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Catalysis Today 130 (2008) 439–445

CATALYSIS TODAY

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Hydroprocessing peculiarities of Fischer–Tropsch syncrude

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Abstract

When catalysts developed for crude oil hydroprocessing are used for syncrude, there are syncrude-specific peculiarities to consider. These relate to differences in the nature and abundance of heteroatoms, olefins, metal species, waxes and aqueous products. Some important aspects are (a) heat release during naphtha and distillate hydroprocessing is very high, but wax hydrocracking is almost isothermal; (b) syncrude is sulphur-free and the use of sulphided base-metal hydroprocessing catalysts require the addition of sulphur-containing compounds to the syncrude; (c) oxygenates strongly adsorb on some catalytic surfaces to affect catalytic behaviour; (d) carbonyl–carboxylic acid interconversion and water produced by hydrodeoxygenation (HDO) may result in catalyst degradation by acid and hydrothermal attack; (e) carboxylic acids in syncrude result in equipment corrosion and catalyst leaching; (f) metal carboxylates are the main metal-containing species in syncrude and are not removed by hydrodemetallation (HDM) catalysis, but by thermal decomposition.

Keywords: Hydroprocessing; Fischer–Tropsch syncrude; Refining; Hydrodeoxygenation; Oxygenates; Metal carboxylates; Olefins

1. Introduction

There is a small number of commercial Fischer–Tropsch syncrude based refineries worldwide, namely Sasol 1 (Sasolburg, South Africa), Sasol Synfuels East & West (Secunda, South Africa), PetroSA (Mossel Bay, South Africa), Shell Middle Distillate Synthesis (Bintulu, Malaysia) and Oryx GTL (Ras Laffan, Qatar). The commercial Fischer–Tropsch facilities make use of different technologies and the syncrudes being produced in the different plants are not the same [1]. Considering the small refining market segment that each syncrude type represents, it is not surprising that little technology has been developed specifically for the hydroprocessing of syncrude. This may lead to the erroneous conclusion that hydroprocessing of crude oil and syncrude is similar, considering that the same basic principles and commercial hydroprocessing catalysts are used for both.

Refining of syncrude is easier and can result in a more environmentally friendly refinery design if cognisance is taken of the unique properties of syncrude [2]. This does not imply that a crude oil refining approach cannot be followed, it can, but it is less efficient. However, even in using a crude oil refining approach there are syncrude-specific issues that have to be taken into account. These aspects will be discussed, focussing specifically on their impact on hydroprocessing.

2. Fischer–Tropsch syncrude

The properties of Fischer–Tropsch syncrude are mainly determined by the Fischer–Tropsch catalyst type and operating conditions. There are two main classes of Fischer–Tropsch technology, namely high-temperature Fischer–Tropsch (HTFT) [3] and low-temperature Fischer–Tropsch (LTFT) [4] technology. Although HTFT is presently practised exclusively with a fused iron-based Fischer–Tropsch catalyst in fixed fluidised and circulating fluidised bed reactors, there is much more variation in LTFT practice. At the Sasol 1 facility, two different iron-based LTFT catalysts are used in fixed bed (Arge) and slurry bed (Sasol Slurry Phase Distillate^{TM}) processes, respectively. The Shell Middle Distillate Synthesis facility uses a cobalt-based LTFT catalyst in a fixed bed process and the Oryx GTL plant uses a cobalt-based LTFT catalyst in a slurry bed process.

The syncrude from all Fischer–Tropsch processes is sulphur- and nitrogen-free and contains percentage levels of oxygenates [1]. The nature of the oxygenates is determined

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doi:10.1016/j.cattod.2007.10.006

by both the catalyst type and the operating conditions. Alcohols, aldehydes and carboxylic acids are all primary Fischer–Tropsch products that can be viewed as partially hydrogenated products from the Fischer–Tropsch chain growth step. Ketones and esters are secondary Fischer–Tropsch products formed at more severe operating conditions and are mainly found during HTFT synthesis. Various models have been proposed to describe oxygenate formation during Fischer–Tropsch synthesis and a consensus view has not yet emerged. However, it can be noted that side reactions, such as hydroformylation, play a minor role [5]. The hydrocarbon fraction consists of linear paraffins and linear α-olefins as primary products. Aromatics, branched paraffins, as well as internal and branched olefins are all secondary products, mainly produced during HTFT synthesis. The ratio of paraffins to olefins is determined by the hydrogenation propensity of the Fischer–Tropsch catalyst, with cobalt being more hydrogenating than iron. The carbon number distribution of the syncrude is determined by the chain propagation probability (α-value) of the catalyst. The α-value of HTFT catalysts is generally in the range 0.65–0.70 and is limited by the dew point of the product (higher α-values would cause condensation at synthesis conditions and impair fluidisation of the catalyst). The α-value of LTFT catalysts is generally in the range 0.90–0.95 to maximise distillate and wax production. The carbon number distribution and typical syncrude properties are listed in Table 1 [6,7]. It will be noticed that syncrude contains an oil product and an aqueous product. The latter is often ignored in discussions on Fischer–Tropsch technology, despite being a significant fraction of the total syncrude.

In comparison to crude oil [8], syncrude is clearly different in terms of its heteroatom composition, olefin content and aqueous product. Less obvious are the differences in heavy end composition and the nature of dissolved metals. In the subsequent discussion on the hydroprocessing of Fischer–Tropsch syncrude, the impact of these differences will be highlighted.

Table 1
The carbon number distribution of high-temperature Fischer–Tropsch [6] and low-temperature Fischer–Tropsch [7] products, excluding C_1–C_2 hydrocarbons, as well as the typical compound classes

Description	HTFT (Synthol)	LTFT (Arge)
Carbon number distribution (mass %)		
C_3–C_4, LPG	30	10
C_5–C_{10}, naphtha	40	19
C_{11}–C_{22}, distillate	16	22
C_{22} and heavier	6	46
Aqueous products	8	3
Compound classes		
Paraffins	>10%	Major product
Olefins	Major product	>10%
Aromatics	5–10%	<1%
Oxygenates	5–15%	5–15%
S- and N-species	None	None
Water	Major by-product	Major by-product

3. Hydroprocessing HTFT syncrude

3.1. Oxygenates

The main oxygenate classes present in syncrude are alcohols, carbonyls and carboxylic acids, with other oxygenate classes present in smaller amounts. These are different to the heavy naphthenic acids found in some crude oils. Hydrogenation of oxygenates can be divided into partial hydrogenation, such as typically found in chemicals production, or complete hydrodeoxygenation, as is more often found in refining of syncrude and biomass to transportation fuels [9]. For isostructural compounds the ease of hydrogenation of heteroatoms is typically in the order hydrodesulphurisation (HDS) > hyhydrodeoxygenation (HDO) > hydrodenitrogenation (HDN). It should consequently be possible to do HDO with catalysts that are capable of HDN and it seems that syncrude hydroprocessing design can be done accordingly.

Furimsky [10] reviewed the progress in HDO catalysis and concluded that more stable catalysts are needed to make production of fuels from oxygenate-rich materials more attractive. More recently, this view was reinforced by Corma and co-workers [11] in a review on biomass conversion to transportation fuel. The hydroprocessing of oxygenate-rich feed materials on their own is therefore quite challenging and different to the hydroprocessing of crude oil where some oxygenates may be present in crude oil matrix.

Refining objectives will significantly affect the hydroprocessing approach followed. When hydroprocessing is used as a pre-treatment step before catalytic reforming, it is imperative that complete HDO is achieved. Catalytic reformers use chlorided Pt/Al_2O_3 catalysts and oxygenates in the feed will be hydrogenated to produce water. The Al–Cl bonds that are responsible for the acidity of the reforming catalyst are not stable in the presence of water and chlorine is lost as hydrochloric acid to reduce the catalyst activity and cause downstream corrosion problems [12]. The same is true for feed pre-treatment to C_5/C_6 hydroisomerisation units that use chlorided Pt/Al_2O_3 catalysts, since they are also sensitive to water [13]. Conversely, during distillate hydrotreating it would be preferable to retain the long chain carboxylic acids and 1-alcohols present in the syncrude, since these are known to give lubricity to the fuel [14,15]. There are other benefits too, since the hydrogen consumption is reduced, less feed mass is lost and improvements in vehicle emissions might be obtained (it was shown that alcohol addition to diesel fuel is beneficial [16]). Efficient hydroprocessing therefore requires a good understanding of competitive hydrogenation of various compound classes and it is not always preferable to achieve complete heteroatom removal.

Heat release during HDO is more than that of HDS (Table 2). Heat management is often an issue in a Fischer–Tropsch refinery and attention should be paid to hydrotreater design, especially for naphtha hydrotreating. For example, HTFT naphtha contains about 2–3% oxygen by mass as oxygenates, while crude oil derived naphtha seldom contains more than 0.1% sulphur by mass, mostly as mercaptans. The

Table 2
Heat release during the hydrogenation of oxygen- and sulphur-containing aliphatic compound classes

Hydrogenation reaction type	ΔH_r (kJ g^{-1} O)	ΔH_r (kJ g^{-1} S)
R–CH_2–OH → R–CH_3 + H_2O	−5.7	
R–CHO → R–CH_3 + H_2O	−10.1	
R–CO–R → R–CH_2–R + H_2O	−8.1	
R–CH_2–SH → R–CH_3 + H_2S		−1.9
R–CH_2–S–CH_2–R → 2R–CH_3 + H_2S		−3.3

adiabatic temperature rise during HDO of HTFT naphtha is therefore at least 50 times more than HDS of crude oil naphtha. This also has implications for pilot plant and laboratory scale evaluations of hydrogenation catalysts.

Oxygenate chemistry is especially important at elevated temperatures in the presence of some acidity, such as typically found during hydroisomerisation and hydrocracking processes. Acid-catalysed oxygenate reactions such as alcohol dehydration, aldol condensation and esterification can all take place and influence HDO efficiency. One especially important, but lesser known oxygenate reaction, is carbonyl–carboxylic acid interconversion (Fig. 1) [17]. The formation of short chain carboxylic acids, which are more corrosive and reactive than the beneficial longer chain carboxylic acids, could cause problems if their formation is not anticipated.

Metal leaching by short chain carboxylic acids precludes the use of hydrogenation catalysts containing metals susceptible to acid attack, such as nickel. In laboratory studies significant metal leaching has been demonstrated and may even be responsible for the selective loss of the metal function reported during aromatisation of HTFT naphtha [18]. To prevent carboxylic acid metal leaching, syncrude hydrogenation is commercially done with sulphided base metal catalysts, which requires the addition of a sulphiding agent to keep the catalyst in a sulphided state. The addition of sulphur compounds to the sulphur-free Fischer–Tropsch feed is not only costly, but in the present refining context where <10 ppm sulphur-containing fuels are required, this seems inappropriate. Metal leaching is not necessarily limited to metal sites and amphoteric or basic metal oxides can also be leached by carboxylic acids.

Hydrothermal attack of the hydrotreating catalyst is possible if the catalyst support material and binder is not resistant to water, since water is invariably produced during oxygenate hydrogenation. Hydrothermal dealumination of alumina-containing materials can take place and the effect depends on the steaming temperature, time and water partial pressure [19]. At normal hydrotreating conditions hydrothermal attack by water is negligible, but it is debatable whether dealumination by steaming is equivalent to dealumination by oxygenates. When oxygenates are decomposed on an alumina surface the water generated by the reaction is already in an activated adsorbed state.

Preferential adsorption of oxygenates on the catalyst may result in activity and selectivity changes. This has been reported for various acid and acid-metal catalysed processes such as oligomerisation [20,21], skeletal isomerisation [22], etherification [23], dehydration [24] and hydrocracking [25,26]. In most instances a hydrophobic catalyst surface reduces the influence of oxygenates. Yet, the preferential interaction of carboxylic acids with metal sites, as noted during hydrocracking [26], is still likely. Carboxylates can coordinate with metals, as well as oxidise metals to form metal carboxylate complexes and there are examples of such reactions with most metals [27]. If the metal is oxidised and the operating temperature is below the metal carboxylate decomposition temperature, leaching of the metal may occur. If the metal carboxylate is decomposed, it is likely that the oxidised metal will be reduced at hydrotreating conditions and the carboxylic acids will only be seen as having an inhibiting effect on metal site catalysed reactions. Although catalyst stability can be related to the metal carboxylate stability [28], the nature of the metal–support interaction may modify the decomposition behaviour [29].

3.2. Olefins

The hydrogenation of olefins, apart from diene saturation, is not practised in crude oil refining. Olefins do not occur naturally in crude oil and the olefins that are produced by residue conversion processes have synthetic value in motor-gasoline production by aliphatic alkylation, etherification and olefin oligomerisation. In a syncrude refinery, olefins are abundant and the motor-gasoline is highly olefinic. The olefin content of motor-gasoline is limited by fuel specifications (Euro IV olefin content is maximum 18%). Although this specification is aimed at reducing light olefins (C_4–C_5), the specification does not differentiate between light and heavy olefins. The excess olefinic C_6+ product in a syncrude refinery must therefore be hydrogenated to meet fuel specifications.

Refining objectives make olefin hydrogenation challenging, since olefinic motor-gasoline that is low in α-olefins, like that produced by olefin oligomerisation, is considerably less structure sensitive to octane number than paraffinic motor-gasoline [30]. For example, the variation in research octane number between linear internal olefins and tri-branched olefins is 32, while that of the corresponding paraffins is 112 (Table 3) [31]. The quality of the hydrogenated product is consequently dependent on the way in which olefin hydrogenation is performed, especially during partial olefin hydrogenation.

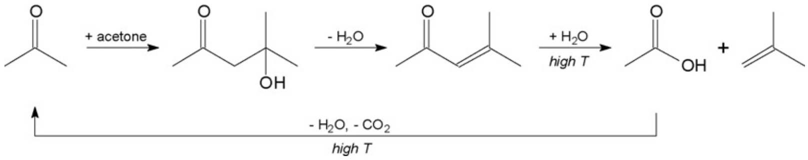

Fig. 1. Acid-catalysed carbonyl–carboxylic acid interconversion reaction.

Table 3
Research octane number (RON) and motor octane number (MON) of selected C_7 olefins and paraffins

Compound	RON	MON
Olefins		
1-Heptene	54.5	50.7
trans-2-Heptene	73.4	68.8
2-Methyl-1-hexene	90.7	78.8
2-Methyl-2-hexene	91.6	79.2
2,3-Dimethyl-1-pentene	99.3	84.2
2,3-Dimethyl-2-pentene	97.5	80.0
2,3,3-Trimethyl-1-butene	105.3	90.5
Paraffins		
n-Heptane	0	0
2-Methylhexane	42.4	46.4
2,3-Dimethylpentane	91.1	88.5
2,2,3-Trimethylbutane	112	101.3

Preferential hydrogenation of the most branched olefins during partial hydrogenation would be beneficial, since it would result in the least octane loss. In practice, unfortunately, the opposite is true, namely that steric hindrance cause the most branched olefins to have a lower hydrogenation rate than less branched olefins. Hydrogenation catalysts that would result in skeletal isomerisation or hydrogenolysis to decrease the degree of branching of the paraffin should be avoided because it is detrimental to the fuel quality. Conversely, hydrogenation catalysts that are active for double bond isomerisation, such as Ni and Pd [32–34], can be beneficial for the partial hydrogenation of straight run Fischer–Tropsch syncrude. Straight run syncrude is rich in linear α-olefins and the octane number can be improved by isomerising the double bond to an internal position (Table 3).

Heat release during olefin hydrogenation is in the order of $120\ \mathrm{kJ\ mol^{-1}}$ and the hydrotreater design should make provision for this. Like in the case of HDO, the high adiabatic temperature rise has implications for pilot plant and laboratory scale evaluations of hydrogenation catalysts too [35]. A further complication is introduced by the facile nature of olefin hydrogenation. High activity catalysts may cause the rate of heat release due to olefin hydrogenation to exceed the heat transfer capability of the catalyst or catalyst bed and result in hot spots (local overheating of the catalyst or catalyst bed). When the hydrogenation rate exceeds the hydrogen mass transfer rate, the reaction becomes hydrogen starved and at the prevailing high temperatures, the catalyst is deactivated by coking, since aromatics formation is favoured. When the catalyst is not hydrogen starved, a runaway reaction may result.

Hydrogen availability is relevant during normal operation too. Hydrogenation catalysts in their reduced, unsulphided state are more reactive than their sulphided analogues. The catalyst activity and operating temperature profile of the catalyst bed should therefore be matched to avoid excessive reaction rate. Even so, the hydrodynamic operation of the hydrotreater should ensure hydrogen availability throughout the catalyst bed. This is also important during plant upsets. Hydrogen availability during such situations may be improved by using catalysts that have hydrogen storage capacity, but it may require a different shutdown procedure and safety interlocks due to this property. An example of such a catalyst system is a palladium on carbon catalyst (Fig. 2) [36].

3.3. Metals

The deactivation of hydroprocessing catalysts is initially caused by the formation of carbonaceous deposits that rapidly reaches a pseudo steady state, whereafter longer term deactivation is mainly caused by metal deposits [37]. It is industrial practice to load a hydrodemetallation (HDM) catalyst as the top layer in hydrotreaters to remove as much metals as possible from the feed. The main crude oil derived metal contaminants are nickel and vanadium that are mostly contained in porphyrine structures. The HDM catalyst disrupts the porphyrine structure, which is easy to hydrogenate, to deposit the metal in the porous structure of the HDM catalyst. Crude oil derived metals are also contained in non-porphyrine structures that are more difficult to hydrogenate, which are not as effectively removed by the HDM catalyst. In HTFT syncrude the main metal contaminants are iron and sodium [38]. These metals are present in the syncrude as metal carboxylates and HDM catalysts are ineffective for their removal.

Metal carboxylate stability depends on both the metal, as well as the chain length of the carboxylate and metal carboxylates can be stable under hydrotreating conditions. Removal of metal carboxylates does not require hydrogenation (as do metal porphyrines), but follows a thermal decomposition pathway. Although the nature of the decomposition is dependent on the metal carboxylate, most metal carboxylates decompose by decarboxylation and ketonisation (Eq. (1)) [39,40].

$$\mathrm{M(RCOO)_2 \rightarrow MO + CO_2 + R_2C{=}O} \qquad (1)$$

At temperatures below their decomposition temperature (Table 4) [41–43] metal carboxylates can cause scaling in

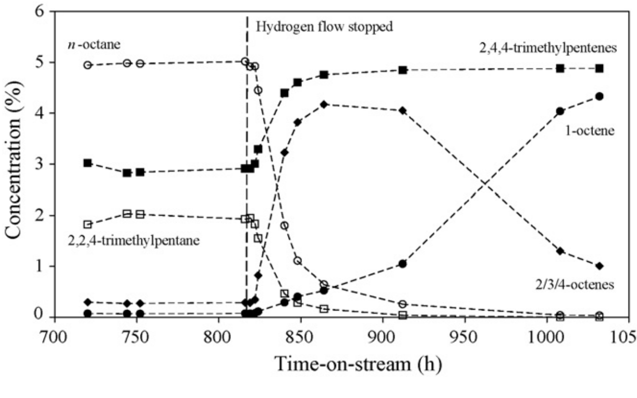

Fig. 2. Hydrogenation of a mixture of 1-octene (5%) and 2,4,4-trimethylpentene (5%) in *n*-heptane (90%) over a 0.25% Pd/C catalyst at 30 °C, 2 MPa and WHSV of $1.9\ \mathrm{h^{-1}}$. In the first part of the experiment, hydrogen was co-fed at $5\ \mathrm{l\ h^{-1}}$ ($0.45\ \mathrm{g\ h^{-1}}$) and in the second part of the experiment, after 817 h on-stream, the hydrogen was stopped and replaced with nitrogen at $5\ \mathrm{l\ h^{-1}}$ ($6.3\ \mathrm{g\ h^{-1}}$). The concentration of the C_8-hydrocarbons in the product was determined by gas chromatography with flame ionisation detection: 2,2,4-trimethylpentane (□), 2,4,4-trimethylpentenes (■), *n*-octane (○), 1-octene (●) and 2/3/4-octenes (◆).

Table 4
Metal carboxylate decomposition temperatures (T_d)

Compound	T_d (°C)	Reference
Sodium acetate	400	[41]
Potassium acetate	440	[41]
Aluminium acetate	>200	[42]
Iron(III) acetate	180–300	[43]

preheaters and result in catalyst bed plugging. The metal oxides formed by decomposition may be reactive under hydrotreating conditions and can be reduced, or when a sulphiding agent is added to keep the catalyst in a sulphided state, stable sulphides can be formed (Fig. 3) [44]. The formation of sodium-containing deposits affects the regenerability of hydroprocessing catalysts, while iron-containing deposits mainly result in increased pressure drop over the catalyst bed. This is a serious operational problem, since the run length that can be obtained by hydroprocessing units in a HTFT refinery is often determined by pressure drop constraints, not by catalyst deactivation. It has been shown that the iron carboxylates can be decomposed thermally prior to hydrotreating, but such a pre-treatment step may also result in thermal oligomerisation of the olefins present in the Fischer–Tropsch syncrude [45].

Surface-active behaviour displayed by the metal carboxylates can also result in refining problems. Longer chain metal carboxylates are metal soaps. Micelle and reverse micelle formation to trap non-polar material in a polar medium, or to trap polar material in a non-polar medium can easily happen. The refining problems associated with stable salt containing emulsions are well-known and desalting is usually the first refining step in crude oil refineries. However, when the emulsions are due to *n*-alkanoic carboxylic acids, as is the case in Fischer–Tropsch syncrude and some crude oils, the conventional approach for de-emulsifying naphthenic acid rich oils does not work well [46].

3.4. Aqueous products

During Fischer–Tropsch synthesis, water is formed as a major product. When the synthesis product is condensed, the polar short chain oxygenates preferentially dissolve in the water, rather than the oil. These short chain oxygenates found in the aqueous product, constitute almost 10% of the total HTFT syncrude mass (including methane). The main products are C_2–C_4 alcohols, carbonyls and carboxylic acids, which are present as a dilute aqueous solution that in the jargon of the industry is called ‘‘reaction water’’ [47]. When these products are hydrogenated, the feed consists only of oxygenates and water. In this respect there is a striking similarity between the hydroprocessing of Fischer–Tropsch syncrude and that of bio-derived materials.

Aqueous medium hydrogenation catalysts must by definition be water-resistant. The hydrotreating of short chain oxygenates in the HTFT aqueous product has much in common with treatment of natural products in bio-refineries. Of especial importance is selective carbonyl to alcohol hydrogenation, since it reduces refinery complexity. In practice it has been found that aldol condensation reactions cannot be prevented, even with almost neutral catalysts and catalyst support materials. The engineering design should therefore make provision for a hot hydrogen strip (>220 °C) to periodically remove such aldol condensation products. This has been found to extend catalyst lifetime considerably, as shown by commercial experience in the PetroSA refinery.

4. Hydroprocessing LTFT syncrude

The heavy product from LTFT synthesis is an *n*-paraffin wax with little olefins, oxygenates and aromatics. This makes it significantly different from HTFT material. Depending on the α-value of the LTFT catalyst, the product may contain C_{100} and heavier waxes, such as commercial Fe-LTFT reactor wax [48]. These waxes can be fractionated to produce medium (candle) wax and hard wax, with the latter having a congealing point as high as 105 °C [49]. This complicates laboratory scale hydroprocessing investigations, since it requires all surfaces in contact with the wax to be heated to well above the congealing point of the wax. Nevertheless, hydrotreating can be done with conventional hydrotreating catalysts [50], but some important differences can be noted.

Heat release during hydrotreating is little on account of the high *n*-paraffin content, resulting in almost isothermal commercial operation. Likewise, hydrocracking of LTFT

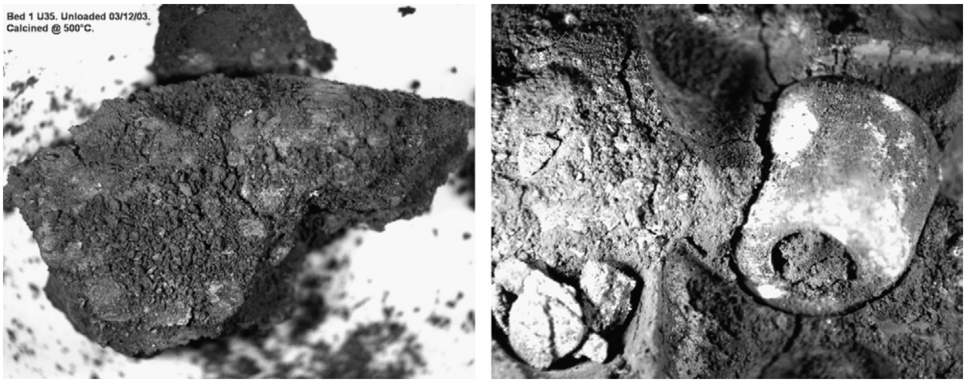

Fig. 3. Deposits rich in iron removed from an HTFT syncrude distillate hydrotreater. On the left are the deposits after calcination in air at 500 °C to convert the triolite (FeS) into hematite (Fe_2O_3) and on the right is the same sample magnified under a stereomicroscope (10× magnification).

wax is almost isothermal, with cracking (endothermic) and olefin saturation (exothermic) balancing each other. This is in contrast to the hydroprocessing of crude oil residues, which is exothermic on account of their high aromatic and heteroatom content.

Catalyst coking during hydroprocessing of LTFT waxes is slow. This can be understood in terms of the reaction network that describes coke formation, which indicates that *n*-paraffins are the molecules requiring the most conversion steps to be converted to coke [51]. This allows wax hydrocracking to be done at a lower pressure, because the wax is *n*-paraffinic and does not contain the same coke precursors that are present in crude oil derived residue fractions. Conventional crude oil hydrocrackers typically operate at temperatures >350 °C and pressures >10 MPa [52,53], while wax hydrocracking can be done at lower temperature and pressure to achieve the same conversion [48,54,55]. For example, in the commercial Shell Middle Distillate Synthesis process the wax hydrocracker is operated in the range 300–350 °C and 3–5 MPa [56].

Hydrogen availability during wax hydroprocessing is considerably higher than during crude oil derived residue hydroprocessing. There is little aromatics or heteroatom compounds to consume hydrogen. Since hydrogen availability is high throughout the catalyst and catalyst bed, catalyst coking is suppressed and hydroprocessing can be done at lower pressures than is possible with crude derived material. Furthermore, there is no need for feed pre-treatment to improve hydrocracking efficiency and unsulphided noble-metal hydrocracking catalysts can be used directly with beneficial results [54,56–59].

5. Conclusions

Hydroprocessing of Fischer–Tropsch syncrude can be performed with catalysts developed for crude oil refining, but there are syncrude-specific issues that have to be taken into account. The differences between syncrude and crude oil relate mainly to the nature and abundance of heteroatoms, olefins, metal species, waxes and aqueous products. Some of the aspects that have been noted are as follows:

(a) Heat release during hydroprocessing is either considerably more, like during olefin hydrogenation or hydrodeoxygenation, or it is much less, like during wax hydrocracking. In both instances it influences the engineering design. It also indirectly influences hydrogen availability in the catalyst particles and along the catalyst bed.
(b) Fischer-Tropsch Syncrude is sulphur-free. The use of sulphided base-metal hydroprocessing catalysts therefore requires the continuous addition of sulphur-containing compounds (such as dimethyl disulphide) to the syncrude.
(c) Oxygenates may strongly adsorb on some catalyst surfaces to affect both catalytic activity and selectivity. Furthermore, oxygenate reactions such as carbonyl–carboxylic acid interconversion and the production of water during hydrodeoxygenation may result in catalyst degradation by acid leaching and hydrothermal attack.
(d) When Fischer–Tropsch aqueous products are hydrogenated, the feed consists only of oxygenates and water. In this respect there is a striking similarity between Fischer–Tropsch syncrude hydroprocessing and the hydroprocessing of bio-derived materials.
(e) Carboxylic acids that are produced as primary Fischer–Tropsch products can result in corrosion of process equipment, as well as leaching of catalysts, including the Fischer–Tropsch catalyst itself. This precludes the use of catalysts with readily leachable metals or metal oxides for the processing of lighter syncrude cuts containing short chain carboxylic acids.
(f) The metal carboxylates that are produced during corrosion and leaching, such as iron carboxylates, are the main metal-containing contaminants in syncrude. Metal carboxylates are not removed by hydrodemetallation catalysts. The impact of these surface-active compounds on syncrude hydroprocessing units is mainly determined by their thermal decomposition behaviour.

Acknowledgements

The author is indebted to his colleagues Thomas. N. Mashapa and Margaret J. Strauss for the use of their unpublished data. Permission from Sasol Technology Research and Development to publish is appreciated.

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