CHAPTER V

Fischer-Tropsch Syncrude

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

1.   Introduction

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

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[a] The Kaiser Wilhelm Institute for Coal Research was established in 1913 in Mülheim in the Ruhr, Germany. The aim of the research of Fischer and Tropsch was to find a way of making fuels and chemicals from coal-derived gas. Their work only started to yield positive results in the 1920's and the first commercial application of their technology was in 1935 in an atmospheric fixed bed reactor, 10 years after the process was patented.
[b] Ruthenium is also too expensive and scarce to be considered for industrial applications.
[c] Nickel is difficult to use industrially, because nickel is lost as nickel carbonyl, $Ni(CO)_4$.

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

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

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

2.   Fischer-Tropsch catalysis

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

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

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[d] Strictly speaking this is true only if the trace components in the synthesis gas are ignored. Depending on the trace components, further cleaning steps may be required to ensure adequate Fischer-Tropsch catalyst lifetime.
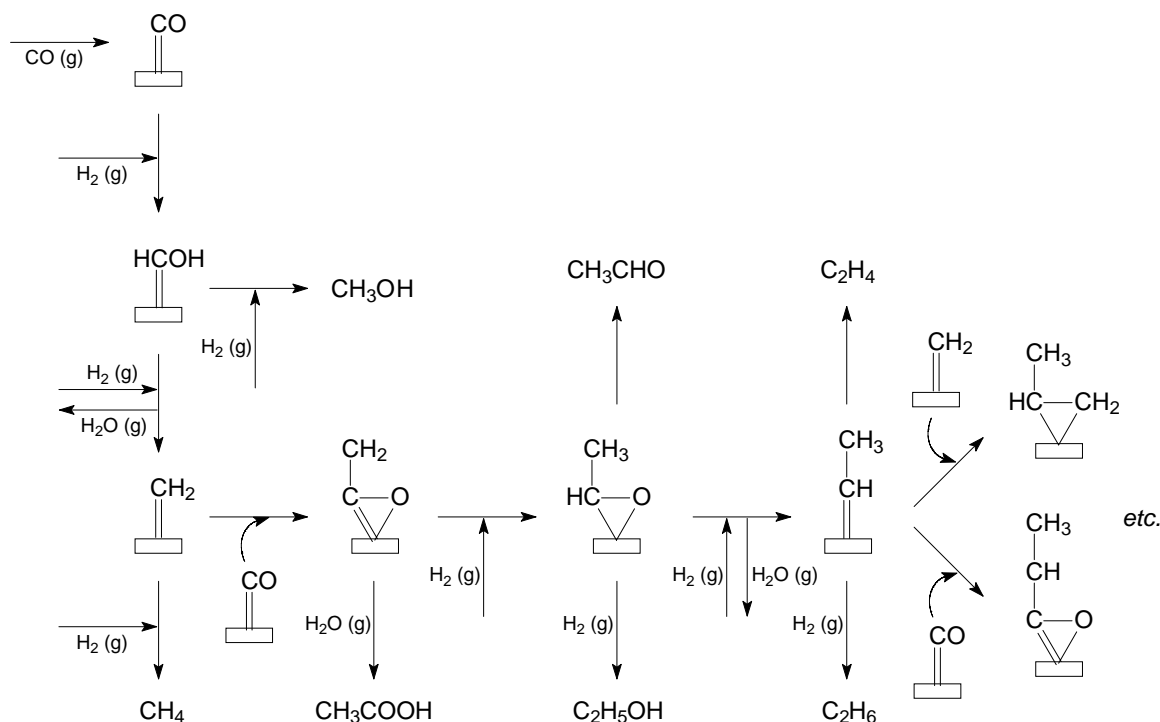
Figure 1. Simplified mechanism of the Fischer-Tropsch reaction showing the formation of the primary products, namely paraffins, olefins, alcohols, aldehydes and carboxylic acids.

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

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

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

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

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

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

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

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

2.1. Catalyst properties

2.1.1. Probability of chain growth

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

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

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

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

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

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

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

2.1.2. Hydrogenation activity

The different metals active for the Fischer-Tropsch reaction have different hydrogenation propensities. Iron is the least active for hydrogenation, followed by cobalt, nickel and

ruthenium. Nickel and ruthenium are both very active methanation catalysts and produce heavy hydrocarbons only at low temperatures.[4] Due to the difference in hydrogenation activity the products from iron based Fischer-Tropsch synthesis are in general more olefinic than those from cobalt based synthesis.

2.1.3. Water gas shift activity

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

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

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

2.1.4. Sensitivity to promoters

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

2.2. Influence of operating conditions

2.2.1. Synthesis gas composition

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

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

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

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

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

2.2.2. Pressure

The reactor pressure and feed gas composition determine the partial pressure of the reagents, hydrogen and carbon monoxide. Since CO is more strongly adsorbed on the catalyst than H_2,

the concentration of CO on the catalyst surface is increased when the pressure is increased. High CO concentration on the catalyst surface promotes chain growth and increases the observed α-value of the catalyst. A high CO concentration also favours CO incorporation and consequently the production of oxygenates.

2.2.3. Temperature

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

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

a) Interconversion of aldehydes, alcohols and carboxylic acids reach equilibrium.

b) Ketone formation by the decomposition of carboxylic acids increases.

c) Iso-alcohol formation by hydrogenation of ketones increases.

d) Alcohol dehydration to produce olefins increases.

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

3. Syncrude composition

Syncrude is produced from synthesis gas and the compounds that can be produced by a Fischer-Tropsch process must therefore be limited to those containing the elements hydrogen, carbon and oxygen. Consequently, Fischer-Tropsch products are either hydrocarbons, or oxygenates. This is reflected in literature on Fischer-Tropsch[4][15][16] that list hydrocarbons (paraffins, olefins and aromatics) and the main oxygenate classes (alcohols, aldehydes, carboxylic acids and ketones) as the only constituents of syncrude. In practise syncrude is

more complex than it would appear from the discussion thus far and many isomers and minor compound classes can be identified (Figure 2). Some compound classes not normally associated with Fischer-Tropsch synthesis, such as cyclic dienes and alkynes, are indeed found in low concentration in the syncrude.
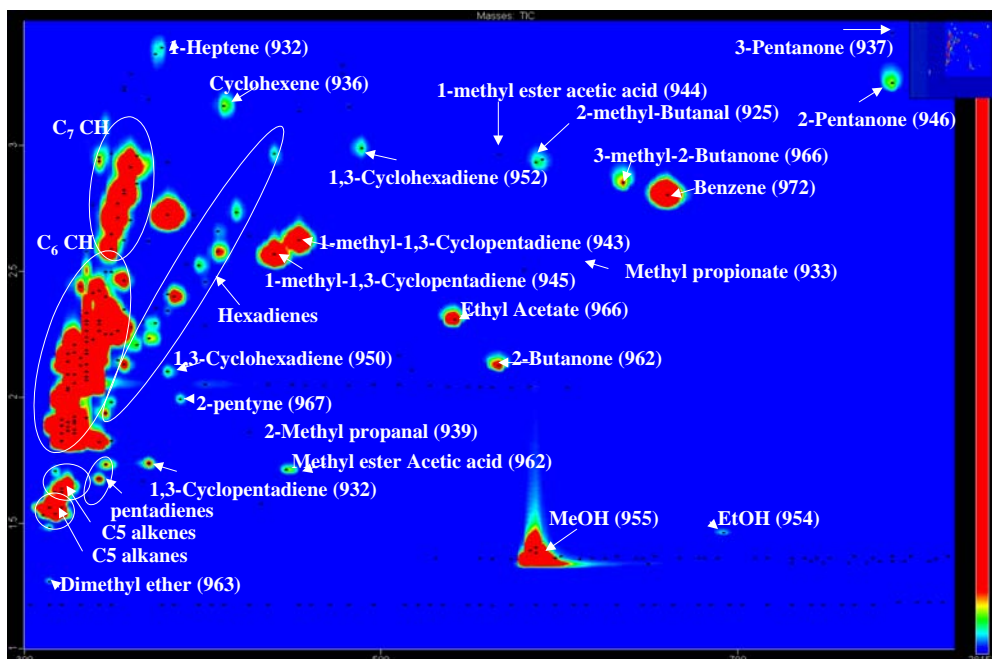

Figure 2. Two dimensional GC-GC-TOFMS chromatogram of C_6/C_7 HTFT derived stabilised light oil. Compound identification is based on similarity index (given in brackets) compared to the mass spectra of known compounds. Separation on the vertical axis is based on boiling point, while separation on the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

3.1. Hydrocarbons

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

a) *Paraffins*. The saturated hydrocarbons are mostly *n*-paraffins, especially the high molecular weight products, like waxes. Branched paraffins are present too and are more prevalent in HTFT processes than in LTFT processes. A mathematical description of chain branching in Fischer-Tropsch synthesis has been given by Weitkamp, et al.[17] that describes data for short chain hydrocarbons well, but the assumptions on which it is based do not hold true for longer chain hydrocarbons. The probability of chain branching does not remain constant, but decreases with increasing chain length and monomethyl branches, randomly

situated along the chain, exceed all other forms of branching by an order of magnitude.[18] Syncrude also contains cyclo-paraffins (naphthenes) in low concentration, typically in the order of 0.1-1% of the total paraffin content.

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

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

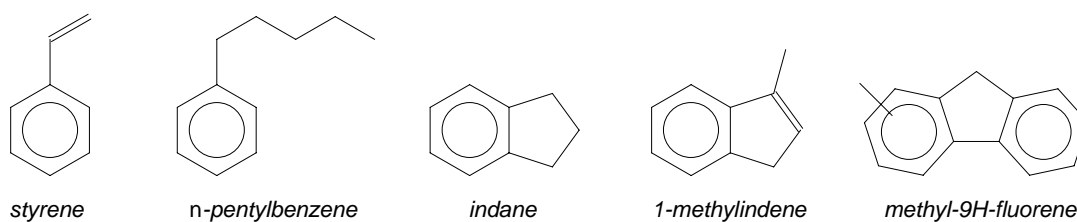| styrene | n-*pentylbenzene* | *indane* | *1-methylindene* | *methyl-9H-fluorene* |

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

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

3.2. Oxygenates

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

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

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

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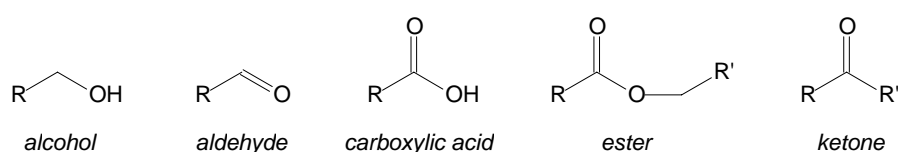

Figure 4. Major oxygenate classes found in Fischer-Tropsch syncrude.

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

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

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

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

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

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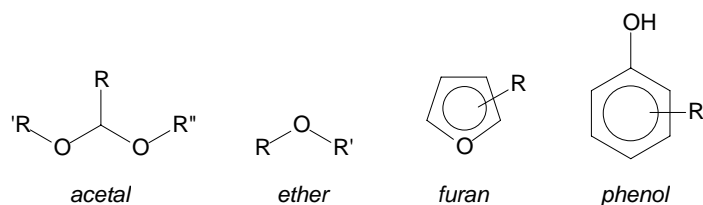

Figure 5. Minor oxygenate classes found in Fischer-Tropsch syncrude.

3.3. Metal containing compounds

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

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

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

4. Properties of commercial syncrudes

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

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

Type	Catalyst	Reactor-type	Technology	Operator	Location
HTFT	Fused Fe	Fluidized bed	Synthol	PetroSA	Mossel Bay, South Africa
HTFT	Fused Fe	Fluidized bed	SAS	Sasol	Secunda, South Africa
LTFT	Precipitated Fe	Fixed bed	ARGE	Sasol	Sasolburg, South Africa
LTFT	Precipitated Fe	Slurry bed	SSBP	Sasol	Sasolburg, South Africa
LTFT	Co-SiO$_2$	Fixed bed	SMDS	Shell	Bintulu, Malaysia
LTFT	Co-Al$_2$O$_3$	Slurry bed	SSBP	Sasol	Ras Laffan, Qatar

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

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

The properties of some commercial syncrudes are given in Table 3.[4][24][25] From this it is clear that catalyst pretreatment and reactor type play significant roles, since a similar catalyst is used in the LTFT ARGE and LTFT SSBP reactors.[26] However, these are not the only parameters differentiating ARGE and SSBP.
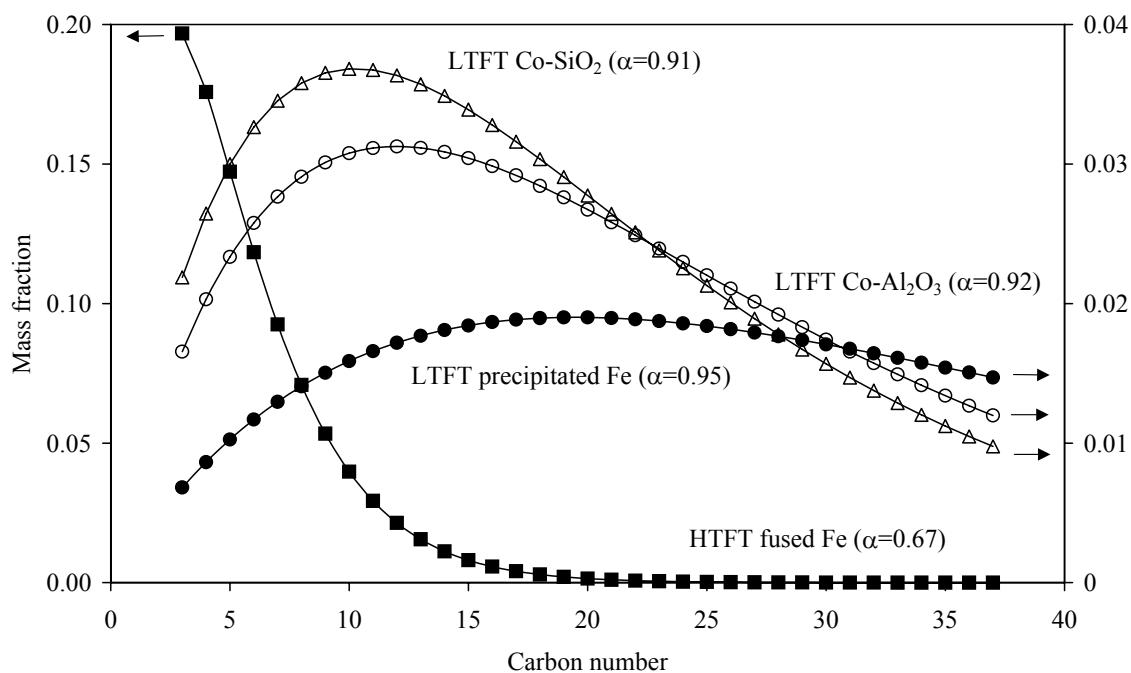
Figure 6. Carbon number distribution of some commercial Fischer-Tropsch technologies.

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

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

5. Comparison of crude oil and syncrude

The composition of crude oil and syncrude differs in some crucial aspects (Table 4). There are obvious differences, with syncrude containing large amounts of olefins and oxygenates, but no sulphur or nitrogen compounds, while crude oil contains no olefins and mostly heavier oxygenates, as well as significant amounts of sulphur and nitrogen compounds. LTFT syncrude contains no aromatics, which is also different to crude oil, while syncrude in general

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has comparatively little naphthenes compared to crude oil. The nature of the metal containing compounds is different and although crude oil may contain associated water, it is a major by-product from Fischer-Tropsch synthesis. The physical properties of crude oil[27] and that of syncrude[28] are also very different.

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

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

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

Something that is less obvious from the comparison in Table 4 is the impact this has on hydrotreating in the refinery. Not only is the focus of hydrotreating different, but also the heat release during hydrotreating.[31][32][33] Crude oil has a hydrodesulphurisation (HDS) and a hydrodenitrogenation (HDN) focus, while syncrude has a hydrodeoxygenation (HDO) and olefin saturation focus. The energy associated with the different compound classes is very different (Tables 5 and 6).[34] Hydrotreating a sulphurous atmospheric residue typically has a heat release of around 450 kJ·kg⁻¹, while hydrotreating a HTFT naphtha has a heat release of around 1000 kJ·kg⁻¹, more than double that of a difficult to hydrotreat crude oil. Heat management during Fischer-Tropsch syncrude refining is consequently much more of an issue than during crude oil refining. This can be viewed in a positive light, since it implies

scope for beneficial heat recovery to improve the overall thermal efficiency of a Fischer-Tropsch refinery. This can be extended to the CO_2 footprint of the refinery, which becomes smaller when the high heat release associated with Fischer-Tropsch syncrude refining is beneficially used.

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

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

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

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

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

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