinery design than presently used for commercial LTFT GTL plants that achieve 70% diesel selectivity.

Two oligomerisation technologies have been evaluated for the conversion of the C_3-C_{10} olefins to naphtha and distillate, namely H-ZSM-5 based and ASA based. The properties and yield structure of these two processes differ, although both are considered distillate production processes. The C_{11}-C_{22} distillate fraction is only hydrotreated in order to maximise the distillate yield, full-knowing that the cold flow properties of this product will be poor. The heavier material (heavier than C_{22}) is hydrocracked to produce mainly distillate. The refinery design therefore makes use of carbon number growth, as well as carbon number reduction technologies to maximise distillate yield.

The impact of the oligomerisation technology selection was evaluated, which is reflected in the yield structure (Table 34). The refinery designs using H-ZSM-5 and ASA based oligomerisation process had distillate selectivities of 78% and 76% respectively, indicating the benefit of including a carbon number growth technology to move some material from the naphtha into the distillate boiling range. The diesel yield was 69%.

Table 34. Yield structure of the LTFT diesel fuel refinery shown in Figure 21, with ZSM-5 and ASA based olefin oligomerisation technologies. The refineries have a liquid fuel yield of 94% (mass) and diesel fuel yield of 69% (mass).

Product	H-ZSM-5 based refinery				ASA based refinery			
	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)	($kg \cdot h^{-1}$)	($m^3 \cdot h^{-1}$)	(bpd)	(vol %)
Liquid fuels								
Motor-gasoline	89848	127	19132	20.1	98123	139	20940	22.1
Jet fuel	0	0	0	0.0	0	0	0	0.0
Diesel fuel	347030	446	67382	70.8	343927	440	66431	70.0
LPG	31238	57	8644	9.1	27095	50	7498	7.9
Other products								
Fuel gas	11375				10287			
Unrecovered organics	22396				22396			
Hydrogen	-3202				-3144			
Water	1316				1316			
Σ	500000	630	95159	100	500000	628	94870	100

Table 35. Diesel fuel and motor-gasoline quality from the LTFT diesel fuel refinery shown in Figure 21 illustrating the impact of oligomerisation technology selection, namely H-ZSM-5 versus ASA.

Fuel properties	Refinery in Figure 21		Fuel specification	
	H-ZSM-5	ASA		
Diesel fuel			*Euro-4*	
Density ($kg \cdot m^{-3}$)	777	782	820-845	Range
Cetane number	78	75	51	Min
Motor-gasoline			*Euro-4*	
RON	28	41	95	Min
MON	26	31	85	Min
Vapour pressure (kPa)	19	33	60	Max
Density ($kg \cdot m^{-3}$)	709	707	720-775	Range
Olefins (vol %)	22.4	46.4	18	Max
Aromatics (vol %)	0	0	35	Max
Oxygenates (vol %)	0	0	15	Max
Benzene (vol %)	0	0	1	Max
Ethanol (vol %)	0	0	5	Max

The oligomerisation technology selection influenced the properties of the products too (Table 35). In both instances the distillate has a cetane number better than 70 and density around 780 kg·m^{-3}, typical of commercial LTFT GTL distillate. Likewise, both H-ZSM-5 based and ASA based refinery designs resulted in a naphtha with poor motor-gasoline quality. The difference in the olefinic motor-gasoline quality between the ASA based (better of the two) and H-ZSM-5 based oligomerisation processes are directly reflected in the properties of the motor-gasoline from the refinery. It is consequently clear why commercial LTFT GTL naphtha is used as naphtha cracker feedstock.

5.4.2. Flowscheme 15

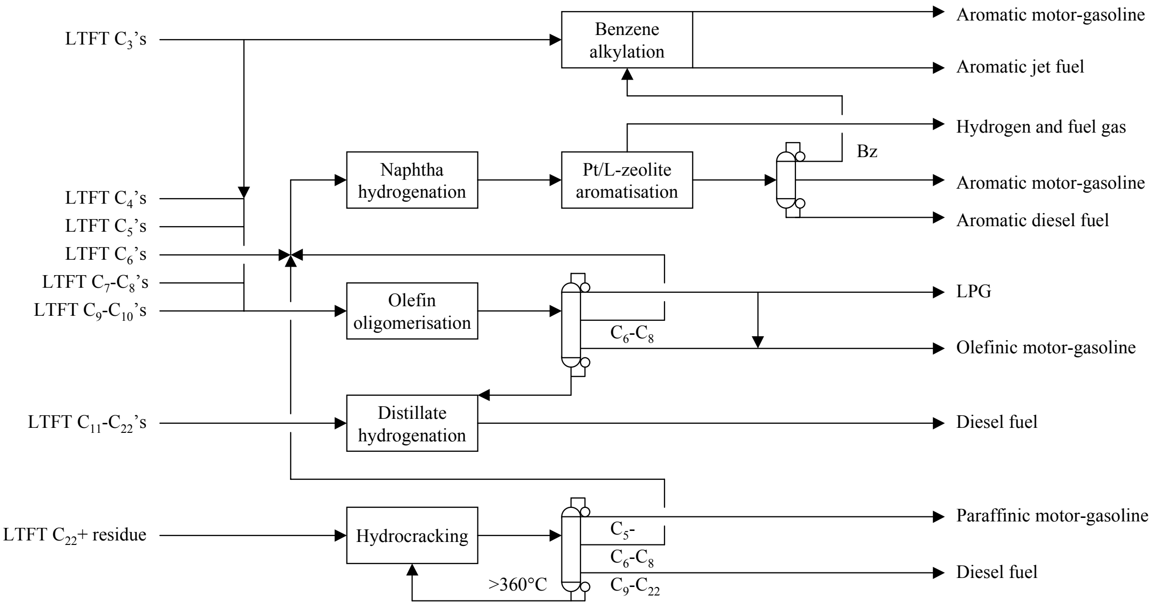

Figure 22. LTFT diesel fuel refinery, flowscheme 15.

The absence of an aromatisation unit in flowscheme 14 (Figure 21) makes the refinery dependent on hydrogen from the Fischer-Tropsch gas loop (Table 34). The inclusion of an appropriate aromatisation unit will not only make the refinery self-sufficient in terms of hydrogen, but also provide aromatics to improve the motor-gasoline quality and increase the diesel density. Furthermore, by converting some of the naphtha into aromatics, the diesel yield may be improved. In this refinery design (Figure 22) these premises were explored by incorporating an aromatisation unit and an aromatic alkylation unit with the objective of increasing the diesel yield beyond that of flowscheme 14, while improving the fuel quality.

It was found that the combination of a platinum promoted non-acidic L-zeolite based aromatisation technology with SPA based cumene production achieves the aforementioned objective. The C_6 LTFT syncrude and C_6-C_8 naphtha fractions from hydrocracking and oligomerisation are used as feed to the aromatisation process, which is benzene selective. The benzene is then alkylated with the LTFT C_3's that is rich in propene, to produce mainly cumene. Although a SPA based cumene process has been selected for benzene alkylation in this design, a slightly better diesel yield is possible if a zeolite-based technology is selected, on account of its lower mono-alkylation selectivity. The rest of the refinery design is similar to flowscheme 14.

The yield structure of the refinery (Table 36) shows that the aim to improve distillate yield was met, with a distillate selectivity of 80% and overall diesel yield 76%. The quality of the naphtha and density of the distillate were also improved (Table 37), but both were far from meeting fuel specifications. Relative to flowscheme 14, the small increase in diesel density (from 782 to 785 $kg{\cdot}m^{-3}$) that was found, was accompanied by a much larger decrease in cetane number (from 75 to 70). This does not bode well for the possibility to refine syncrude in such a way that operation can be achieved in the small operating window shown in Figure 20 where diesel specifications can theoretically be met.

Table 36. Yield structure of the LTFT diesel fuel refinery shown in Figure 22, which has a liquid fuel yield of 93% (mass) and diesel fuel yield of 76% (mass).

Product	Refinery production			
	($kg{\cdot}h^{-1}$)	($m^3{\cdot}h^{-1}$)	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	52395	70	10574	11.5
Jet fuel	0	0	0	0.0
Diesel fuel	382193	487	73477	79.7
LPG	29283	54	8164	8.9
Other products				
Fuel gas	12785			
Unrecovered organics	22396			
Hydrogen	-369			
Water	1316			
Σ	500000	611	92214	100

Table 37. Diesel fuel and motor-gasoline quality from the HTFT diesel fuel refinery shown in Figure 22.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	785	820-845	Range
Cetane number	70	51	Min
Motor-gasoline		*Euro-4*	
RON	77	95	Min
MON	64	85	Min
Vapour pressure (kPa)	33	60	Max
Density (kg·m^{-3})	748	720-775	Range
Olefins (vol %)	39.4	18	Max
Aromatics (vol %)	26.0	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.6	1	Max
Ethanol (vol %)	0.0	5	Max

5.4.3. Flowscheme 16

The quality of the motor-gasoline in flowscheme 15 (Figure 22 and Table 37) is quite poor and despite the limited volume being produced, the refinery complexity may have to be increased in order to meet motor-gasoline specifications. The lowest octane material is typically the heaviest motor-gasoline compounds (C_9-C_{10}), which fall within the kerosene range. Motor-gasoline quality can therefore be improved by producing jet fuel. Diesel fuel quality can likewise be improved by producing jet fuel, since the lightest diesel fuel compounds (C_{11}-C_{14}) have the lowest density and cetane number. The C_{11}-C_{14} material also falls within the kerosene range. However, using the kerosene range material for jet fuel will inevitably reduce the diesel fuel yield, thereby posing a trade-off between yield and overall fuel quality.

In flowschemes 14 and 15 the fuel quality was deliberately ignored in order to maximise diesel fuel production and this design (Figure 23) is an attempt to redress the quality deficiency.

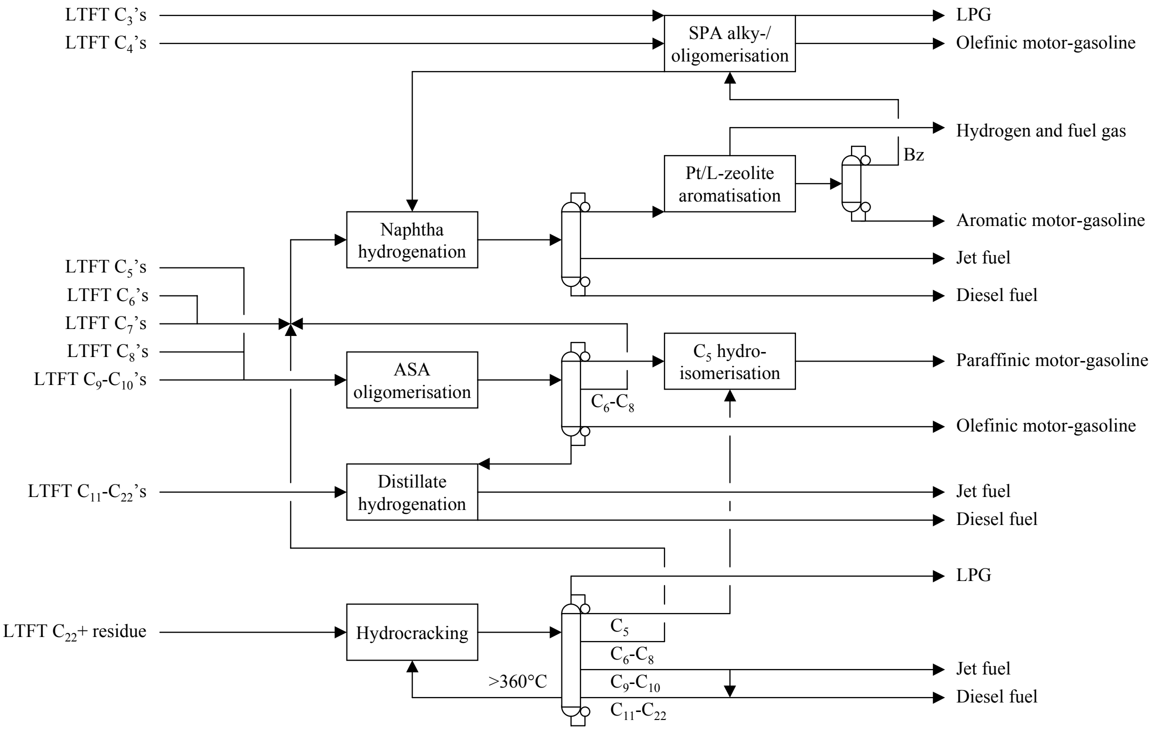

Figure 23. LTFT diesel fuel refinery, flowscheme 16.

Table 38. Yield structure of the LTFT diesel fuel refinery shown in Figure 23, which has a liquid fuel yield of 92% (mass) and diesel fuel yield of 69% (mass).

Product	Refinery production			
	(kg·h^{-1})	(m^3·h^{-1})	(bpd)	(vol %)
Liquid fuels				
Motor-gasoline	72183	97	14617	15.8
Jet fuel	18078	23	3518	3.8
Diesel fuel	345119	442	66649	72.2
LPG	27313	50	7504	8.1
Other products				
Fuel gas	13866			
Unrecovered organics	22505			
Hydrogen	-484			
Water	1420			
Σ	500000	611	92288	100

To improve the octane number of the motor-gasoline a C_5 hydroisomerisation unit was included in the refinery design. With the C_6-C_8 naphtha being used as aromatisation feed and the C_9-C_{10} naphtha being used as jet fuel, the motor-gasoline became very light. Good octane C_6-C_8 motor-gasoline had to be produced, which is why SPA based oligomerisation was included in the refinery design. In order not to duplicate oligomerisation units (both SPA and ASA), it was investigated whether only SPA oligomerisation, or a combined SPA oligomerisation and benzene alkylation unit could be used. The latter proved to be a better design optimisation and the final refinery design (Figure 23) required only one more conversion unit than in flowscheme 15 (Figure 22).

As expected, the diesel yield (Table 38) was lower than in the previous design (69% compared to 76%), but it was similar to that of flowscheme 14. The fuel quality (Table 39) was significantly better, with the motor-gasoline and jet fuel meeting fuel specifications. Only the diesel fuel did not meet fuel specifications and resembled a typical commercial LTFT GTL distillate with better than 70 cetane number and density of around 780 kg·m^{-3}.

Table 39. Diesel fuel, jet fuel and motor-gasoline quality from the LTFT diesel fuel refinery shown in Figure 23.

Fuel properties	Refinery	Fuel specification	
Diesel fuel		*Euro-4*	
Density (kg·m^{-3})	782	820-845	Range
Cetane number	74	51	Min
Jet fuel		*Jet A-1*	
Density (kg·m^{-3})	776	775-840	Range
Aromatics (vol %)	17.9	8-25	Range
Flash point (°C)	38	38	Min
Vapour pressure (kPa)	1.2	-	
Motor-gasoline		*Euro-4*	
RON	95	95	Min
MON	87	85	Min
Vapour pressure (kPa)	60	60	Max
Density (kg·m^{-3})	745	720-775	Range
Olefins (vol %)	18.0	18	Max
Aromatics (vol %)	32.8	35	Max
Oxygenates (vol %)	0.0	15	Max
Benzene (vol %)	0.5	1	Max
Ethanol (vol %)	0.0	5	Max

The refinery design reiterated the difficulty inherent in satisfying the density-cetane-yield triangle. It also illustrated that it is possible to produce on-specification motor-gasoline and jet fuel in a Fischer-Tropsch distillate refinery, but that Fischer-Tropsch syncrude is not suited for the production of on-specification diesel fuel.

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APPENDIX A

Design basis for conceptual refinery development

Background

The modelling of a Fischer-Tropsch refinery is somewhat different to the modelling of a crude oil refinery, since the physical property correlations and distillation profile based separations are not directly applicable to syncrude. This situation is exacerbated by the need to consider the modified conversion technologies to make it suitable for Fischer-Tropsch syncrude, which is one of the aims of the present study. It was therefore necessary to provide all the data, ranging from the characterisation of the different syncrude fractions and syncrude specific conversion profiles for the different technology blocks, up to the fuel properties of the synthetic fuels. Needless to say, the decision on the platform to use for the refinery design and modelling was crucial to the success of this study, since one could easily miss the wood for the trees.

Modelling platform

Three different modelling platforms were considered for the study, namely a process simulation package, spreadsheet and custom designed software. The decision was based on the following train of thought:

a) *Process simulation package*. The process simulation packages currently available on the market, such as those from AspenTech™ and SimSci™, are very powerful. Complex flow sheets with numerous recycles and detailed compound-based calculations can easily be developed. Conversion calculations can be coded and linked into the simulation package as custom function blocks, enabling proper Fischer-Tropsch specific calculations. These packages are geared for the calculation of mass and energy balances with realistic separation steps, rather than for the calculation of fuel properties, although it is possible to do so. However, the emphasis of the software is to provide an accurate simulation or representation of a process and much effort has to be spent on selecting appropriate thermodynamic models, compound or pseudo-compound based feed compositions and separation steps. This was not the aim of the investigation, which is focussed on syncrude specific conversion and fuels refining. Furthermore, the information that is necessary to build custom conversion steps for syncrude is not always available in the format required by the process simulation package. The level of detail necessary for conceptual refinery development, and that required and provided by a process simulation package, is clearly ill matched.

b) *Spreadsheet.* In a spreadsheet all the information and calculations necessary to build a refinery model has to be provided. It is not possible to calculate any of the separation steps with the level of detail that is possible in a process simulation package, nor is it possible to incorporate such detailed physical and thermodynamic property calculations. However, the complexity of the refining blocks can easily be adapted to the information available and the compound based description can be varied between blocks. It is also possible to have more information on the assumptions available "at a glance" in a spreadsheet than in a process simulation package, making the model far more accessible. No special coding is necessary, although Visual Basic routines can be incorporated if such complexity is needed. As a tool for focussing on refining concepts, rather than slogging out the finer details of separation steps and heat integration, a spreadsheet can be an excellent tool.

c) *Custom software.*[u] With custom software it is possible to achieve some compromise between the detail (and restrictions of such detail) found in process simulation packages and the much lower level of detail inherent in spreadsheet based modelling. Unfortunately it may also result in having the worst of both worlds, since the user-interface can easily be the programming interface and much time can be wasted on coding aspects of the model that are already provided by process simulators and spreadsheets.

It was decided to make use of a spreadsheet for modelling the refinery designs. This decision was made mainly on the ability to match conversion blocks with different levels of detail and the ease of reviewing assumptions at a glance. In this way the focus remained on the conversion technologies and their interaction, with the tacit assumption that the separation steps implied by the product routings can be achieved in practise. To mitigate this shortcoming, the implied separations were kept simple and conceptual designs were steered clear of configurations implying fancy tricks of separation. The plausibility of the implied separation steps was qualitatively checked for all designs and in most cases separation involved only carbon number cuts. Where more involved separations were needed, such as in hydroisomerisation, the availability of the required technology has been confirmed from literature.

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[u] Software for estimating physical properties was developed (ChemDB Ver.2.00).

Syncrude feed definition

The composition of the HTFT syncrude has been based on Sasol Synfuels (Secunda, South Africa) production data, using the averaged values over the period 1 January 1998 to 30 April 1998. The source data[v] included detail at compound level (representative compounds); this level of detail was not used. Compound specific detail was only retained for the C_1-C_3 hydrocarbons and aqueous chemicals. For the C_4-C_8 carbon range, the flows were lumped as *n*-paraffins, iso-paraffins, *n*-olefins, iso-olefins, aromatics and oxygenates. For higher carbon numbers, compounds were classified only as paraffins, olefins, aromatics or oxygenates. The C_9-C_{10}, C_{11}-C_{14}, C_{15}-C_{22} and C_{22}+ compounds were lumped.

The composition of the LTFT syncrude has been based on the data for the Sasol China CTL LTFT base case.(42) The source data, which implies an Fe-based LTFT process, such the commercial SSBP at Sasol 1 (Sasolburg, South Africa), was simplified in a similar way to the HTFT syncrude data. It should nevertheless be noted that the source data was of a lower level of detail compared to the HTFT source data.

Due to reasons of confidentiality,[w] this data may unfortunately not be provided. It can nevertheless be noted that it similar to the syncrude compositions previously given (HTFT in Chapter VI, Table 12 and LTFT in Chapter VI, Table 10).

Capacity

To ensure that all the conceptual refinery designs are on the same feed basis, the Fischer-Tropsch syncrude production has been scaled to a flow rate of 500 $t \cdot h^{-1}$ of C_2 and heavier material. This is roughly equivalent to a 100 000 bpd crude oil equivalent refinery.[x] Reference to refinery yield is always expressed on a mass basis relative to the C_2 and heavier syncrude feed to the refinery. Is allows refinery comparisons, but implies that the total Fischer-Tropsch syncrude production may be different, depending on the methane-make.

It should also be noted that the impact of the refinery hydrogen requirement has not been taken into consideration. This is not an omission. Translation of the hydrogen surplus or deficiency into increased or decreased syncrude production requires detailed Fischer-

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[v] Sasol Synfuels PI data historian that logs the field instrument values and compound based analyses from the quality control laboratories.

[w] The Sasol Technology Intellectual Property group requested that this data be removed from the thesis.

[x] The conversion of barrels per day (bpd) crude oil equivalent = 0.1589873 m^3 per day syncrude. Since these numbers are on a volumetric basis, they are density dependent.

Tropsch gas loop modelling, which falls outside the scope of the present work. The actual refinery yield values can therefore not be directly compared if the refinery hydrogen requirements are widely differing.

Fuel specifications and property assumptions

The Euro-4 standards (Chapter II) have been used as benchmark to determine whether the motor-gasoline and diesel fuel meet fuel specifications. For jet fuel the international Jet A-1 specifications (Chapter II) were used. However, not all fuel properties can be calculated accurately, which is reflected by the limited property values reported in this chapter. For example, there is no accurate estimation method for freezing point, a key property for jet fuel. It was consequently necessary to manually check that the compounds included in the jet fuel were likely to result in a fuel that met the freezing point specification (Table 19).

The fuel properties reported for the refinery designs have been calculated by linear blending of the fuel components on a volumetric basis (Equation A1), where V_j is the volume of component j and X_j is the fuel property of the component. The estimated fuel properties are therefore only indicative, since this is an approximation of the non-linear blending nature of fuel properties found in practice.

$$X = \frac{\sum X_j V_j}{\sum V_j} \qquad \ldots \text{(A1)}$$

The ASTM DS 4B tables(21) were used for all compound specific property values except cetane numbers, which were taken from the paper by Santana and co-workers.(28) In cases where the product was similar to that for which syncrude specific property data is known, the property data for the specific conversion process was used.(10)(23)(24) The fuel property values for oligomerisation products, which played an important role in all refinery designs, were feed composition dependent in some instances and had to calculated. The assumptions made for modelling are listed in Table A1.

The octane values of hydrogenated motor-gasoline from SPA oligomerisation are very sensitive to the feed composition, unlike the octane values of unhydrogenated motor-gasoline, which are feed insensitive. The feed significantly affects the degree of branching and carbon number distribution of the product. The hydrogenated motor-gasoline RON

(Equation A2) and MON (Equation A3) were calculated based on a correlation developed from literature data,(14) showing the dependence on the fraction of propylene (f_{C3}), iso-butene (f_{iC4}) and pentenes (f_{C5}) in a butene feed:

$$RON = 86 - 37.\left[f_{C3} + \frac{f_{C5}}{2} \right] + 25.\left[\exp\left(f_{iC4} - 0.08 \right) - 1 \right] \quad \text{... (A2)}$$

$$MON = 86 - 30.\left[f_{C3} + \frac{f_{C5}}{2} \right] + 10.\left[\exp\left(f_{iC4} - 0.08 \right) - 1 \right] \quad \text{... (A3)}$$

Table A1. Fuel property values of the olefin oligomerisation products that were used for refinery modelling.

Refinery source	Density (kg·m^{-3})	RON	MON	RVP (kPa)	Flash pt. (°C)	Cetane number
Butanes	581.4	94.7	90.6	380	-	-
SPA motor-gasoline (unhydrogenated)	719.6	95.9	82.1	5.5	-	-
SPA motor-gasoline (hydrogenated)	720	Eq. A2	Eq. A3	5.5	-	-
SPA kerosene	750	-	-	1.2	40	-
SPA distillate	760	-	-	-	-	30
ASA motor-gasoline (unhydrogenated)	Eq. A4	Eq. A5	Eq. A6	72	-	-
ASA motor-gasoline (hydrogenated)	700	80	80	72	-	-
ASA C_9-C_{10} kerosene	760	-	-	1.2	40	-
ASA C_{11}-C_{16} kerosene	790	-	-	0.1	73	-
ASA distillate	810	-	-	-	-	29
ZSM-5 motor-gasoline (unhydrogenated)	738	85	75	57	-	-
ZSM-5 motor-gasoline (hydrogenated)	700	55	55	50	-	-
ZSM-5 kerosene	Eq. A7	-	-	1.2	40	-
ZSM-5 distillate	Eq. A8	-	-	-	-	54

A similar situation exists for ASA oligomerisation, but in this instance the octane values of unhydrogenated motor-gasoline is sensitive to the feed composition, while the octane values of hydrogenated motor-gasoline are insensitive enough to assume it to remain constant. The feed does not significantly change the degree of branching of the product, but the paraffin content in the feed lowers the octane value of the unhydrogenated motor-gasoline. Linear correlations for density (Equation A4), RON (Equation A5) and MON

(Equation A6) and were developed from literature data,(43) showing the dependence on the C_3-C_6 olefin fraction ($f_{C3\text{-}C6}$) in the feed:

$$\rho = 707 \cdot f_{C3\text{-}C6} + 711 \cdot (1 - f_{C3\text{-}C6}) \quad \text{... (A4)}$$

$$RON = 93 \cdot f_{C3\text{-}C6} + 80 \cdot (1 - f_{C3\text{-}C6}) \quad \text{... (A5)}$$

$$MON = 71.5 \cdot f_{C3\text{-}C6} + 60 \cdot (1 - f_{C3\text{-}C6}) \quad \text{... (A6)}$$

The base octane values for ZSM-5 oligomerisation are listed in table A2. Similarly to the ASA derived oligomers, the octane numbers of the motor-gasoline were dependent on the feed paraffin content and had to be calculated on a compound basis.

More general correlations were derived from literature data(31) to calculate the density of the kerosene (Equation A7) and the distillate (Equation A8) from an H-ZSM-5 oligomerisation process. The density was related to the kerosene fraction of the distillate (f_{kero}) before fractionation:

$$\rho_{kero} = 748.5 + 40 \cdot f_{kero}\text{ , valid for } f_{kero} = \{0 \,..\, 0.5\} \quad \text{... (A7)}$$

$$\rho_{distillate} = 800 - 40 \cdot (0.5 - f_{kero})\text{ , valid for } f_{kero} = \{0 \,..\, 0.5\} \quad \text{... (A8)}$$

Although not explicitly stated, the property values for all conversion processes were adjusted if the feed contained inert compounds that would significantly affect the fuel properties.

Conversion technologies

The conversion data reported in literature, as discussed in Chapter VII, were used for the modelling of the conversion units.

Mass balance closure

Proper mass balance closure was ensured for every conversion unit, as well as for the refinery as a whole. In some tables it may seem as if mass balance closure was not obtained, but this is only due to rounding. In instances where it is known that some material had to be purged, such material was reported as “Unrecovered organics”. Material not recovered, such as carboxylic acids dissolved in the Fischer-Tropsch aqueous product, was similarly reported as "Unrecovered organics".

Due to the importance of hydrogen in a refinery, as well as the importance of water as by-product from hydroprocessing of Fischer-Tropsch materials, these compounds were listed separately in the mass balance. Hydrogen was recovered only from product streams with a significant hydrogen content. It was assumed that 85% hydrogen recovery is possible, based on Sasol experience, although Chauvel and Lefebvre(44) reported a lower average value (75%). The remainder of the hydrogen was reported as fuel gas. No restrictions were placed on the composition of the fuel gas, which generally consisted of a mixture of hydrogen, methane, ethane and ethylene.

Separation of Fischer-Tropsch primary products

An advantage of Fischer-Tropsch syncrude refining over crude oil refining that has been pointed out,(6) is that the stepwise condensation of the Fischer-Tropsch primary products act as a pre-separation step. This advantage has not been fully exploited in current commercial designs, but a significant energy saving is possible if the designs of the Fischer-Tropsch synthesis block with its stepwise condensation is integrated with the primary separation in the refinery. In the model realistic assumptions were made for product separation,[y] without modelling each separation step as a unit operation. Proper separation design is implied, with inefficiencies in product separation affecting only one carbon number from the cut point.

One assumption that may be considered unrealistic, is the implied separation between methane and C_2 hydrocarbons in the LTFT refinery designs. On account of the high light hydrocarbon production during HTFT synthesis, the inclusion of cryogenic separation in the design is almost implied, but this is not necessarily true for LTFT. The C_2 hydrocarbons from LTFT synthesis are reported as part of the fuel gas, but in practise the C_2 hydrocarbons can be recycled in the Fischer-Tropsch gas loop. The reason for this "unrealistic" assumption during LTFT modelling is purely to enable reporting of all refinery yields in terms of C_2 and heavier syncrude feed. In instances where ethylene conversion technology is specifically used for an LTFT refinery design, the necessary separation will of course be required.

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[y] For example, the separation efficiency for the carbon number separation between C_3 and C_4 took cognisance of the Linde detailed separation efficiency values, namely 0.8% C_3's in C_4 and 1.4% C_4's in C_3.