CHAPTER VII

Refining technologies evaluated in Fischer-Tropsch context

Refining technologies for olefin conversion, hydrogen addition, carbon rejection and hydrogen rejection are discussed. The objective of each technology, as well as the chemistry and catalysis involved, is described to allow an analysis of its compatibility with Fischer-Tropsch syncrude. This has shown that key crude refining technologies such as fluid catalytic cracking and Pt/Al_2O_3 catalytic reforming have poor compatibility with Fischer-Tropsch feed and refining needs, emphasising the difference between Fischer-Tropsch syncrude and crude oil refining. The technologies are also discussed in terms of their environmental friendliness, since this is considered an important aspect for future selection.

1.   Introduction

In the past there has been little incentive to develop Fischer-Tropsch specific refining technologies, due to the small number of Fischer-Tropsch refineries. This situation has not changed much and commercial Fischer-Tropsch operators had to adapt crude oil refining technology to make it compatible with Fischer-Tropsch feed materials. This often took the form of hydrogenating the olefins and oxygenates to hydrocarbons, so that the Fischer-Tropsch feed becomes similar to a paraffinic crude oil feed.

Some exceptions are noted, such as the development of a technology and catalyst for the hydrocracking of Fischer-Tropsch wax by Shell[1] and the development of the conversion of olefins to distillate (COD) process by the Central Energy Fund of South Africa.[2] The former process is employed in the Shell Bintulu refinery, while the latter process is employed in the PetroSA (Mossgas) refinery. In addition to these two technologies, there is also the development of the especially dry C84/3 solid phosphoric acid catalyst by Süd-Chemie Sasol Catalysts for use in the Synfuels olefin oligomerisation units.[3] Other Fischer-Tropsch specific technology developments were mostly done for chemicals production, such as those applied in the Sasol linear α-olefin purification processes.[4]

Technology selection for use with Fischer-Tropsch streams is not a trivial exercise and the commercial implementation of technologies in Fischer-Tropsch refineries does not

imply a good technology fit. The devil is in the details. A thorough understanding of the composition of the Fischer-Tropsch feed, including its trace components, the chemistry of the process and the catalysis involved, are all required to make a proper technology selection. This type of analysis is available from neither literature, nor technology licensors.

The refining technologies that are evaluated in this chapter, will be discussed in terms of the: a) Objective of the technology; b) chemistry involved; c) catalysts; d) feed requirements; e) environmental issues; f) compatibility to Fischer-Tropsch products and g) its prospects for future application in Fischer-Tropsch refineries.

2. Olefin conversion

2.1. Double bond isomerisation

The octane numbers of olefins are dependent on the position of the double bond. In general the octane numbers of linear α-olefins are much worse than that of linear internal olefins (Table 1).[5] When a feed material has a high linear α-olefin content, double bond isomerisation can be used to improve the octane number significantly. The same is not true of branched olefins, where there is much less gain in doing so.

Table 1. Octane numbers of some linear olefins.

Compound	RON	MON	½(RON+MON)	Δ Relative to α-olefin
1-hexene	76.4	63.4	69.9	-
trans-2-hexene	92.7	80.8	86.8	16.9
trans-3-hexene	94.0	80.1	87.1	17.2
1-heptene	54.5	50.7	52.6	-
trans-2-heptene	73.4	68.8	71.1	18.5
trans-3-heptene	89.8	79.3	84.6	32.0
1-octene	28.7	34.7	31.7	-
trans-2-octene	56.3	56.5	56.4	24.7
trans-3-octene	72.5	68.1	70.3	38.6
trans-4-octane	73.3	74.3	73.8	42.1

Double bond isomerisation is a facile reaction that favours the formation of internal olefins from α-olefins at low temperatures, for example, the 1-butene to 2-butenes ratio at

200°C is 0.13:1 and at 450°C it is 0.38:1.[6] It is an almost thermoneutral conversion, with a heat of reaction (ΔH_r) in the order of 5-10 kJ·mol^{-1}. The reaction is acid catalysed and takes place via a carbocation intermediate, but it can also take place via a carbanion intermediate or a radical intermediate[7] (Figure 1) in different reaction environments.
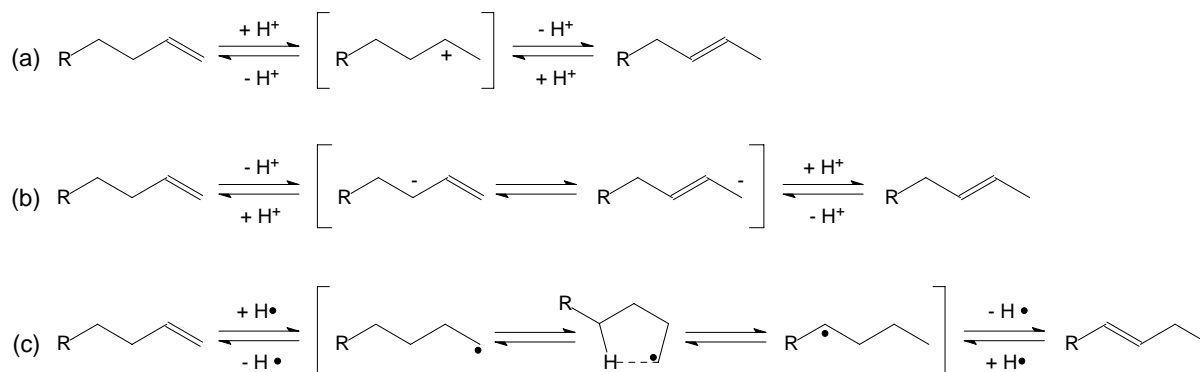

Figure 1. Double bond isomerisation mechanisms by (a) carbocation, (b) carbanion, and (c) radical intermediates.

Industrially, double bond isomerisation is generally catalysed by solid acid catalysts with sufficient Brønsted acidity for olefin protonation. Numerous examples of such catalysts have been recorded in the extensive review by Dunning,[8] with more recent literature reporting studies on catalysts such as sulphonic acid resins,[9] various zeolites[10] and mixed oxides.[11] Isomerisation by other mechanisms are less common, although double bond isomerisation over basic zeolites[12] and in alkaline media,[13] as well as during hydrogenation with palladium[14][15][16] and nickel[17][18][19][20] catalyst have been noted.

Double bond isomerisation as octane enhancing side-reaction during hydrogenation is only relevant when the olefinic feed is being partially hydrogenated. Unless the olefinic feed is highly branched, there is a precipitous drop in octane number when an olefinic feed is hydrogenated. Yet, when the olefinic feed is highly branched, there is little gain in octane number during double bond isomerisation. This form of double bond isomerisation is therefore not especially valuable in refining context.[a]

Acid catalysed double bond isomerisation has previously been used in refineries to upgrade products with a high linear α-olefin content.[21][22] These applications used bauxite or silica-alumina materials and were not environmentally friendly on account of their high operating temperatures (>340°C)[23] and high frequency of regeneration. Such a high

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[a] It could have been beneficial for mixed olefin feeds containing both linear and branched olefins if the hydrogenation catalyst had a higher rate of branched olefin hydrogenation than linear olefin hydrogenation. This is not the case in practice though, with sterically hindered olefins being more difficult to hydrogenate.

operating temperature is not a prerequisite for double bond isomerisation, but were used since these processes also doubled as heteroatom conversion technologies. It is possible to conduct double bond isomerisation at milder operating conditions. By using a catalyst with stronger acidity, such as acidic resins, or even silica-alumina materials, double bond isomerisation can be performed at <100°C.[24][25] However, with more acidic catalysts olefin oligomerisation can become a significant side-reaction.[26] Furthermore, unless the catalyst is only weakly acidic, the process can only be considered for C_4-C_6 olefin feeds, since C_7 and heavier olefins are prone to catalytic cracking.[27]

Since naphtha range Fischer-Tropsch primary products are rich in linear α-olefins, there is a good technology fit with double bond isomerisation. Catalyst selection is crucial though, since Fischer-Tropsch derived naphtha feeds contain oxygenates. The oxygenates are not necessarily detrimental and when silica-alumina based catalysts are employed, catalyst activity may be improved by the water that is being produced during oxygenate conversion.[28]

Although double bond isomerisation technology has been proven with Fischer-Tropsch derived feed, its prospect for future application is slim. From Table 1 it is clear that even with the significant gain in octane that can be achieved, linear internal olefins still have moderate to poor octane numbers. The octane deficit cannot be corrected by the addition of tetraethyl lead, as was the case when this technology was developed. Its usefulness is further restricted by the fuel specifications that limit the olefin content of motor-gasoline. It will consequently not be practical to employ a process relying only on double bond isomerisation to upgrade Fischer-Tropsch syncrude.

2.2. Oligomerisation

The solubility of short chain hydrocarbons in naphtha is quite high and on account of their high octane number, it is desirable to include these compounds in motor-gasoline (Table 2).[5] The amount of short chain hydrocarbons that can be accommodated in motor-gasoline is, however, limited by their vapour pressure and the vapour pressure specification of the fuel. Olefin oligomerisation[b] provides a way to convert the normally gaseous short chain olefins into liquid products.

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[b] Oligomerisation is preferred as term over dimerisation, since it refers to the addition of 2-10 olefin monomers.

Table 2. Octane numbers and Reid vapour pressure (at 37.8°C) of short chain aliphatic hydrocarbons.

Compound	RON	MON	RVP (kPa)
Paraffins			
ethane	111.4	100.7	-
propane	112.1	97.1	1301
n-butane	93.8	89.6	357
isobutane	101.3	97.6	500
Olefins			
ethylene	100.4	75.6	-
propene	102.5	84.9	1569
1-butene	97.4	80.8	436
cis-2-butene	100.0	83.5	315

The oligomerisation of olefins is a highly exothermic reaction, with a heat of reaction of each dimerisation step typically being in the order of 85-105 kJ·mol^{-1}. Low temperatures and high pressures therefore thermodynamically favour oligomerisation. The mechanism by which olefin oligomerisation takes place is dependent on the type of catalysis. If only the main commercial oligomerisation processes are considered,[29] three different mechanisms are represented (Figure 2).

Acidic resin and zeolite-based processes follow a classic Whitmore-type carbocation mechanism (Figure 2.a), solid phosphoric acid (SPA) based processes follows an ester based mechanism (Figure 2.b) and homogeneously catalysed organometallic based processes catalyses olefin oligomerisation by a 1,2-insertion and β-hydride elimination mechanism (Figure 2.c). It should be noted that this is a simplified mechanistic description. Other mechanistic variations have been suggested to account for specific types of oligomerisation catalysis.[30]

It is necessary to consider the different olefin oligomerisation technologies separately, since they have different processing aims, different feed requirements and yield different products.
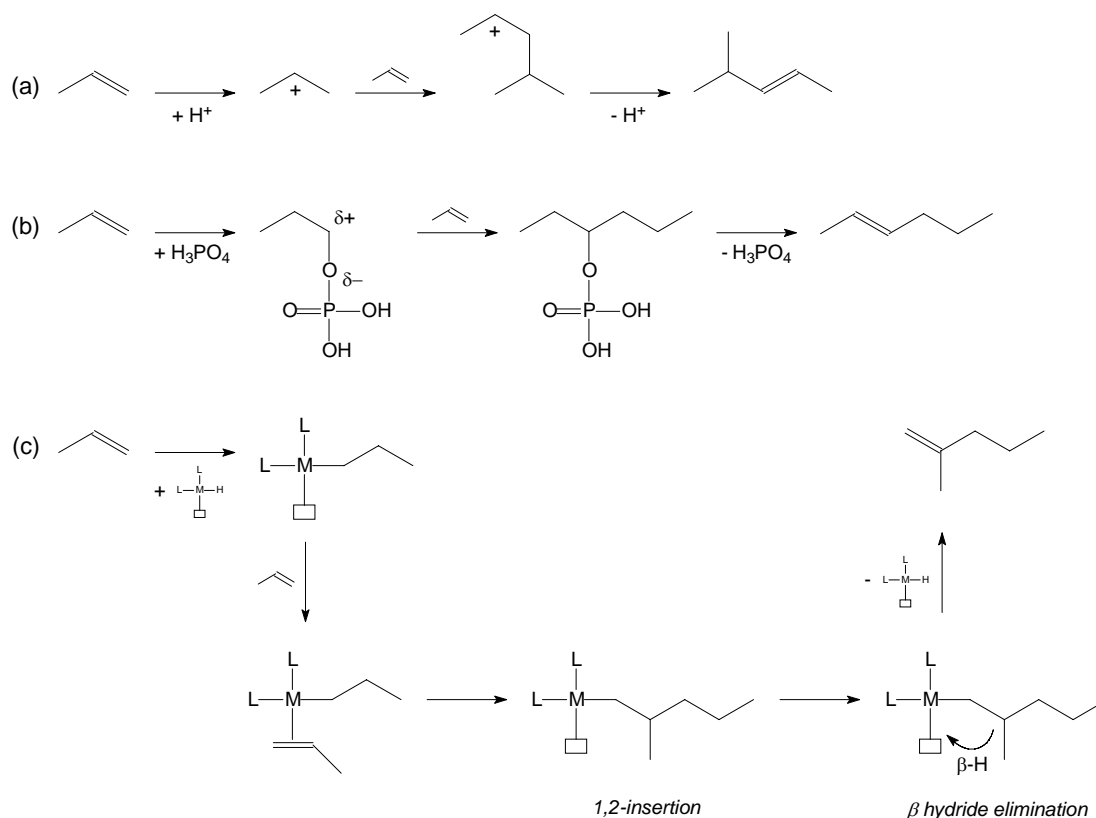
Figure 2. Olefin oligomerisation by the (a) classic Whitmore-type carbocation mechanism, (b) ester-based mechanism, and (c) organometallic catalysis by a 1,2-insertion and β-hydride elimination.

Acidic resin. The use of sulphonated styrene-divinylbenzene based resins for olefin oligomerisation, such as Amberlyst 15 (Rohm and Haas), is a fairly recent development. Resin based oligomerisation technology development received a boost with the phase out of MTBE.[31] Processes like NExOCTANE™ (Fortum Oy)[32] was developed to convert MTBE units to dimerisation units that operated at similar conditions (<100°C, liquid phase) and used the same catalyst. Other technology suppliers include Snamprogetti/CDTech, UOP and Lyondell.[33] Instead of etherifying the iso-butene, it is dimerised to trimethylpentenes that can be hydrogenated to give high-octane trimethylpentanes. This makes the technology an environmentally friendly alternative to aliphatic alkylation for the production of alkylate-quality high-octane paraffins. To maximise dimerisation selectivity and limit heavy oligomer formation, the reaction is moderated by the addition of polar compounds, typically *tert*-butanol.[34][35] Only branched olefins are targeted for conversion, with iso-butene and iso-amylene being the main feed materials. The feed needs to be free of typical acid catalyst poisons, but oxygenates in general does not seem to be a problem, with limited side-reactions being noted during conversion over Amberlyst 15 at 70°C and 0.4 MPa.[36] The application

of acidic resin catalysed oligomerisation of Fischer-Tropsch feed benefits from the oxygenate tolerance of this system, but it is only of limited use in a Fischer-Tropsch refinery, since Fischer-Tropsch olefins are mostly linear (not branched).[c]

Zeolite. The Mobil Olefins to Gasoline and Distillate (MOGD)[37] and Conversion of Olefins to Distillate (COD)[2] processes make use of a ZSM-5 based catalyst. The chemistry and catalysis of olefin oligomerisation over ZSM-5 has been studied extensively, with the pioneering work of Garwood[38] clearly showing its equilibration properties at high temperature. At low temperature, H-ZSM-5 catalyses oligomerisation with limited cracking, resulting in the formation of oligomers that are multiples of the monomer, but above temperatures of around 230°C[d] it equilibrates the carbon number distribution of the product.[39][40] In the temperature region where the feed is "equilibrated", the process is insensitive to the carbon number distribution of the olefins in the feed and the operating conditions (temperature and pressure), as well as product recycle can be used to determine the product distribution.[41] Oxygenates are known to reduce catalyst activity,[42] but this does not preclude the use of ZSM-5 with Fischer-Tropsch feed material. The COD process operates commercially with an oxygenate containing HTFT feed. Both the MOGD and COD processes employ conditions around 200-320°C and 5 MPa. The distillate produced by oligomerisation is hydrogenated to a high quality diesel, with >51 cetane number and good cold flow properties.[2][37][43] The motor-gasoline is of a lower quality (RON = 81-85, MON = 74-75).[2] The linearity of the oligomers, which is responsible for the good cetane number of the diesel fuel and poor octane number of the olefinic motor-gasoline, is due to the pore constraining geometry of the ZSM-5 catalyst.[44] Despite the low coking propensity of ZSM-5, the catalyst has to be regenerated every 3 months by controlled coke burn-off. The catalyst lifetime extends over multiple cycles and overall the process is environmentally friendly. Another zeolite based process that has recently been introduced is the ExxonMobil Olefins to Gasoline (EMOGAS™) technology. In the absence of nitrogen bases, it is claimed to have a catalyst lifetime of 1 year and has been designed for retrofitting SPA-units.[45] The zeolite-type (not H-ZSM-5) has not been stated explicitly, although ExxonMobil patents[e] suggest that it is a zeolite of the MFS-type (H-ZSM-57) or TON-type (Theta-1 / ZSM-22). The carbon number distribution of the product is similar to that of SPA, with little material boiling

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[c] Linear olefins can be oligomerised, but the product will have a lower degree of branching and consequently a lower hydrogenated octane number.
[d] The exact temperature is dependent on the catalyst acid strength and other operating conditions.
[e] Patent applications WO 2001083407, WO 2003035583 and WO 2003035584.

above 250°C.[46] Other zeolites have also been investigated for oligomerisation, but generally deactivates too fast to be of commercial value in this type of service.[47]

Amorphous silica-alumina (ASA). The IFP Polynaphtha™ process was originally designed to use an amorphous silica-alumina catalyst.[f] The difference between ASA and its zeolitic counterparts, relates mainly to its lower acid strength and the less pore constraining geometry of ASA, since it is not crystalline. However, there are other differentiating features too, such as its hydrogen transfer propensity[48] and reaction by a different mechanism to the classic Whitmore-type carbocation mechanism. The latter is evidenced by its *cis*-selective nature for double bond isomerisation and the differences in products obtained from the oligomerisation of linear α-olefins and linear internal olefins.[49] It has been found that ASA catalysts work well with Fischer-Tropsch feeds, including oxygenate containing feed materials, yielding a distillate with higher density (810 kg·m^{-3}; much needed in Fischer-Tropsch refining) than any of the other oligomerisation catalysts. However, the hydrogenated distillate has good cold flow properties, but with a cetane number of only 28-30.[50][51] The naphtha properties are feed dependent and short chain olefins yield a better quality motor-gasoline (RON = 92-94, MON = 71-72) than ZSM-5, although the distillate cetane is of poorer quality. Similar cycle lengths and regenerability as ZSM-5 has been demonstrated in service as olefin oligomerisation catalyst, making ASA based oligomerisation technology as environmentally friendly as ZSM-5 based technology. There is also a fair amount of interest in the more structured ASA derivatives, like MCM-41, for olefin oligomerisation, but these catalysts have not yet been applied commercially.[52][53][54] One variation on ASA catalysts that deserve special mention is the Hüls Octol process, which uses a nickel promoted silica-alumina molecular sieve (montmorillonite)[g] catalyst.[55] For fuels applications the Octol A catalyst, which gives a more branched product, is preferred.[56] The addition of nickel to the catalyst introduces a different reaction mechanism, namely 1,2-insertion and β-hydride elimination, which implies that more than one mechanism is operative in parallel.

Solid phosphoric acid (SPA). The Catalytic Polymerisation (CatPoly) technology of UOP was the first of many solid acid catalysed olefin oligomerisation technologies to be commercialised.[57][58] The catalyst is manufactured by impregnating a natural silica source such as kieselguhr (diatomaceous earth) with phosphoric acid. The active phase is a viscous layer of phosphoric acid on the support, with the support itself being inactive.[59] Olefin

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[f] The Axens IP 501 catalyst that is now being licensed for the Polynaphtha™ technology is different from the ASA based catalyst on which the technology has originally been developed.
[g] Personal communication with Dr. Karl-Heinz Stadler (Süd-Chemie).

oligomerisation takes place via an ester mechanism, whereby a phosphoric acid ester stabilises the polarised hydrocarbon intermediate.[60][61] The operating temperature and amount of water in the feed determine the ratio of different phosphoric acid species on the catalyst, which in turn determines its activity and selectivity behaviour.[62] The technology was nevertheless reported to be insensitive to the feed composition (C_2-C_5 olefins)[h] and the olefinic motor-gasoline thus produced invariably has a RON in the range of 95-97 and MON in the range of 81-82.[63][64][65][66] However, this does not imply that the olefin oligomers produced by different type of feed are isostructural. It was found that the quality of the hydrogenated motor-gasoline is very dependent on feed and operating conditions.[67] This is relevant to Fischer-Tropsch refining, since it is likely that at least some of the olefinic motor-gasoline will have to by hydrogenated to meet the olefin specification of motor-gasoline. Surprisingly it was found that a low temperature isomerisation pathway is operative during 1-butene oligomerisation that results in the formation of a significant fraction of trimethylpentenes.[68] It is consequently possible to produce a hydrogenated motor-gasoline with 86-88 octane from a 1-butene rich Fischer-Tropsch feed. SPA oligomerisation is not a distillate producing technology,[69] although distillate yield can be improved by manipulating the water content and operating conditions.[70] The distillate has a low cetane number (25-30), but excellent cold flow properties, making it a good jet fuel, but poor diesel fuel. Since the catalyst is influenced by water, only a limited amount of oxygenates can be tolerated in the feed and catalyst activity is inhibited at high oxygenate concentration. This limits application of SPA in a Fischer-Tropsch refinery to the conversion of the condensate streams. Attempts to use SPA catalysed oligomerisation with stabilised light oil (SLO) gave poor results[71] and some oxygenate classes were found to be especially detrimental to the catalyst.[72] SPA is a cheap catalyst and spent SPA catalyst is therefore not regenerated. The process is nevertheless environmentally friendly, because the catalyst is produced from natural silica and the spent catalyst can be neutralised with ammonia to produce ammonium phosphate plant fertiliser, rather than a solid waste.

Homogeneous catalysts. Olefin oligomerisation by the IFP Dimersol™ process,[29] is the only refinery technology where homogeneous organometallic catalysis is applied industrially.[i] The Dimersol™ process makes use of a nickel-based Ziegler-type catalyst system and oligomerisation takes place by a β-hydride elimination mechanism.[73] There are

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[h] This statement holds true only for feed materials that are not very rich in iso-butene, which gives a somewhat higher octane value.
[i] Aliphatic alkylation also employs homogeneous catalysis, but not organometallic catalysis.

a number of variants of the Dimersol™ process:[74] a) Dimersol™ E for the oligomerisation of ethylene and FCC off-gas (C_2/C_3 olefin mixture) to motor-gasoline;[j] b) Dimersol™ G for the oligomerisation of propylene and C_3/C_4 olefin mixtures to motor-gasoline;[75][76] and c) Dimersol™ X for butene oligomerisation to linear octenes for plasticiser alcohol manufacturing.[77][78] Because the technology makes use of a homogeneous organometallic catalyst system, it is sensitive to any impurities that will complex with the nickel. Amongst other, it is sensitive to dienes, alkynes, water and sulphur, that should not exceed 5-10 $\mu g \cdot g^{-1}$ in the feed.[76] Conversely, the advantage of a process based homogeneous catalyst system, is that the catalyst dosing can be increased to offset deactivation by feed impurities. The catalyst has to be removed from the reaction product by a caustic wash, which makes this a less environmentally friendly technology. In a more recent incarnation of this technology, called Difasol™, the catalyst is contained in an ionic liquid phase,[73] which makes catalyst separation easier. The Difasol™ process does not generate the same amount of caustic effluent as the Dimersol™ process. In a lifetime test conducted over a period of 5500 hours, it was found that the nickel catalyst consumption in the Difasol™ process was only 10% of that found with the Dimersol™ process, while that co-catalyst consumption was half.[79] There may be a competitive advantage to use the Dimersol™ X and Difasol™ technologies for the oligomerisation of Fischer-Tropsch butenes on account of their low iso-butene content, but such an application is for chemicals production, not fuels refining.

Thermal. The thermal oligomerisation of cracker gas streams to motor-gasoline had been practised widely in the past,[80][81] but has since been completely replaced by catalytic oligomerisation. This happened not only due to the higher efficiency of the catalytic processes, but also due to the lower octane number (MON = 77)[81] obtained by thermal oligomerisation. The reaction takes place by a radical mechanism,[82] which results in the formation of products that have a low degree of branching. This explains the low octane number of motor-gasoline produced by thermal oligomerisation. Branching is not introduced by isomerisation of radicals and there is consequently similarities to Lewis acid catalysed oligomerisation, such as with BF_3.[84] Thermal oligomerisation of linear α-olefins, as is prevalent in HTFT products, results in lubricating oils with good viscosity properties.[85] Mechanistically thermal oligomerisation is better suited to the production of distillates and lubricating oils from Fischer-Tropsch products, as was indeed shown.[86] The technology

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[j] This type of technology was in commercial operation at the Sasol Synfuels site to convert excess ethylene to motor-gasoline. It was originally installed as a risk-mitigation option to avoid flaring of ethylene. The plant became redundant in the 1990's and was officially written off early in the 2000's.

unfortunately requires high temperatures. A method to overcome this shortcoming by heat-integrating thermal oligomerisation with high temperature Fischer-Tropsch synthesis has been suggested,[86] which makes the overall process more energy efficient. Attempts to further reduce the energy requirements by making use of radical initiators, such at di-tertiary butyl peroxide (DTBP), failed due to low initiator productivity.[87]

2.3. Olefin skeletal isomerisation

In a refinery the skeletal isomerisation of olefins is mainly used to convert linear olefins to branched olefins for etherification with alcohols to produce fuel ethers such as methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). There was consequently a lot of activity in the early 1990's in this field when oxygenated motor-gasoline was introduced. Industrial skeletal isomerisation processes have been developed with mostly *n*-butenes and *n*-pentenes in mind.[88][89][90][91] Studies on the skeletal isomerisation of *n*-hexenes are more limited,[92][93] since these compounds are not generally used as fuel ethers.
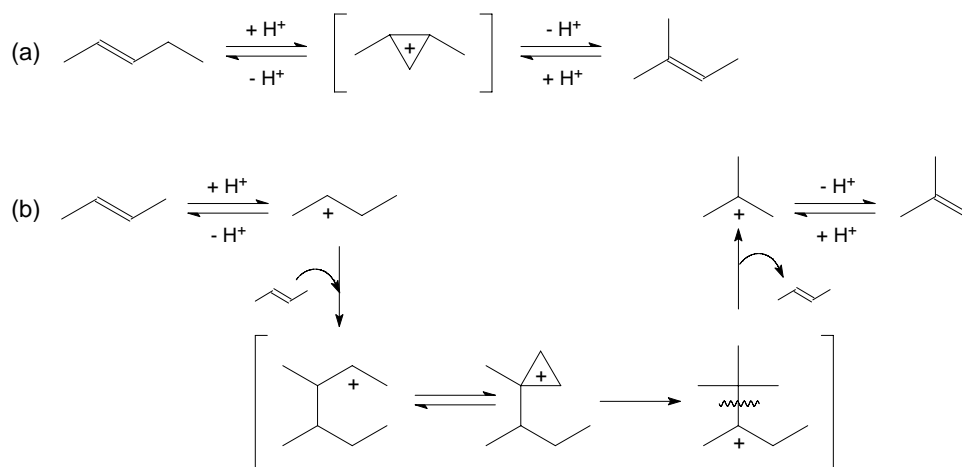

Figure 3. Skeletal isomerisation by (a) monomolecular rearrangement through a protonated cyclopropane intermediate, and (b) bimolecular mechanism involving dimerisation, isomerisation and cracking.

There are two mechanistic routes by which the skeletal isomerisation takes place (Figure 3), namely monomolecular isomerisation via a protonated cyclopropane intermediate and a bimolecular process involving dimerisation, followed by skeletal isomerisation and cracking.[88][90][91] The relative contribution of these two mechanisms depend on the feed material. Skeletal rearrangement via a monomolecular mechanism requires a carbon chain length of at least 5 carbon atoms to avoid the formation of a primary carbocation intermediate

and is the dominant mechanism whereby pentene and heavier feeds are isomerised. The bimolecular mechanism is expected to be the dominant mechanism for butene isomerisation, but despite this seemingly simplistic explanation, the butene skeletal isomerisation mechanism is still actively being debated.[94][95][96][97]

Butene skeletal isomerisation. Various catalysts have been investigated for the skeletal isomerisation of *n*-butene,[98] and it has been shown that ferrierite is by far the most selective for high temperature isomerisation, but requires operating temperatures of 350°C and higher.[90] With ferrierite it is possible to come close to the equilibrium conversion, which is a maximum at around 50% *n*-butene conversion at 350°C. At typical operating temperatures there is a gradual loss of catalyst activity due to coking.[99] For commercial processes cycle lengths in the order of 500 hours have been reported.[89] Catalyst activity is generally restored by controlled carbon burn-off. Although butene skeletal isomerisation is a fairly clean process in terms of solid waste, the high operating temperature and frequent catalyst regeneration makes it energy intensive, which increases its environmental footprint. There is no advantage in processing Fischer-Tropsch butenes over cracker-derived raffinate-II butenes and with the decline in MTBE use globally, it is not seen as an important Fischer-Tropsch refining process.[k] Nevertheless, it may be considered as feed pretreatment step for indirect alkylation,[31][32][34][100] if the refinery is very octane constrained.

Pentene skeletal isomerisation. The skeletal isomerisation of *n*-pentene is more facile and a wider selection of commercial technologies is available, using different catalysts, such as acidic molecular sieves (UOP),[88] ferrierite (Lyondell)[89] and alumina (IFP).[91] From a thermodynamic, as well as an environmental point of view, it is better to operate at lower temperatures. At lower temperatures the process is less energy intensive, the equilibrium concentration of branched olefins is higher and catalyst coking is reduced. The UOP Pentesom™ process, which uses an acidic molecular sieve catalyst, makes use of this advantage and has a start-of-run temperature of less than 300°C. However, it was found that oxygenates typically present in feed materials derived from Fischer-Tropsch synthesis, adsorbs on the catalyst and requires a temperature of at least 320°C to desorb.[101] This reduces the cycle length from 1 year, that is obtainable with cracker-derived feed, to only 1-2 months with Fischer-Tropsch derived feed. Ferrierite is also negatively affected by oxygenates, but conversely, oxygenates were actually found to be beneficial during alumina

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[k] Sasol considered building a butene skeletal isomerisation plant to improve the octane number from their olefin oligomerisation process. However, after it was shown that little benefit over butene-only SPA oligomerisation could be obtained, the project was shelved. Ref.(67)

catalysed skeletal isomerisation.[102]   This was indeed found in practice and after initial teething trouble,[103] the alumina based ISO-5™ process that was implemented at Sasol Synfuels was found to work well with Fischer-Tropsch pentenes. The ISO-5™ process has an operating temperature around 410°C and makes use of continuous catalyst regeneration (CCR) to burn off coke formed on the catalyst. On account of the high temperature and significant side-product formation (10-15%) of this alumina based process, it is not considered environmentally friendly. Despite its commercial implementation in a Fischer-Tropsch refinery, it is not seen as important refining technology for the future, unless future motor-gasoline specifications mandate the inclusion of fuel ethers.

2.4. Etherification

With the mandatory inclusion of oxygenates in reformulate fuels, as promulgated in legislation such as the Clean Air Act Amendment of 1990 in the USA, refiners mainly had a choice between alcohols and ethers (Table 3).[104] Ethers were preferred over alcohols for a number of reasons:

a) Ethers have a lower vapour pressure than the alcohols;

b) Ethers have a lower phase separation tendency in the presence of small amounts of water that gives it better storage and transport stability; and

c) The production of fuels ethers was a convenient way to reduce the volatile short chain olefin content in motor-gasoline.

Table 3. Blending vapour pressure (VP) at 37.8°C, boiling point (T_b) and blending octane numbers of fuel alcohols and ethers.

Compound	VP (kPa)	T_b (°C)	RON	MON
Fuel alcohols				
methanol	524	64.7	>120	95
ethanol	154	78.3	120	99
2-propanol	95	82.4	117	95
2-methyl-2-propanol	103	82.2	105	95
Fuel ethers				
2-methoxy-2-methylpropane (MTBE)	55	55.3	118	101
2-ethoxy-2-methylpropane (ETBE)	40	72.8	118	101
2-methoxy-2-methylbutane (TAME)	25	86.3	115	100

Etherification as practised industrially, is an equilibrium limited reaction between an alcohol and an olefin containing a C=C bond on a tertiary carbon (Figure 4). The reaction is catalysed by an acid and is generally performed at low temperature to favour the etherification equilibrium. The catalyst most often used for etherification is Amberlyst 15, a sulphonic acid exchanged divinylbenzene-styrene copolymer resin catalyst from Rohm and Haas, although other acidic resin catalysts[104] and zeolites[105] can also be used. The process has to be operated with an excess of alcohol to reduce olefin oligomerisation as side reaction. When an excess of alcohol is used, the catalyst protonates the alcohol and the alcohol becomes the protonating agent,[106] thereby preventing the formation of oligomers. The alcohol also acts as solvating agent, breaking the hydrogen bonds between sulphonic acid groups and thereby reducing the acid strength of the catalyst.[107] This helps to reduce oligomerisation as side-reaction.
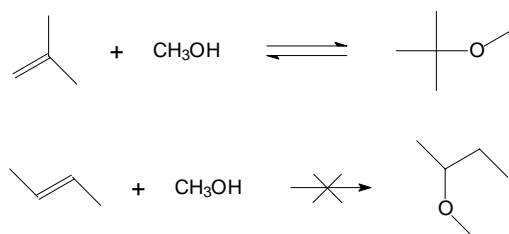

Figure 4. Etherification reaction between an olefin and an alcohol.

From a technical point of view, methanol is the preferred alcohol for etherification, since it does not form an azeotrope with water[1] and it results in a higher equilibrium ether concentration. For example, the equilibrium constant for MTBE is 32 at 70°C, but for ETBE it is only 18 at 70°C.[108] The olefin feed is refinery dependent, but isobutene that is derived from naphtha steam cracking and/or fluid catalytic cracking (FCC), is most often used on account of its high volatility. The second choice is the reactive isoamylenes, which is less volatile and therefore more easily assimilated in motor-gasoline. Rather than preparing a carbon number cut by distillation, the etherification of all reactive olefins in FCC naphtha to ethers has been investigated.[109][110] This simplifies feed preparation, but it complicates product separation. Furthermore, it has been shown that most hexyl ethers have a low octane number.[111]

When a cracker-derived feed material is used, diene removal is a prerequisite. The dienes are very reactive and can form heavy polymers under etherification conditions. This is

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[1] Water is produced as side-product by alcohol etherification: $2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$.

not a problem when using Fischer-Tropsch derived feed, but the presence of oxygenates other than alcohols are potentially problematic. The oxygenates inhibit the etherification reaction and participate in side-reactions,[36] often forming water, which is known to inhibit the reaction.[112]

Etherification is an environmentally friendly technology. It is not energy intensive and is quite selective. However, it became a victim of politics, which resulted in a ban on MTBE in fuel in many States of the USA.[113] It is therefore doubtful that much new etherification capacity will be installed in future.

2.5. Aliphatic alkylation

Aliphatic alkylation is one of the most important technologies for the production of high octane paraffins. With fuel specifications putting increasingly tighter limits on non-paraffinic compound classes in motor-gasoline, the viability of motor-gasoline production in a refinery becomes more and more reliant on the paraffin quality of the base stock.
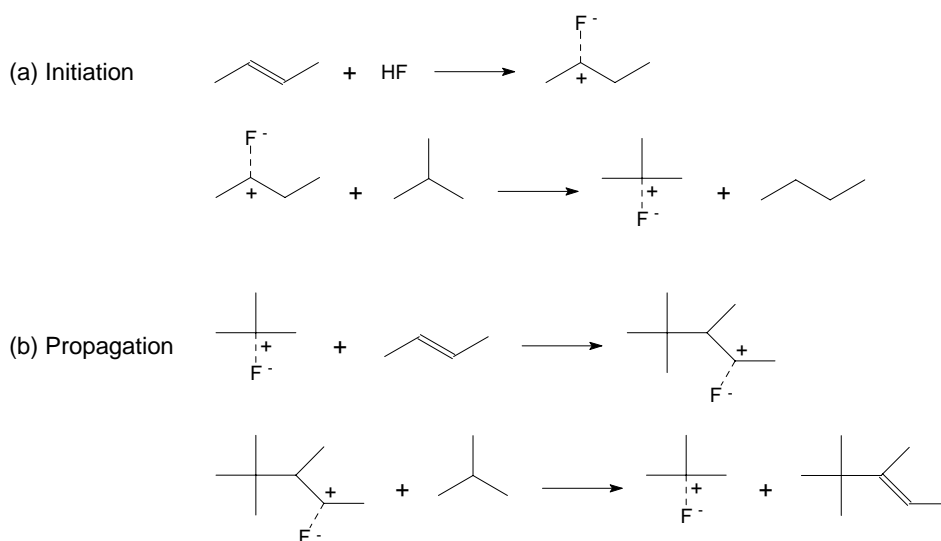

Figure 5. Aliphatic alkylation mechanism illustrated by the initiation and propagation steps involved during hydrofluoric acid catalysed alkylation of isobutane with 2-butene.

Aliphatic alkylation entails the alkylation of isobutane with an olefin (usually butene) to produce a highly branched paraffin (Figure 5). There are mainly two technology types to accomplish this, both making use of liquid acids, namely HF and H_2SO_4 alkylation.[114][115] The field of aliphatic alkylation has seen incremental advances since its development, but a comparison of reviews shows that the same technologies that were commercially available in

the 1950's,[116] are still the commercial technologies available today.[117] The projected development of solid acid catalysts for this process "[t]he trend is definitely toward solid catalysts operating at temperature that do not require refrigeration" (1958),[116] has not yet come to pass.[118][119] The main reasons that solid acid catalysed aliphatic alkylation processes have not yet found commercial use can be traced to the rapid deactivation of solid acid catalysts that runs contrary to the high on-stream availability that is required from alkylation units.

Aliphatic alkylation units based on HF is more feed sensitive and the feed has to be dried (<20 $\mu g \cdot g^{-1}$) to limit corrosion. Other olefinic feed impurities, such as ethylene and dienes, increase the acid consumption, but can generally not justify the cost of a selective hydrogenation feed pretreatment step. The type of olefin that is used for alkylation has a significant influence on the octane number of the product (Table 4),[117] as well as acid consumption.[120] A high isobutene content in the feed is detrimental, because it rapidly oligomerises to form heavy products. The effect of oxygenates as feed impurities are still inadequately understood.[114]

Table 4. Influence of the olefin feed on the research octane number (RON) of the product obtained by isobutane alkylation with HF and H_2SO_4 alkylation processes.

Olefinic feed	Research Octane Number (RON)	
	HF-process	H_2SO_4-process
propene	90-91	88-90
1-butene	94	92-94
2-butene	>97	92-94
pentenes	-	91
mixed olefins	93	91-93

It is interesting to note that at 99% H_2SO_4 concentration, the quality of the alkylate being produced from 1-butene is better than that from 2-butene.[121] Sulphuric acid, like phosphoric acid, is capable of forming esters with olefins. It is speculated that a similar low temperature skeletal isomerisation pathway may be operative as was previously noted for solid phosphoric acid.[68] Since HTFT derived butenes are rich in 1-butene, contain little isobutene and have a low concentration of dienes, there may be some competitive advantage to use Fischer-Tropsch butenes with an H_2SO_4 alkylation process. Conversely, since HF is

not isomerising and very sensitive to water, Fischer-Tropsch butenes will have a disadvantage compared to cracker-derived feedstocks.

Aliphatic alkylation not only requires olefins, but also requires isobutane and there is little isobutane in Fischer-Tropsch syncrude. This is quite the opposite of crude oil refining, where olefin availability is constraining. Even if all the n-butane in syncrude is isomerised, only part of the total butene product could be used for alkylation.[m]

The biggest drawback of current aliphatic alkylation technologies is their significant environmental footprint. Liquid acid processes are not considered environmentally friendly, especially not HF processes. Due to the current lack of alternative technologies for alkylate production in crude oil refining context, these liquid acid processes are tolerated. This may well change in future. There is luckily a more environmentally friendly Fischer-Tropsch specific alternative to liquid acid aliphatic alkylation, namely SPA catalysed oligomerisation combined with olefin hydrogenation.[122][123]

2.6. Aromatic alkylation

Aromatic alkylation is not normally associated with refining, but rather with petrochemical production. However, with the reduction in the amount of benzene that may be included in motor-gasoline, various options for benzene reduction have been presented, amongst other benzene alkylation.[124] One of the advantages of benzene alkylation over alternatives such as benzene extraction and benzene hydrogenation, is that it retains the octane value of benzene.
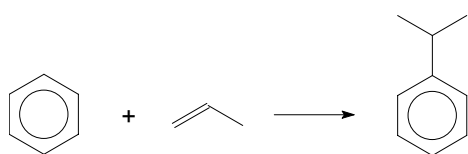
Figure 6. Aromatic alkylation with an olefin.

The alkylation of benzene with an olefin is an acid catalysed reaction (Figure 6). Various commercial processes exist for the alkylation of benzene with either ethylene or propene and the catalysts most often used are solid phosphoric acid and zeolite-type materials such as ZSM-5 (Mobil-Badger 1980's), MCM-22 (Mobil-Ratheon / Mobil-Badger 1990's), Y-zeolite (CDTech) and modified-Beta (Enichem).[125][126] The main difference between

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[m] The PetroSA HTFT refinery is an exception, since it has an HF alkylation unit. Additional butane is available from the associated gas condensate that is landed with the natural gas. Ref.(122)

SPA and zeolite catalysed processes is that SPA has a low multiple alkylation tendency, while zeolite-based processes require a transalkylation reactor after the alkylation reactor to increase the yield of mono-alkylated products.[127] In a refining context multiple alkylation is not necessarily a problem and the choice of alkylating olefin and degree of alkylation is more a function of the desired product properties (Table 5)[5][128] for the target fuel, namely motor-gasoline, jet fuel or diesel. The degree of alkylation can also be controlled by the aromatic to olefin ratio in the process. Aromatic alkylation processes are generally operated at an aromatic to olefin ratio of around 1:5 to 1:8 to limit multiple alkylation. This results in a benzene conversion of less than 20% per pass and necessitates recycling of the benzene. It also implies that the benzene should be purified sufficiently to enable such recycling. The other feed requirements are catalyst specific, with zeolites being more sensitive to heteroatom compounds in the feed than SPA.

Table 5. Fuel properties of some alkylbenzenes that can be prepared by benzene alkylation with olefins.

Compound	Density (kg·m^{-3})	RON	MON	Cetane
ethylbenzene	874.4	107.4	97.9	8
cumene	868.5	113	99.3	15
sec-butylbenzene	866.2	106.8	95.7	6
tert-butylbenzene	870.7	>115	107.4	-1
m-diethylbenzene	868.3	>115	97	9

It has been shown that aromatic alkylation can play an integral part in Fischer-Tropsch refinery design.[129] This allows the synthesis of specific high octane motor-gasoline components, while creating a platform for chemical growth. Since the purpose of benzene alkylation in refining context is to reduce benzene in motor-gasoline, the objective of the technology is "environmentally friendly". SPA-based alkylation is more environmentally friendly than zeolite-based processes, since the SPA is operated at a lower temperature, requires no transalkylation reaction and can be operated at a lower aromatic to olefin ratio,[130] making it less energy intensive. This is contrary to the trend for chemicals production by benzene alkylation that is moving more towards zeolite based processes.[125] SPA alkylation has also been shown to have specific benefits for application in a Fischer-Tropsch refinery, since it enables the production of on-specification fully synthetic jet fuel.[131]

2.7. Metathesis

A review of metathesis technologies shows that metathesis has not been developed with fuels refining in mind. It is used mainly in the olefins business to produce propene from ethylene and 2-butene, and vice versa (Olefins Convertion Technology - OCT, ABB Lummus and Meta-4™, IFP), as well as for the production of linear α-olefins (Shell Higher Olefins Process - SHOP, Shell).[132] Application of the OCT-process for the production of 3-hexene that is isomerised to 1-hexene has also been commercialised.[133]

The ability to change the carbon number distribution of an olefin pool may be of interest to Fischer-Tropsch refining, due to the high olefin content of the syncrude. Unlike oligomerisation that only produces heavier olefins from lighter olefins, or cracking that only produces lighter olefins from heavier hydrocarbons, metathesis produces heavier and lighter olefins, while retaining the same average molecular mass in the product as in the feed.[n]
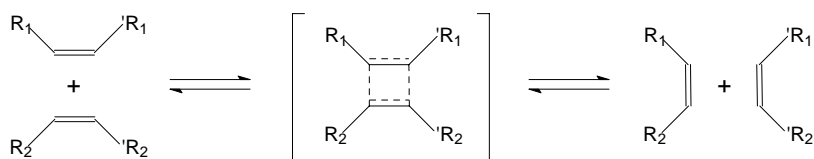

Figure 7. Olefin disproportionation (metathesis) reaction.

The metathesis reaction, which is a form of olefin disproportionation, requires an unsymmetric olefin or a mixture of olefins to result in productive disproportionation (Figure 7).[134] The most commonly used heterogeneous catalysts are based on WO_3 (OCT), MoO_3 (SHOP) and Re_2O_7 (Meta-4™). The need for frequent catalyst regeneration[135] increases the energy consumption of the process and makes it less environmentally friendly. It has also been noted that oxygenates change the catalytic behaviour of metathesis catalysts,[136] which detracts from its use in a Fischer-Tropsch environment.

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[n] Metathesis does not change the number of moles in the feed, it is a pure disproportionation reaction. When the average molecular mass of the product is different to that of the feed, it is indicative of side reactions such as oligomerisation and/or cracking.

3.   Hydrogen addition

3.1. Hydrotreating

Hydrotreating is the mainstay of refining. It is the primary method to convert heteroatom containing compounds into hydrocarbons. Hydrotreating fulfils two functions in the refinery, both related to the removal of specific functional groups. Firstly it is useful as a feed pretreatment step for refinery operations that are sensitive to impurities. For example, hydrogenation of dienes to mono-olefins as feed pretreatment before aliphatic alkylation reduces gum formation during alkylation. Secondly it is used to meet final product specifications in terms of composition. For example, the hydrogenation of sulphur containing compounds to meet the sulphur specification of transportation fuel.[137] Hydrotreating is therefore often classified in terms of its function, namely hydrodesulphurisation (HDS),[138] hydrodenitrogenation (HDN),[139][140] hydrodeoxygenation (HDO),[141] hydrodearomatisation (HDA),[142] hydrodemetalisation (HDM) and hydrogenation of olefins (HYD).[143]

Hydrotreating is invariably exothermic and the specific heat release is related to the compound type being hydrogenated (see Chapter V, Tables 5 and 6). When Fischer-Tropsch naphtha and distillate cuts are hydrotreated, the heat release can be very high.[144] This not only requires a reactor design that is capable of proper heat management, but also necessitates careful catalyst selection ensure that the reaction rate is not too high. In this respect the hydrotreating of Fischer-Tropsch materials tend to require less active catalysts in order to avoid hot spot formation and hydrogen starvation at the catalyst surface. This presents a problem, since catalyst manufacturer are discontinuing lower activity catalysts in favour of very high activity catalysts.

During hydrotreating hydrogen addition occurs. In the case of HDS, HDO and HDN, hydrogen sulphide (H_2S), water (H_2O) and ammonia (NH_3) are co-produced, which have to be removed downstream of the hydrogenation reactor. The rate of heteroatom removal for isostructural compounds is generally in the order HDS > HDO > HDN.[141] This order may change when the compounds are not isostructural.

Most commercial refinery hydrotreating catalysts are bi- or trimetallic, with Ni/Mo, Ni/W, Co/Mo, Ni/Co/Mo on alumina being the main type encountered in practice.[145] On account of the sulphur content of crude oil, these catalysts are all designed to be operated as sulphided metal catalysts and are called sulphided catalysts for short.[146] A smaller group of

hydrotreating catalysts are used for selective hydrogenation and are used in the absence of sulphur. These unsulphided catalysts are generally based on Ni, Pd or Pt on alumina.[o]

The selection of hydrotreating catalysts is very application specific.[147] In practice hydrotreaters are not loaded with a single type of catalyst, but with different layers, each performing a specific function. However, it is not only the catalyst activity that is important, but also its deactivation behaviour with the intended feed.[148] Special catalyst types are often loaded on top of the main catalyst beds to help with feed distribution and to remove feed impurities that can lead to deposit formation. Catalyst grading with an HDM catalyst on top to trap metals and avoid pressure drop problems is therefore common practice.

In a Fischer-Tropsch refinery, HDO and HYD are the main hydrotreating duties required. However, the absence of sulphur in the feed creates a problem for most hydrotreating catalysts, since they have been designed as sulphided catalysts. Standard crude oil refinery hydrotreating technology is consequently ill-suited to Fischer-Tropsch feeds. This can be overcome in two ways, by either using only unsulphided catalysts, or by adding sulphur compounds to the feed to keep the sulphided catalysts in a sulphided state. It is clear that from an environmental point of view the latter is undesirable. Ironically, it is the latter approach that is followed. This is mainly due to the action of the carboxylic acids in Fischer-Tropsch syncrude that necessitates special catalyst properties, but oxygenates in general may cause problems with unsulphided catalysts not designed for HDO.[149][150] Since the market for Fischer-Tropsch specific hydrotreating catalysts is still small, such catalysts have not yet become commercially available.

Another aspect relevant to the hydroprocessing of Fischer-Tropsch syncrude is demetallisation. In syncrude the metals are present mainly as metal carboxylates that are produced during corrosion and catalyst leaching. These metal carboxylate species can be stable under hydrotreating conditions and are not removed by standard HDM catalysts. The stability of the metal carboxylates depend on both the metal, as well as the chain length of the carboxylate. Removal of the metal carboxylates does not require hydrogenation, since it follows a thermal decomposition pathway.[151][152] At temperatures below their decomposition temperature the metal carboxylates can cause scaling in preheaters and result in catalyst bed plugging. When the metal carboxylates decompose the metal oxide that is formed will deposit on the catalyst and may be reactive under hydrotreating conditions. When a

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[o] There are many more hydrotreating catalyst types if selective hydrogenation of specific functional groups is also considered. Such transformations are mostly found in the petrochemical industry and not in refineries, although it should be noted that many compounds present in Fischer-Tropsch syncrude are seen as chemicals.

sulphiding agent is added to keep the catalyst in a sulphided state, stable sulphides can be formed and the decomposition of iron carboxylates to yield stable iron sulphides is especially troublesome in Fischer-Tropsch refineries.[150]

3.2. Hydroisomerisation

The process of hydroisomerisation can increase the degree of branching of paraffins. This is achieved by rearrangement of the carbon chain in an analogous way to olefin skeletal isomerisation. Hydroisomerisation is divided into four categories based on the type of feed material being processed, namely isobutane production (for use in aliphatic alkylation), C_5/C_6 hydroisomerisation (for octane improvement of light straight run naphtha), C_7 isomerisation (for octane improvement, but not yet commercially available) and hydroisomerisation of waxy paraffins (for lubricating oil production). This classification may initially seem arbitrary, but it is actually based on fundamental catalytic considerations.
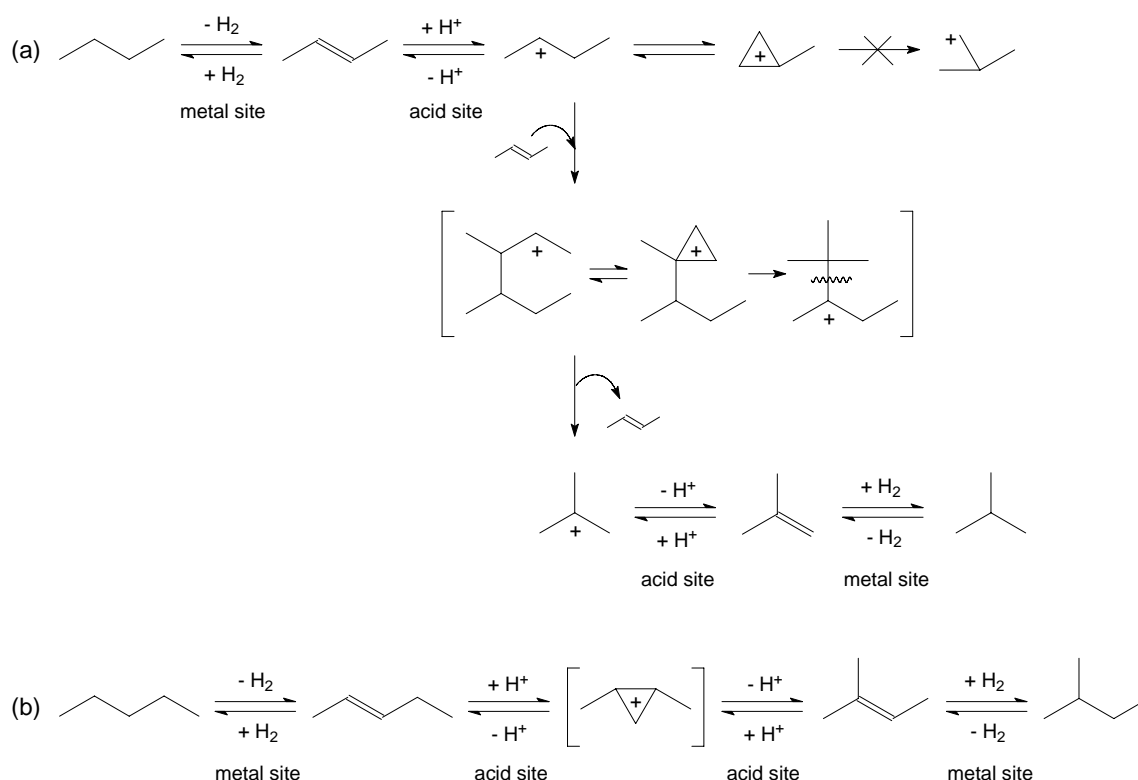

Figure 8. Hydroisomerisation of (a) butane that proceeds through a bimolecular mechanism to avoid the formation of a primary carbocation, and (b) C_5 and heavier paraffins that can proceed through a monomolecular mechanism.

Hydroisomerisation catalysts are bifunctional, since both metal sites and acid sites are necessary for the reaction to proceed (Figure 8). The metal sites are responsible for dehydrogenation of the paraffin to produce an olefin. The olefin can then be skeletally isomerised on the acid site, which is the rate determining step. The metal sites are then again responsible for the hydrogenation of the olefin.[153] The balance between metal and acid sites are important for catalyst performance, since it determines partial pressure of olefins on the catalyst surface and thereby the probability that acid catalysed side-reactions can take place, such as olefin oligomerisation and cracking.[154] The optimum metal to acid ratio, as well as acid site strength is different for the different classes of hydroisomerisation catalysts and other isomerisation mechanisms may even be operative, like in the case of butane isomerisation.[155][156] The cracking propensity of C_6 and lighter aliphatics is low. The C_6 and lighter aliphatics cannot crack to produce a tertiary carbocation intermediate and the probability of cracking to produce less stable secondary or primary carbocation intermediates is correspondingly lower. However, a C_4 aliphatic cannot rearrange without passing through a primary carbocation intermediate, which is very unstable. The same mechanistic limitations as discussed for olefin skeletal isomerisation applies (see section 2.3). Once the carbon chain length is C_7 or longer, cracking can readily proceed, which is why there are no commercially available C_7 hydroisomerisation processes. Hydroisomerisation of waxy paraffins is always accompanied by some losses due to cracking, but this is not necessarily negative, since it is a residue upgrading technology and cracking results in the production of mainly naphtha and distillate range material. It can therefore be seen as a form of mild hydrocracking, which it indeed is.

C_4 isomerisation.[157] The principal technology for *n*-butane isomerisation to isobutane is the chlorinated Pt/Al_2O_3 catalysed Butamer™ process of UOP. It operates at 180-220°C,[p] 1.5-2.0 MPa, space velocity of 2 h^{-1} and with hydrogen to hydrocarbon ratio of 0.5-2.0. The conversion is thermodynamically limited and side-product formation is less than 2%. To maintain the acidity of the catalyst, constant chlorination is required. It is consequently important to ensure that the feed is water-free and free of oxygenates that can potentially form water at reaction conditions. The need for constant chlorination also increases the environmental footprint of this technology.

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[p] There are generally two reactors, the first reactor operating at a higher temperature to increase reaction rate and the second reactor at a lower temperature, which is thermodynamically more favourable for isobutane formation. (Equilibrium concentration of isobutane at 180°C is 60%, but at 300°C it is only 40%).

C_5/C_6 isomerisation.[157][158][159][160]   There are mainly three catalyst types currently being used for C_5/C_6 paraffin isomerisation, namely chlorinated Pt/Al_2O_3 (for example UOP I-8/I-80, Procatalyse IS 612, Albemarle AT-20), Pt/mordenite (for example Süd-Chemie Hysopar, Procatalyse IS 632, UOP HS-10) and sulphated zirconia (UOP LPI-100).   The chlorinated Pt/Al_2O_3 catalysts have similar requirements, advantages and drawbacks as those already listed for C_4 isomerisation.   The main advantage is the low operating temperature (120-180°C), which favours the isomerisation equilibrium.   The main drawback, apart from the environmental concern related to the use of a chlorinated system, is the sulphur and water sensitivity of the catalyst.[161]   This led to the development of Pt/mordenite zeolite catalysts, which are resistant to sulphur and water.[q]   The drawback of a Pt/mordenite catalyst is that it requires a higher operating temperature (250-270°C), which is less favourable in terms of the isomerisation equilibrium.   Although sulphur is not a problem in a Fischer-Tropsch environment, oxygenates and water are ever-present, giving Pt/mordenite a competitive feed advantage.   This catalyst type is also more environmentally friendly, since it requires no chlorination and exceptionally long catalyst lifetimes (>8 years)[r] have been reported. Sulphated zirconia catalysts have some tolerance to water (<35 µg·g^{-1})[163] and operate at lower temperature (180-240°C) than the zeolitic system.   A catalyst cycle length of 18 months before regeneration has been reported.[159]   The isomerisation equilibrium advantage gained by a catalyst operating at low temperature, can be offset by the recycling of unconverted *n*-paraffins.   Various process options are possible.[164][165][166]   In most refineries the C_5/C_6 paraffins are present as a light straight run (LSR) naphtha mixture and in all C_5/C_6 isomerisation processes there is a feed specification to limit inclusion of C_7 paraffins to less than 2%.[s]   In practise the conversion of the *n*-pentane is equilibrium limited, but the isomerisation of the C_6 paraffins are slower and kinetically controlled.   Of all the C_5/C_6 compounds in LSR, *n*-hexane has by far the worst octane number (Table 6) and most process configurations aim at maximising the conversion of *n*-hexane.

C_7 isomerisation.[167][168]   The C_7 content of feed to C_5/C_6 isomerisation processes is limited, due to the high cracking propensity of C_7 and heavier material.   Yet, *n*-heptane has an octane number of 0 (by definition) and skeletal isomerisation would clearly be beneficial. Although progress has been made in the search for catalysts that reduce cracking and have sufficient pore diameter to allow multi-branched C_7 paraffins to diffuse, a catalyst and

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[q] New developments in this field are noted. Ref.(162)
[r] Personal communication with Dr. Karl-Heinz Stadler of Süd-Chemie (Germany).
[s] For recycle processes the inclusion of benzene and cyclohexane in the feed is also limited.

process for this purpose at this stage remains on the wish-list of refiners. The field is nevertheless actively being researched.

Table 6. Octane numbers of C₅/C₆ paraffins.[5]

Compound	RON	MON	½RON + ½MON	Relative to *n*-paraffin
C₅ paraffins				
n-pentane	61.7	62.6	62.2	-
2-methylbutane	92.3	90.3	91.3	29.2
2,2-dimethylpropane	85.5	80.2	82.9	20.7
C₆ paraffins				
n-hexane	24.8	26	25.4	-
2-methylpentane	73.4	73.5	73.5	48.1
3-methylpentane	74.5	74.3	74.4	49.0
2,2-dimethylbutane	91.8	93.4	92.6	67.2
2,3-dimethylbutane	103.5	94.3	98.9	73.5

Waxy paraffin isomerisation.[169][170][171][172] Hydroisomerisation and hydrocracking of long chain paraffins always occur in parallel. The co-production of lighter products during waxy paraffin hydroisomerisation is therefore inevitable. The reaction conditions and catalyst selection can be optimised to maximise lubricating oil production. The sulphur-free nature of LTFT waxes makes them ideal feed materials for unsulphided noble metal catalysed hydroisomerisation, which is similar to that used for hydrocracking.

3.3. Hydrocracking

The shrinking market for residues (boiling point >360°C) as heavy fuels, necessitated refiners to convert residues into products in the distillate and naphtha boiling ranges. One way of accomplishing this is by hydrocracking. The aim of hydrocracking is threefold, it removes heteroatoms by hydrotreating, it cracks the heavy material to lighter material and it reduces the aromatic content, especially polynuclear aromatics content, to meet final product specifications.

The conversion of residue material into lighter boiling fractions requires C-C bond scission, which in turn requires high temperatures, even in the presence of a catalyst. In order to convert the residue at lower temperatures than required for acid catalysed paraffin

cracking, hydrocracking employs bifunctional catalysts. These bifunctional catalysts have both metal and acid sites, similar to that used for hydroisomerisation. As mentioned previously, the performance of the bifunctional catalyst is determined by the balance between the metal and the acid sites.[154] The mechanism of hydrocracking follows the same basic steps as hydroisomerisation, but rather than hydrogenating the branched olefin directly, the branched olefin is cracked by β-scission before being hydrogenated (Figure 9).[173][174][175] Cracking by β-scission of the olefin is not the only mechanism that is operative, but it is the dominant mechanism during hydrocracking.[t] It can nevertheless be expected that the metal to acid site ratio of hydrocracking catalysts will be less than that of hydroisomerisation catalysts.
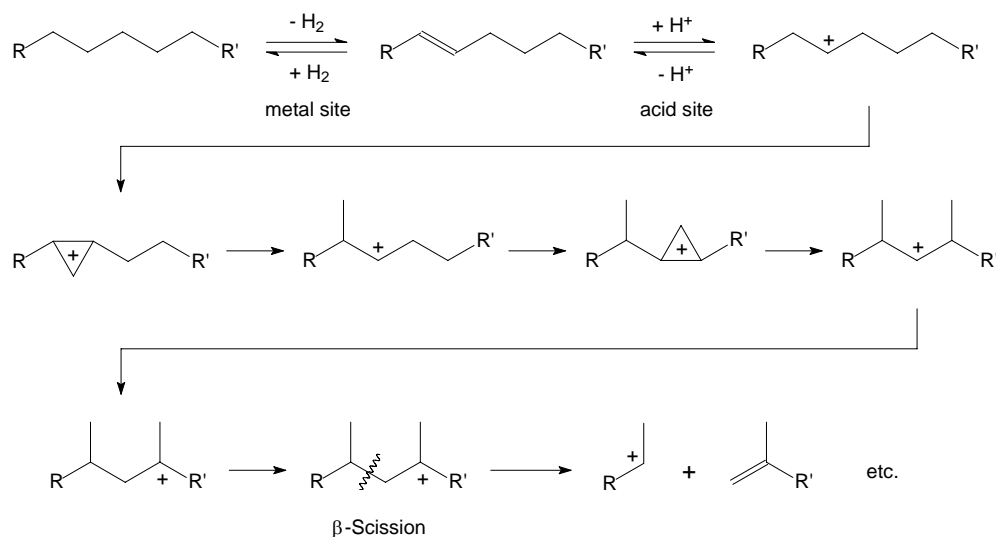

Figure 9. Hydrocracking mechanism.

The metal sites on hydrocracking catalysts are also responsible for heteroatom removal by HDS, HDO and HDN. The metal sites are similarly responsible for the hydrogenation of coke precursors, by hydrogenating aromatics that are thermodynamically favoured at high temperatures.

The conditions necessary for hydrocracking is determined by the feed quality and catalyst type, but in general hydrocrackers are operated at 360-440°C, 7-15 MPa and a space velocity of around 0.3-2.0 h^{-1}.[176] Hydrogen is co-fed in a ratio of 800-1800 normal $m^3 \cdot h^{-1}$ per 1 $m^3 \cdot h^{-1}$ of liquid feed.

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[t] During high temperature catalytic cracking of paraffins, cracking via a pentacoordinated carbocation is an important mechanistic route too. However, cracking of a carbocation that is formed by olefin protonation is much faster and therefore dominant during hydrocracking.

Hydrocracking catalysts can be divided into sulphided base-metal catalysts and unsulphided noble metal catalysts. Typical sulphided hydrocracking catalysts employ Ni/Mo or Ni/W (Co/Mo less often used) on an amorphous silica-alumina (ASA) or zeolitic support. Sulphur acts as a poison for noble metal catalysts, but with proper feed pretreatment, unsulphided noble metal hydrocracking catalysts using Pd or Pt on ASA or zeolitic supports can also used.

Hydrocracking of LTFT waxes is unique in that the feed is sulphur-free and consists of mainly linear paraffins, with small amounts of olefins and oxygenates. Unsulphided base metal hydrocracking catalysts seem to be ideal for this application, but both Ni-based and Co-based hydrocracking catalysts display high methane selectivity.[177][178] In contrast, unsulphided noble metal catalysts seem to work very well, not only on small scale,[179] but also on commercial scale, as used in the Shell Middle Distillate Synthesis (SMDS) process in Bintulu, Malaysia.[180] The hydrocracking of LTFT waxes is much more facile that crude derived residues and lower temperatures (300-370°C) and lower pressures (3-7 MPa) can be used.[179][180][181][182] The oxygenates that are present in Fischer-Tropsch products adsorb strongly on hydrocracking catalysts to cause some inhibition, but this can be beneficially used as selectivity modifier.[183][184] In general it can therefore be said that hydrocracking has a good fit with Fischer-Tropsch product refining and although it is a fairly energy intensive processing step, unsulphided hydrocracking is otherwise an environmentally friendly technology.[u]

4. Carbon rejection

4.1. Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) is used for the conversion of heavy residues to lighter material that is more hydrogen rich in comparison to the feed. It is often the main source of short chain olefins in a crude oil refinery and its operation is generally focussed on motor-gasoline production. In larger refineries that it is close to petrochemical producers, additional revenue can be generated by selling the propylene as chemical feedstock. Refinery propylene, mainly

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[u] It is somewhat surprising that the Oryx GTL facility uses Chevron's Isocracking™ technology, which employs a sulphided base metal hydrocracking catalyst operating at medium pressure. Since the wax is sulphur free, the process requires sulphur addition to the LTFT feed.

derived from FCC, presently supplies 25% of the European propylene market, 50% of the North American market and 20% of the Asian market.[185]

Catalytic cracking is a high temperature acid catalysed process. Most FCC catalysts are based on Y zeolite (10-50%) mixed with a diluent, such as kaolin, to reduce the catalyst cost. The zeolite and diluent are contained in a matrix or binder made from silica, alumina or silica-alumina. The catalyst may additionally contain additives such as pseudoboehmite to increase cracking activity and various other promoters. During FCC operation various other catalysts (catalyst additives) may be added to the catalyst mixture to customise it for the specific feed.[186] The additives are not necessarily incorporated into the catalyst, but are co-fed with the catalyst. Some of these additives are combustion promotors (Pt or Pd salts), SO_x transfer agents (basic metallic oxides), metal traps and octane improvers (H-ZSM-5 zeolite).
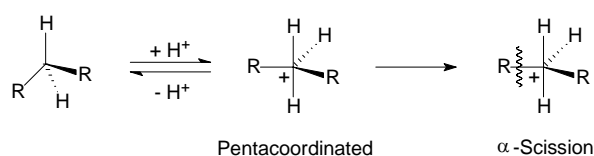

Figure 10. Cracking by protolysis involving the direct protonation of a paraffin to form a pentacoordinated carbocation that cracks by α-scission.

Catalytic cracking is similar to hydrocracking in that it uses acid catalysed cracking by β-scission to break C-C bonds and reduce the molecular weight of the product. The ease of cracking increases with the degree of branching,[27] which is introduced by skeletal isomerisation of the carbocation (Figure 9). In addition to the β-scission mechanism, cracking can also take place by protolysis, or α-scission (Figure 10). Protonation of a paraffin will yield a pentacoordinated carbon that can crack by α-scission to yield products different from β-scission, including products that would otherwise require a primary carbocation intermediate to form via β-scission. The contribution of protolysis is determined by the availability of other carbocation creating pathways and is especially important during initial conversion, before a carbocation covered catalyst surface is created.[187] Another important process during catalytic cracking is hydrogen transfer. During hydrogen transfer one molecule is dehydrogenated, while the other molecule is hydrogenated. (Acid catalysts in general have poor hydrogen desorbing capability and in instances when molecular hydrogen is detected in FCC products, thermal cracking cannot be ruled out[187]). Hydrogen transfer does not involve C-C bond scission, but affects the product selectivity to paraffins, olefins and aromatics. This process drives the carbon rejection during catalytic cracking,

since heavy aromatics (coke) are formed on the catalyst surface, while the lighter cracked products are hydrogen enriched. This is also the primary catalyst deactivation mechanism[188] and the reason why FCC includes continuous catalyst regeneration (CCR).

FCC is performed at high temperature (480-550°C), low pressure (0.1-0.3 MPa) and short contact time (<10 s). Since this is not a typical fixed bed process, a short process description is necessary. Hot regenerated catalyst (680-750°C) is brought into contact with the preheated feed (200-375°C) to the bottom of a riser. This causes thermal shock and induces some thermal (radical mechanism) cracking in the feed while heat is transferred from the catalyst to the feed. As the catalyst-feed mixture travels up the riser (2-10s), catalytic cracking occurs. At the top of the riser the temperature is typically 500-530°C. The catalyst and product are then separated in a disengager to prevent further reaction. This is quite important, because it is the intermediate cracking products that are of interest. The coked (deactivated) catalyst is then returned to the regenerator where the coke is burned off with air. This provides the energy that drives the process, which is quite energy intensive.

FCC operation is generally optimised for maximum motor-gasoline production, but light gases are invariably co-produced. The light naphtha (C_5-160°C) is olefinic (60%) and contains about 20% aromatics, giving it reasonable octane properties (RON=90-95, MON=75-82). The kerosene or heavy naphtha (160-220°C) typically has 20% olefins and 70% aromatics, with similar octane properties. The distillate cut (220-350°C) is called light cycle oil (LCO) and contains in the region of 80% aromatics. All products still contain sulphur.[186] The yield structure is influenced by the feed. The gasoline yield at constant severity gives some indication of the reactivity of the different hydrocarbon classes during FCC conversion:[186] polynaphthenes ≈ mononuclear aromatics (60%) > mononaphthenes (45) > branched paraffins (28) > n-paraffins (17) > dinuclear aromatics (10).

The small amount of residue from HTFT is too little to justify FCC and the hydrogen rich waxes from LTFT are not typical FCC feedstocks. Catalytic cracking of Fischer-Tropsch waxes has nevertheless been studied.[189][190][191][192][193][194] The paraffinic nature of the feed results in very high motor-gasoline yields being obtained (almost double that with normal crude oil derived feed) and in the presence of ZSM-5, high gas production is obtained too. Although these studies showed that waxes are good feed materials for FCC, the rationale of using FCC for wax upgrading has to be different to that in a crude oil refinery. No carbon rejection is required to enrich the hydrogen content of Fischer-Tropsch residue material, since it is already quite hydrogen rich. FCC is consequently not a technology that will naturally be considered for Fischer-Tropsch refining, unless motor-gasoline production is the main aim.

When wax hydrocracking was compared to FCC of wax for the production of transportation fuels, FCC was more economical.[195] However, the naphtha fraction from Fischer-Tropsch synthesis is already very olefinic and the good octane claimed for the motor-gasoline from FCC of wax[193][194] cannot be realised by direct blending in a Fischer-Tropsch refinery, due to the limitation on the olefin content of motor-gasoline.

FCC technology can in principle also be used in petrochemical applications for the conversion of more oxygenate rich HTFT feed to produce light olefins. Such a unit has recently been commissioned at Sasol Synfuels and is based on the KBR Superflex™ Catalytic Cracking (SCC) technology. The SCC converts oxygenate rich C_6-C_7 HTFT naphtha into ethylene, propene and high octane motor-gasoline. The SCC technology differs from standard FCC technology mainly in terms of operating temperature, which is 50-80°C higher. This implies that there is a significant contribution from thermal cracking.[196] The SCC technology has been designed to operate at even higher end-of-riser temperatures (>600°C) than deep catalytic cracking (DCC) processes that are typically operated in the temperature range 525-595°C.[197]

Despite this commercial development, in fuels refining context, FCC has a poor fit with Fischer-Tropsch feed compared to alternative residue upgrading technologies such as hydrocracking. Furthermore, a shorter catalyst lifetime is predicted due to hydrothermal dealumination of the catalyst by oxygenates in the riser and water produced by the more hydrogen-rich "coke" entering the regenerator.

4.2. Coking

Coking is used to convert heavy residues to coke and lighter fuel products. The coke has a high carbon to hydrogen ratio, making it suitable for metallurgical applications, but it may also be used for heating. It can therefore be seen as an extreme carbon rejection technology, because about 30% of the feed mass is rejected as coke[198] (in FCC it is only about 4%). Since the coke is effectively the rejected carbon and contains most of the sulphur and metals, the lighter products are comparatively hydrogen enriched and partially desulphurised, making them more amenable to conventional refining to transportation fuels. Contrary to what the name suggests, the aim of coking in a refinery is not to produce coke, but to produce hydrogen enriched distillates. The lighter products are rich in olefins, which makes coking also a source of olefins for motor-gasoline production.

Table 7. Homolytic bond dissociation energy of some C-H and C-C bonds at 298 K.

Homolytic bond dissociation reaction	Bond type	Dissociation energy	
		(kcal·mol^{-1})	(kJ·mol^{-1})
Paraffinic C-H bonds			
$CH_4 \rightarrow CH_3• + H•$	C-H	104.9	439
$C_2H_6 \rightarrow CH_3CH_2• + H•$	C-H	101.1	423
$C_3H_8 \rightarrow (CH_3)_2CH• + H•$	C-H	98.6	413
$C_4H_{10} \rightarrow (CH_3)_3C• + H•$	C-H	96.5	404
Paraffinic C-C bonds			
$C_2H_6 \rightarrow CH_3• + CH_3•$	C-C	90.1	377
$C_3H_8 \rightarrow CH_3CH_2• + CH_3•$	C-C	89	372
$C_4H_{10} \rightarrow (CH_3)_2CH• + CH_3•$	C-C	88.6	371
$C_4H_{10} \rightarrow CH_3CH_2• + CH_3CH_2•$	C-C	87.9	368
Olefinic C-H bonds			
$CH_2=CH_2 \rightarrow CH_2=CH• + H•$	C-H	110.7	463
$CH_2=CHCH_3 \rightarrow CH_2=CHCH_2• + H•$	C-H	88.8	372
Olefinic C-C bonds			
$CH_2=CHCH_3 \rightarrow CH_2=CH• + CH_3•$	C-C	101.4	424
$CH_2=CHC_2H_5 \rightarrow CH_2=CH• + CH_3CH_2•$	C-C	100	418
$CH_2=CHC_3H_7 \rightarrow CH_2=CH• + (CH_3)_2CH•$	C-C	99.2	415
$CH_2=CHC_2H_5 \rightarrow CH_2=CHCH_2• + CH_3•$	C-C	76.5	320
Aromatic C-H bonds			
$C_6H_6 \rightarrow C_6H_5• + H•$	C-H	112.9	472
$C_6H_5CH_3 \rightarrow C_6H_5CH_2• + H•$	C-H	89.7	375
Aromatic C-C bonds			
$C_6H_5CH_3 \rightarrow C_6H_5• + CH_3•$	C-C	103.5	433
$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2• + CH_3•$	C-C	77.6	325

Coking is a non-catalytic thermal process that relies on homolytic bond scission to form radicals for the reaction to proceed. The likelihood of bond rupture at a given temperature is determined by the bond dissociation energy (Table 7).[199] The temperature must therefore be high enough to promote bond scission and temperatures of 485-505°C are typically used in cokers. The feed composition determines the coke yield and feed materials with a high Conradson carbon residue produces more coke. The Conradson carbon, as

determined by the ASTM D189 method,[200] is not numerically the same as the Ramsbottom carbon (ASTM D542),[201] but these values as highly correlated. Both are measures of the carbon residue forming potential of a material when subjected to high temperature.

There are mainly two types of coking, namely delayed coking and flexicoking. In delayed coking the process is operated batchwise, with coke being produced as by-product. The feed is heated to cracking temperatures in a furnace and then allowed to soak in drums to complete the thermal conversion of the feed. In flexicoking the process is continuous, with almost complete conversion of the feed into gaseous and liquid products. The coking is done in a fluidised bed, with the coke being fed to a gasifier to produce a low heating value gas, similar in composition to blast furnace gas.[198] Both processes are energy intensive, which is their main drawback from an environmental point of view. Fischer-Tropsch products can be thermally cracked,[202][203][204] but are not suited for coking, because of their low Conradson carbon content.[v]

5.   Hydrogen rejection

5.1. Thermal cracking

Historically thermal cracking processes were classified as gas-phase or mixed-phase. Gas-phase processes typically operated at temperatures around 620°C and at low pressure, while mixed-phase processes operated in the temperature range 450-540°C.[7] Steam cracking (gas-phase) is generally associated with the petrochemical industry for the production of ethylene, as well as for the production of products such as propylene and butadiene.[205] In fuels refineries a less severe form of thermal cracking is found, namely visbreaking (mixed-phase). The term "visbreaking" is derived from "viscosity breaking", since this form of thermal cracking had previously been used to reduce the viscosity of fuel oils.[206][207]

Thermal cracking has also been used in some of the German Fischer-Tropsch plants and has since then found its way into other Fischer-Tropsch refinery strategies. In this respect it is presently considered as upgrading pathway for LTFT naphtha from GTL plants such as Oryx GTL, with specific feed benefits being claimed.[208] Cracking of LTFT waxes has been investigated as way to produce fuels, candle wax and lubricating oils.[202][203][204][209][210]

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[v] The delayed coker plant at Sasol Synfuels makes use of coal pyrolysis material.

The process is non-catalytic and follows a radical mechanism (Figure 11), with propagation steps that may involve reactions such as intermolecular radical transfer, intramolecular decomposition and thermal dimerisation.[w] Hydrogen is rejected as molecular hydrogen during thermal cracking.[212] The mechanism is the same as for coking, but with the difference that aromatics formation (coke precursors) is generally limited. Aromatic compounds can in principle be formed, but thermal cracking processes are operated in such a way that the residence time is limited to avoid excessive formation of aromatics.

(a) Initiation $R-CH_2-CH_2-R' \xrightarrow{\Delta} R-CH_2 \{ CH_2-R' \longrightarrow R-\overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_2-R'$

(b) Propagation $R-\overset{\bullet}{C}H_2 + CH_3-R'' \longrightarrow R-CH_3 + \overset{\bullet}{C}H_2-R''$

$R-CH_2-CH_2-\overset{\bullet}{C}H-R''' \longrightarrow R-CH_2 \{ CH_2-\overset{\bullet}{C}H-R''' \longrightarrow R-\overset{\bullet}{C}H_2 + CH_2=CH-R'''$

$R-\overset{\bullet}{C}H_2 + CH_2=CH-R'''' \longrightarrow R-CH_2-CH_2-\overset{\bullet}{C}H-R''''$

(c) Termination $R-\overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_2-R' \longrightarrow R-CH_2-CH_2-R'$
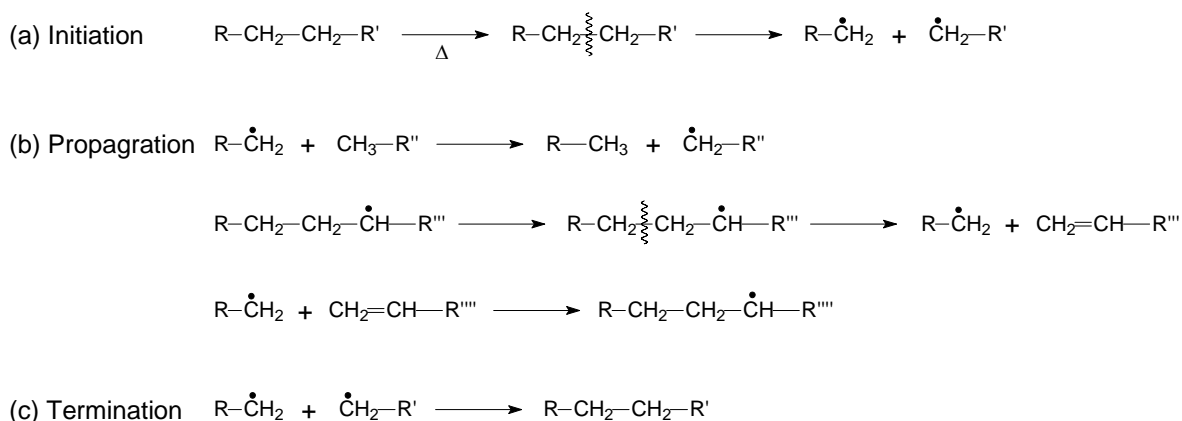
Figure 11. Thermal cracking by a radical mechanism, showing that propagation may take place by hydrogen atom abstraction (radical transfer), intramolecular cracking to produce an α-olefin and radical addition to an olefin (thermal oligomerisation).

At cracking temperatures in the range 420-500°C it was found that the product distribution from the cracking of Fischer-Tropsch waxes can be described by the Rice-Kossiakoff mechanism.[204] Oxygenates can also be thermally cracked and may either be initiated by hydrocarbon decomposition, or direct homolytic bond dissociation of the oxygenate. It should be noted that there are significant differences between the bond dissociation energies of oxygenates and oxygenate radicals. For example, it requires 349 kJ·mol^{-1} to convert butanone (MEK) into an acetyl and ethyl radical,[199] but only 40 kJ·mol^{-1} to liberate CO from the acetyl radical.[213]

Apart from the energy intensive nature of thermal cracking, it is a very clean technology. In comparison to hydrocracking it is less efficient for fuels refining, but has been shown to have some advantages over hydrocracking when it come to chemicals refining. It has been demonstrated that the <370°C boiling fraction has a high linear α-olefin content (about 40%) and that the medium wax fraction could find application as candle wax.[204]

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[w] Intramolecular isomerisation is also possible, although this type of isomerisation is limited to isomerisation of the radical position by 1-4 and 1-5 hydrogen transfer, which does not affect the skeletal structure. Ref.(211)

5.2. Catalytic reforming

Initially catalytic reforming was developed to upgrade low octane naphtha to a high octane product that is rich in aromatic compounds.[214] The hydrogen that is co-produced during this process has since become equally important,[215] due to the increasing pressure on refineries to increase their hydroconversion severity.[216]

The main reaction classes found during catalytic reforming are dehydrogenation-hydrogenation, aromatisation, cyclisation, isomerisation and hydrogenolysis. The reaction network is quite complex and is discussed in detail in literature.[217] The rate limiting step is alkane activation,[218] which is an endothermic process and one of the reasons why catalytic reforming is done at high temperature. By increasing the temperature (severity of operation) the octane number of the final product can be increased and catalytic reformers are typically operated in such a way that the product (reformate) is of sufficiently high octane to meet octane demand in the refinery. Two types of catalytic reforming are distinguished which have markedly different response to the nature of the feed.

Pt/Al₂O₃ reforming. Almost all catalytic reformers found in crude oil refineries uses Pt/Al_2O_3 based bifunctional catalysts. The first platinum based reforming process to be used for refining is the UOP Platforming™ process that came on stream in 1949.[219] The platinum is often stabilised by the addition of a second metal, which in most cases is rhenium, tin or iridium. The support material is acidified by the addition of chloro-alkanes (such as CCl_4 or C_2Cl_4), which also helps to retard platinum agglomeration and aids platinum re-dispersion during regeneration.[215] The acidity of the support is necessary to catalyse skeletal isomerisation reactions such as the conversion of alkylcyclopentanes to cyclohexane species, which is a prerequisite for aromatisation. The feed plays an important role in determining the severity of operation necessary to achieve the desired reformate octane. Cyclo-paraffins (naphthenes) react much faster than acyclic paraffins and feed materials containing a high concentration of naphthenes are called rich naphthas. Rich naphthas require less severe conditions than lean naphthas to obtain the same reformate octane number. The richness of naphtha is often expressed by the number *N+2A,* where *N* refers to the percentage naphthenes in the feed and *A* refers to the percentage aromatics in the feed. Synthetic naphtha, like that from Fischer-Tropsch synthesis, is especially poor feed, since it contains very little naphthenes and aromatics. The conversion of synthetic naphtha therefore results in much higher gas-make and lower aromatics yield compared to crude derived feed at similar

conversion.[214] The carbon chain length of the paraffins in the feed also has an impact, with paraffin reactivity for catalytic reforming by Pt/Al_2O_3 catalysts increasing in the order $C_6 <$ $C_7 << C_8 \approx C_9$ and heavier. The aromatics yield is consequently determined by $N+2A$ number and the nature of the paraffins in the feed. This can only partially be compensated for by the severity of reforming, since coke formation increases rapidly with an increase in temperature. Typical operating ranges are 490-525°C and 1.4-3.5 MPa for semi-regenerative (SR) reforming and 525-540°C and 0.3-1.0 MPa for reformers with continuous catalyst regeneration (CCR).[214][215][220] Although Pt/Al_2O_3 based reforming is a key refining technology that is very important for clean fuels production,[221] it is not an environmentally friendly technology. It is energy intensive and requires continuous addition of chloro-alkanes to keep the catalyst active. It has also been shown that Fischer-Tropsch feeds can be classified as extremely lean naphthas, making them poor feed materials for Pt/Al_2O_3 reforming. Furthermore, Pt/Al_2O_3 reforming catalysts are chlorided, which requires the feed to be dry. This further detracts from the use of Pt/Al_2O_3 reforming with Fischer-Tropsch derived feed, since it requires deep hydrodeoxygenation to remove the oxygenates present in Fischer-Tropsch derived feed.

Pt/L-zeolite reforming. The Aromax™ (Chevron Phillips Chemical company)[222] and RZ-Platforming™ (UOP)[223] technologies use monofunctional Pt/L-zeolite reforming catalysts. These catalysts have no acidity and any residual acidity in the L-zeolite structure is generally removed by ion exchange with potassium and barium. These catalysts have demonstrated very high selectivities for the aromatisation of especially C_6-C_7 paraffins and are in general considerably more active and selective for the aromatisation of *n*-paraffins.[224] The main drawback of these catalysts are their extreme sensitivity to sulphur poisoning.[225] This requires additional precautions to remove sulphur in the feed to levels below 0.05 µg·g^{-1}. Sulphur removal presents no difficulty when this technology is employed with Fischer-Tropsch derived feed, since it is already sulphur-free. The effect of oxygenates on a Pt/KL-zeolite has been studied and it was found that oxygenates and CO suppressed conversion, while water had no effect.[226] This indicated that Fischer-Tropsch feeds, even containing some oxygenates, are good feed materials for Pt/L-zeolite reforming. The suitability of this technology to refine Fischer-Tropsch products has been voiced for quite some time by Mark E. Dry, one of the key figures in the development of Fischer-Tropsch technology.[227][228] Selectivity to aromatics from *n*-paraffins are high and hydrotreated HTFT feed material from Sasol Synfuels has been successfully piloted with the Aromax™ catalyst, yielding better than predicted hydrogen and aromatics yields.[229] Environmentally speaking, Pt/L-zeolite

reforming is a much cleaner reforming technology than Pt/Al$_2$O$_3$ reforming. Although it also requires high operating temperatures, it does not require constant chloro-alkane addition and a catalyst lifetime of around a year has been reported, despite its low operating pressure (0.3-1.0 MPa).

5.3. Aromatisation

The aromatisation of C$_3$-C$_5$ hydrocarbons is related to reforming, but such units are generally not associated with refineries. The aim of LPG aromatisation is to convert normally gaseous paraffins to aromatic-rich liquid hydrocarbons. Like reforming, an added advantage is the co-production of hydrogen.
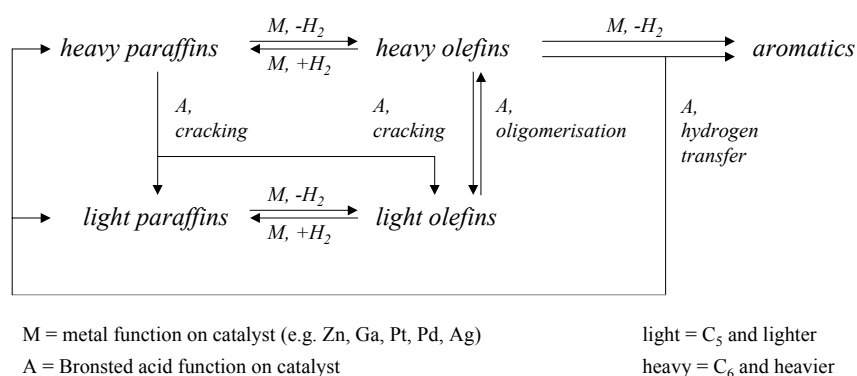

M = metal function on catalyst (e.g. Zn, Ga, Pt, Pd, Ag)   light = C$_5$ and lighter
A = Bronsted acid function on catalyst   heavy = C$_6$ and heavier

Figure 12. Reaction network during aromatisation on a bifunctional metal promoted zeolite (ZSM-5 type) catalyst.

It has been shown that light paraffins can be activated and aromatised on H-ZSM-5, without the rapid catalyst deactivation being seen on many other acidic zeolites.[x] Hydrogen rejection occurs by hydrogen transfer to olefins,[231] which limits the aromatics yield that can be obtained. H-ZSM-5 nevertheless formed the basis of the M2 Forming process (Mobil).[232] However, when a metal is added to produce a bifunctional catalyst, the hydrogen can be desorbed as molecular hydrogen and the aromatics yield is substantially increased.[233] The reaction network shown in Figure 12 illustrates the role of both acidic and metallic sites on the catalyst. Commercial LPG aromatisation processes use bifunctional catalysts and are either based on Zn/ZSM-5 (for example the Alpha process of Asahi) or Ga/ZSM-5 (for example the Cyclar process of BP). Operating conditions are in the range 450-520°C and less

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[x] Although ZSM-5 has a lower coking tendency than β-zeolite and Y-zeolite, it also has a much larger coke capacity than less coking zeolites such as faujasite. More coke lay down is therefore required before complete deactivation occurs. Ref.(230)

than 1 MPa pressure. These processes are characterised by periodic operation. Each production cycle (in the order of 2 days) is followed by a regeneration cycle during which the coke on the catalyst is removed by controlled coke burn-off. During coke burn-off, some water is generated that cause hydrothermal dealumination of the zeolite and result in eventual catalyst deactivation.[234] Numerous reaction-regeneration cycles are nevertheless possible, albeit being dependent on the water partial pressure and exposure time to water vapour during regeneration.[235] Water vapour that is produced during coke-combustion is unavoidable, but the water partial pressure is actually controlled by the water content in the nitrogen recycle gas. Nitrogen is recycled to dilute the air that is used for combustion and it is impractical to remove all the water vapour from this high temperature gas stream. In this respect the application of LPG aromatisation within a Fischer-Tropsch refinery has an advantage. The air separation units associated with synthesis gas production, also produces nitrogen as by-product. It is consequently not necessary to recycle nitrogen, since nitrogen is available as fatal by-product from air separation and can be employed on a once-through basis to reduce the water partial pressure during regeneration.

From the reaction network (Figure 12) it is clear that any hydrocarbon feed material can in principle be used. However, it may not be economical to use a C_5 and heavier liquid hydrocarbon feed. Metal promoted ZSM-5 aromatisation processes have a liquid yield of around 60-70%, which implies a significant loss of liquid volume when the feed material is a liquid hydrocarbon stream.

The use of LPG aromatisation for the upgrading of light Fischer-Tropsch fractions has been suggested[122] and the upgrading of HTFT naphtha has also been investigated. In the latter application it was found that the oxygenates present in HTFT naphtha is detrimental to the catalyst lifetime, causing not only hydrothermal dealumination, but also selective loss of the metal.[236]

The environmental footprint of LPG aromatisation is determined mainly by the high operating temperature and frequent catalyst regeneration. It is not worse that FCC, although it approaches refining from the other end, namely converting light gases into liquid products.

5.4. Alcohol dehydration

Aliphatic alcohols are primary Fischer-Tropsch products and alcohol dehydration technology is therefore a form of conversion that can be considered. It is not a technology that is

associated with crude oil refining, which is hardly surprising considering that alcohols are not found in crude oil.

During alcohol dehydration hydrogen is rejected in the form of water, thereby converting the alcohols into olefins. This can be especially beneficial in reducing the complexity of Fischer-Tropsch aqueous product refining.[237] By converting the alcohols into olefins, the separation of alcohol-water azeotropes can be avoided. The olefins are easily separated from the water and the olefins can then be co-processed with the rest of the Fischer-Tropsch olefins. Another application of alcohol dehydration that is becoming important is the partial dehydration of alcohols to ethers, which are employed as high cetane additives for diesel fuel.[33][238] Since ether formation is accompanied by an increase in molecular mass, it is also a convenient way to shift naphtha range alcohols into distillate.
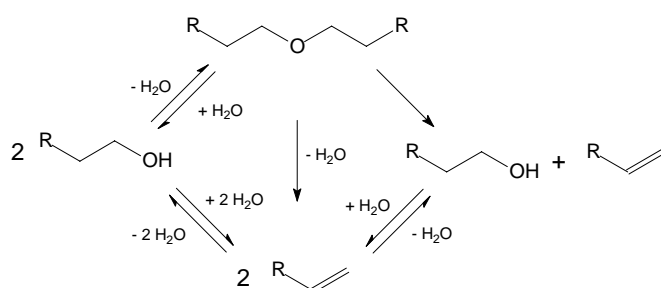

Figure 13. Alcohol dehydration by indirect bimolecular dehydration to an ether and direct monomolecular dehydration to an olefin.

Dehydration is an acid catalysed endothermic reaction. There are two mechanistic pathways (Figure 13), namely direct monomolecular dehydration of the alcohol to an olefin and the bimolecular dehydration to the ether, which can be followed by monomolecular dehydration to produce an olefin.[239] Methanol, because it contains only a single carbon atom, can only dehydrate to the ether and not directly to an olefin. Strictly speaking the dehydration reaction is reversible, but the equilibrium favours dehydration. For example, ethanol dehydration to diethyl ether and ethylene are the least favourable of the dehydration reactions, but at 300°C equilibrium constants are 3.9 and 320 respectively.[240][241]

During commercial operation water is typically co-fed with the alcohols to reduce the adiabatic temperature decrease. The water co-feed also reduces side-reactions, since the water dilutes the surface concentration of the alcohol.[242]

The range of catalysts that can be used for alcohol dehydration is limited to those that are water-tolerant.[243] Industrially the catalyst that is most often employed for alcohol dehydration is alumina.[244] Alumina is stable in the presence of large amounts of water at the

operating conditions required for dehydration, namely 300-400°C and near atmospheric pressure.[y] It is a clean conversion, albeit being energy intensive.

Dehydration to ethers is performed at lower temperatures (<250°C) and higher pressures, with acidic resins being the preferred catalysts to use. This is also a clean conversion, also from an energy usage perspective.

Dehydration of Fischer-Tropsch aqueous product alcohol mixtures to olefins has been practised commercially. The dehydration of alcohols on η-alumina is not affected by the presence of carbonyls and carboxylic acids. These oxygenates are also converted, but it was found that the alumina catalyst deactivated in a matter of days for such conversions, albeit without affecting the catalyst's activity for the alcohol dehydration reaction.[245]

It should be noted that the reverse reaction, namely olefin hydration, may also be relevant in a Fischer-Tropsch context. Ethylene hydration to ethanol is a useful way to convert ethylene into a transportable product when the Fischer-Tropsch refinery is not close to a petrochemical market. The ethanol itself can even be added to the fuel. Ethylene hydration is a commercial phosphoric acid catalysed process.[246] Propylene can also be hydrated to produce isopropanol,[247] but is less important in a refining context, since propylene has numerous other refining pathways. Like dehydration, hydration catalysts also need to be water-tolerant and only a limited number of catalysts have been investigated for this purpose.[248]

6. Discussion

Refining technologies have been evaluated in terms of their compatibility with Fischer-Tropsch syncrude as feed and their environmental friendliness. The selection of technologies for use with Fischer-Tropsch syncrude cannot be done purely on a theoretical basis, but will always to some extent be dictated by the refinery design. Nevertheless, the guiding principle should be to select the most environmentally friendly refining technologies for the task.

Since the term "environmentally friendly" has become charged with emotion and filled with political undertones, its meaning in the present context will be made clear. It is used as a term to describe the collective impact of aspects that would make a technology less efficient or cause it to generate more waste products than necessary for the conversion of

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[y] The dehydration temperature required depends on the feed. The conversion of ethanol to ethylene requires a higher temperature than any of the other alcohol dehydration reactions. It is also far easier to dehydrate

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interest. The following specific aspects have been considered for the different refining technologies previously discussed (Table 8):

a) *Fischer-Tropsch fit*. If a technology is compatible with Fischer-Tropsch syncrude, it implies that the least effort will have to be expended in feed pretreatment and that the conversion itself will be suited to deal with type of molecules present in the feed. Although this does not render the technology environmentally friendly, it is likely to be less wasteful than other technologies having the same aim, but a poorer Fischer-Tropsch fit.

b) *Waste generation*. All irreversible processes or activities generate waste (second law of thermodynamics), whether it be wasted energy or "low energy" by-products. It is therefore not helpful to consider waste generation per se, but to rather focus on the generation of waste in excess of the norm. For example, the solid waste resulting from unloading a spent catalyst from a refinery process is the norm and deviations from this norm would be the generation of excessive amounts of spent catalyst waste, or very hazardous catalyst waste.

c) *Chemicals addition*. The nature of refining is such that it deals with chemicals, some of which are quite hazardous. The type of chemicals that will be highlighted as increasing the environmental footprint of the technology, are those that are either present in very large volumes, or those that are destructively added (non-catalytic) to make the process work. It should be noted that in some instances this is done to gain energy efficiency and a trade-off is involved.

d) *Energy requirements*. Processes that are energy intensive, or operate at high temperature, are considered less environmentally friendly, since they indirectly generate waste. High temperature processes are usually, but not necessarily more energy intensive than low temperature processes.[z]

The summary presented in Table 8 makes it clear that a Fischer-Tropsch refinery will look very different to a crude oil refinery. Technologies such as FCC, coking and Pt/Al_2O_3 catalytic reforming, that are the mainstay of crude oil refineries, have poor compatibility with Fischer-Tropsch syncrude. The design of Fischer-Tropsch refineries, taking cognisance of the technology selection, will be explored in the next chapter.

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branched alcohols than linear alcohols. The operating temperature can be lowered by using a more acidic catalyst, but side-reactions such as olefin oligomerisation may become a problem.

[z] A proper evaluation of the energy use of processes has to take waste heat recovery into account. It is recognised that proper quantitative analysis is necessary to correctly rank technologies with respect to their energy requirements, but such a detailed analysis has not been attempted.

Table 8. Compatibility of refining technologies with Fischer-Tropsch syncrude and their overall environmental friendliness.

Refining technology	Catalyst	FT-fit	Waste	Chemicals	Energy use
Double bond isomerisation	Alumina	Good	Low	None	High
Oligomerisation	Acidic resin	Average	Low	None	Low
	ZSM-5	Good	Low	None	Moderate
	ASA	Good	Low	None	Low
	SPA	Good	Low	None	Low
	Homogeneous	Average	Moderate	Ni-complex	Low
Olefin skeletal isomerisation	Ferrierite	Average	Low	None	High
	Alumina	Good	Low	None	High
	Acidic molsieve	Poor	Low	None	Moderate
Etherification	Acidic resin	Average	Low	None	Low
Aliphatic alkylation	HF	Poor	Low	HF	Low
	H_2SO_4	Average	Moderate	H_2SO_4	Low
Aromatic alkylation	SPA	Good	Low	None	Low
	Zeolite	Average	Low	None	Moderate
Metathesis	Metal oxide	Average	Low	None	Moderate
Hydrotreating	Sulphided	Average	Low	DMDS	Moderate
	Unsulphided	Average	Low	None	Low
Hydroisomerisation	Pt-alumina	Poor	Low	Chloroalkane	Low
	Pt-zeolite	Good	Low	None	Low
	Pt-metal oxide	Good	Low	None	Low
Hydrocracking	Sulphided	Average	Low	DMDS	High
	Unsulphided	Good	Low	None	High
Fluid Catalytic Cracking	Zeolite	Poor	Low	None	High
Coking	Thermal	Poor	Low	None	High
Thermal cracking	Thermal	Good	Low	None	High
Catalytic reforming	Pt/Al_2O_3	Poor	Low	Chloroalkane	High
	Pt/L-zeolite	Good	Low	None	High
LPG aromatisation	Metal/ZSM-5	Average	Low	None	High
Alcohol dehydration	Alumina	Good	Low	None	Moderate
	Acidic resin	Good	Low	None	Low

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