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The Fischer–Tropsch process: 1950–2000

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Abstract

The decision to build a Fischer–Tropsch (FT) plant is still fraught with risk because it has to be based on the perceived future price and availability of petroleum crude oil and on local politics. The most expensive section of an FT complex is the production of purified syngas and so its composition should match the overall usage ratio of the FT reactions, which in turn depends on the product selectivity. The kinetics, reactor requirements, control of selectivity and the life of cobalt and iron catalysts are discussed and compared. Control of the FT conditions coupled with appropriate downstream processes results in high yields of gasoline, excellent quality diesel fuel or high value linear α-olefins. The history of the various FT options and of the improvements in FT reactor technologies over the last 50 years is reviewed. It appears that "new" technologies are re-discovered in cycles of 15–30 years and it often takes the same time for the implementation of new concepts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Viability of FT plants

This review deals mainly with the industrial and practical aspects of the Fischer–Tropsch (FT) process.

Currently the world's fuel and chemical production is based predominantly on petroleum crude oil. The presently known reserves of methane and of coal exceed that of crude oil by factors of about 1.5 and 25, respectively. Production of syngas from methane or coal and conversion of the syngas to a range of fuels and chemicals could become increasingly of interest as the reserves of crude oil are depleted and/or the price of crude rises. The industrial application of the FT process started in Germany and by 1938 there were nine plants in operation having a combined capacity of about 660×10^3 t per year [1]. Even though these plants ceased to operate after the second world war, interest in the FT process remained because at that stage there was the persistent perception that the reserves of crude oil were very limited. Based on syngas produced from methane, an FT plant with a capacity of 360×10^3 t per year was built and operated in Brownsville, TX, during the 1950s but a sharp increase in the price of methane caused the plant to be shut down. During the same time period, based on the world-wide prediction of increasing crude oil prices an FT plant based on coal came on stream in Sasolburg, South Africa. Even before construction of this plant was completed, however, the huge oil fields of the Middle East were discovered and consequently the predicted rise in the price of crude oil did not materialise and interest in the FT process all but disappeared.

The economic viability of the FT process obviously depends on the price of crude oil and as this has varied considerably over the past 30 years (see Fig. 1) the decision to construct an FT complex is clearly fraught with risk. The oil crises of the mid 1970s prompted Sasol to construct two much larger

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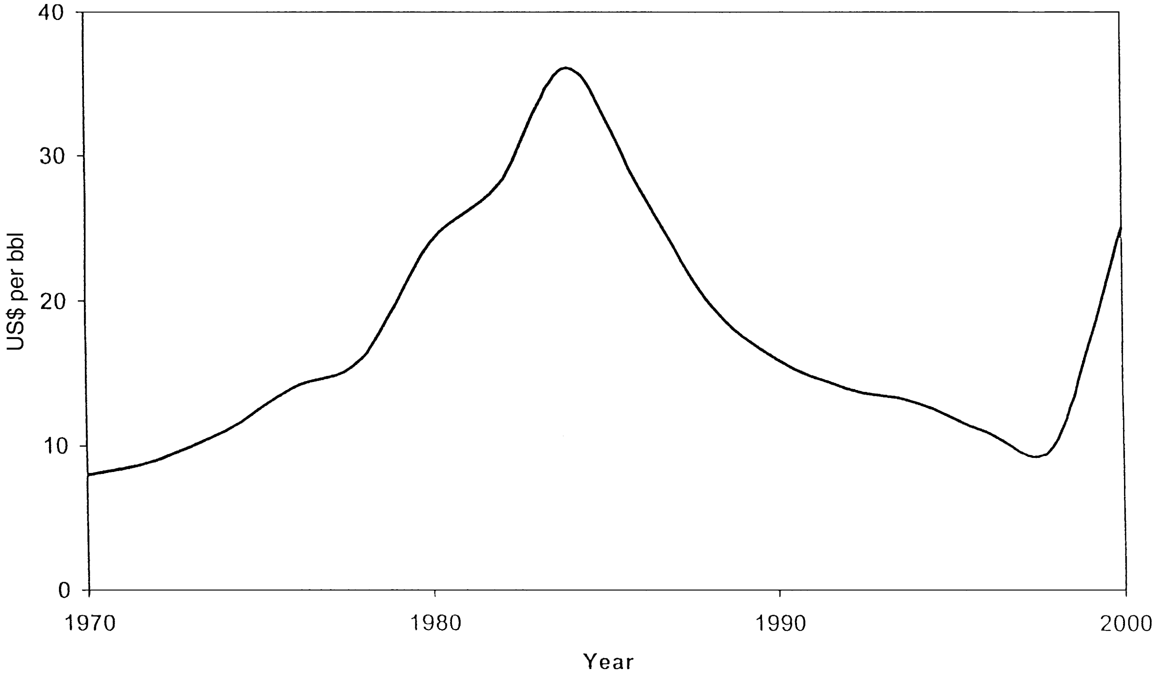

Fig. 1. Variation in petroleum crude oil price.

coal-based FT complexes and this time things worked out better as the two plants came on-line in 1980 and 1982 when the price of crude exceeded US$ 30 per barrel. At that stage the combined capacity of the three Sasol plants was about 6000×10^3 t per year. Based on methane, the Mossgas plant in South Africa and the Shell plant at Bintuli, Malaysia, came on stream in 1992 and 1993, respectively. At that stage, however, the price of crude had dropped to about US$ 15 per barrel and so the timing of these two plants, with capacities of about 1000×10^3 and 500×10^3 t per year, respectively, was not as fortunate as had been the case for the two new Sasol plants. Crude oil prices continued to decline to about US$ 10 per barrel, but in 1999 there was a dramatic increase and at the time of writing the price is again above US$ 30 per barrel. Environmental/political considerations are also factors. Thus, for instance, certain large new oil fields are associated with high levels of natural gas the flaring of which is prohibited. In order to recover the crude oil the construction of FT plants to convert the methane to oil is being considered.

2. Preparation of syngas

In an FT complex the production of purified syngas typically accounts for 60–70% of the capital and running costs of the total plant. Given its availability, methane is preferred to coal for syngas production. Not only is the capital cost of the methane conversion plant about 30% lower but the process is more efficient. In methane reforming about 20% of the carbon is converted to CO_2, whereas with coal gasification the figure is about 50% due to coal's much lower hydrogen content. Since the cost of syngas is high it is important that the maximum amount is converted in the downstream FT reactors. This requires that the composition of the syngas matches the overall usage ratio of the reactions. For cobalt-based FT catalysts the dominant reaction is the FT reaction itself, typically

$$CO + 2.15H_2 \rightarrow \text{hydrocarbons} + H_2O$$

That is, the H_2/CO usage ratio is about 2.15. When iron-based catalysts are used, however, the water-gas shift (WGS) reaction also readily occurs

$$CO + H_2O \rightarrow CO_2 + H_2$$

and so this changes the overall usage ratio. For the low-temperature FT (LTFT) process the H_2/CO usage ratio is typically about 1.7. At higher temperatures the WGS is rapid and goes to equilibrium and this allows CO_2 also to be converted to FT products, via the reverse WGS followed by the FT reaction. Thus if the syngas has a ratio of $H_2/(2CO + 3CO_2)$ equal to about 1.05 all of the H_2, CO and CO_2 can in principle be converted to FT products.

Currently in all three Sasol plants the primary source of syngas is from the gasification of coal in Lurgi dry-ash gasifiers [2]. Where the coal enters the gasifier the temperature is only about 600 °C and hence there is a coproduction of aromatic tars, oils and naphthas and phenols as well as ammonia, all of which have to be separated and worked up into saleable products. In the gasification zone of the gasifiers the temperature is about 1200 °C and hence under the operating pressure of about 3 MPa a considerable amount of methane is also produced. After purification, i.e. removal of excess CO_2 and all of the H_2S and organic sulphur compounds, the syngas contains about 11% methane. The H_2/CO ratio is about 1.8 and so is suitable as feedgas to the wax producing LTFT reactors. In the case of the high-temperature FT (HTFT) synthesis producing gasoline and light olefins the methane contained in the purified Lurgi syngas together with the methane produced in the FT reactor is catalytically reformed in autothermal reactors [2]. The reformed gas together with the Lurgi gas has a $H_2/(2CO + 3CO_2)$ ratio close to the desired value of 1.05 and so is suitable as feed to the HTFT reactors. The complexity of the syngas production from coal accounts for the higher production cost relative to syngas from methane.

The Mossgas plant is based on methane which is catalytically reformed in two stages, primary tubular reactors followed by secondary autothermal reactors [3]. The tailgas from the FT reactors, containing unconverted syngas, CH_4 and CO_2 is recycled to the autothermal reformers. The recycling of CO_2 ensures the attainment of the required $H_2/(2CO+3CO_2)$ ratio for the HTFT reactors.

In the Shell plant the primary source of syngas is from the non-catalytic partial oxidation of CH_4 at high pressure and at about 1400 °C [4]. The CH_4 slip is only about 1%. The H_2/CO ratio is about 1.7 and this is below the 2.15 required for the cobalt-based catalyst used in the FT section. The ratio is raised by adding the H_2 rich gas produced by catalytic stream reforming the tailgas of the FT reactors (after knock-out of the water and heavier FT hydrocarbons).

In the proposed Exxon AGC-21 process which has been demonstrated in a 8000 t per year unit, syngas is prepared by catalytic reforming in a fluidised bed unit [5]. Since the rate of heat exchange is much higher, the differential pressure lower and the gas through-put higher in fluidised bed reactors compared to fixed bed reactors the cost of producing syngas from methane should be significantly lower.

In the proposed Syntroleum process [6] methane is reformed at low pressure in air blown reactors and this eliminates the need for an oxygen plant. FT synthesis is also carried out at low pressure. The viability of these processes needs to be demonstrated on a larger scale.

3. FT reactor options and developments

Currently there are two FT operating modes. The high-temperature (300–350 °C) process with iron-based catalysts is used for the production of gasoline and linear low molecular mass olefins. The low-temperature (200–240 °C) process with either iron or cobalt catalysts is used for the production of high molecular mass linear waxes.

Since the FT reactions are highly exothermic it is important to rapidly remove the heat of reaction from the catalyst particles in order to avoid overheating of the catalyst which would otherwise result in an increased rate of deactivation due to sintering and fouling and also in the undesirable high production of methane. High rates of heat exchange are achieved by forcing the syngas at high linear velocities through long narrow tubes packed with catalyst particles to achieve turbulent flow, or better, by operating in fluidised catalyst bed reactor. Fig. 2 depicts a multitubular reactor and Fig. 3 shows three types of fluidised bed reactors.

3.1. *High-temperature operation*

The commercial FT reactors in the Brownsville, TX, plant [7], which only operated for a brief period in the mid 1950s, were of the fixed fluidised bed (FFB)

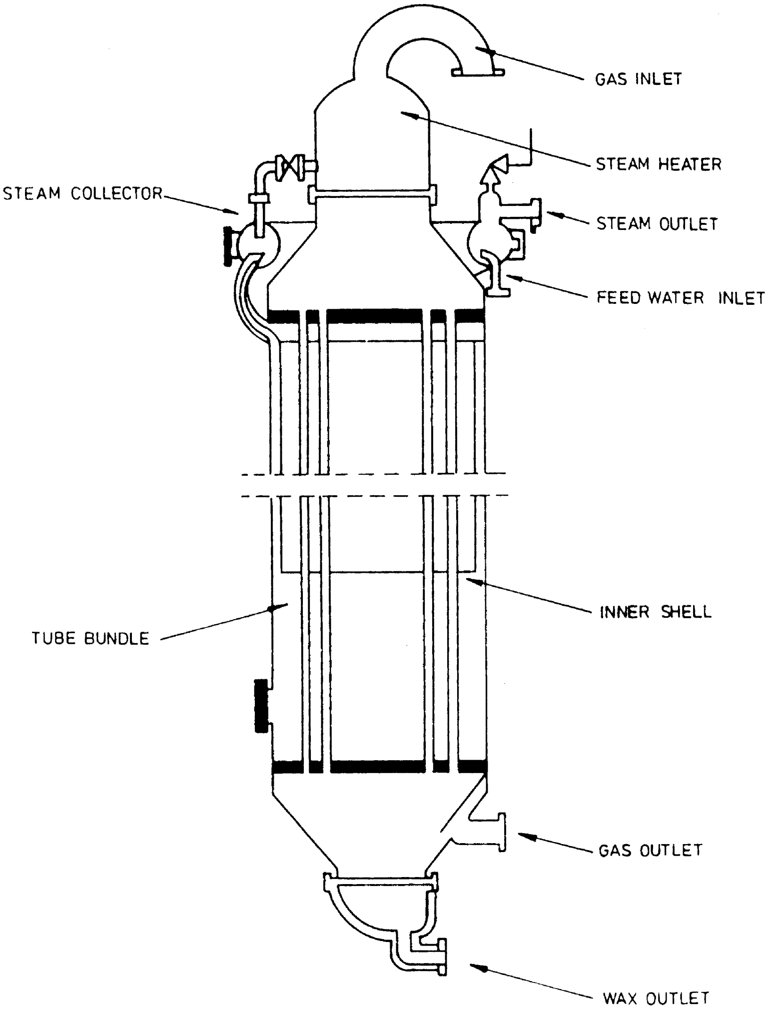

Fig. 2. Multitubular fixed bed FT reactor.

type (Fig. 3B). The reactors operated at about 2 MPa and 300 °C, i.e. they were HTFT reactors. For the first Sasol plant at Sasolburg the Kellogg-designed circulating fluidised beds (CFBs) (Fig. 3A) were chosen. These reactors operated at about 2 MPa and 340 °C. After making some process and catalyst improvements these reactors operated very well for many years. The improved reactors were named Synthol reactors. For the two new Sasol plants constructed about 25 years later at Secunda the same type of reactors were installed but with improved heat exchangers and the capacity per reactor was increased three-fold (wider diameter and higher operating pressure). The same larger type of CFB reactors, with further improved heat exchangers, were installed in the Mossgas FT complex. It should be noted that in CFB reactors there are two phases of fluidised catalyst. Catalyst moves down the standpipe in dense phase while it is transported up the "reaction" zone (left-hand side of Fig. 3A) in lean phase. To avoid the feedgas going up the standpipe the differential pressure over the standpipe must always exceed that over the reaction zone. At the high operating temperature carbon is deposited on the iron-based catalysts and this lowers the bulk density of the catalyst

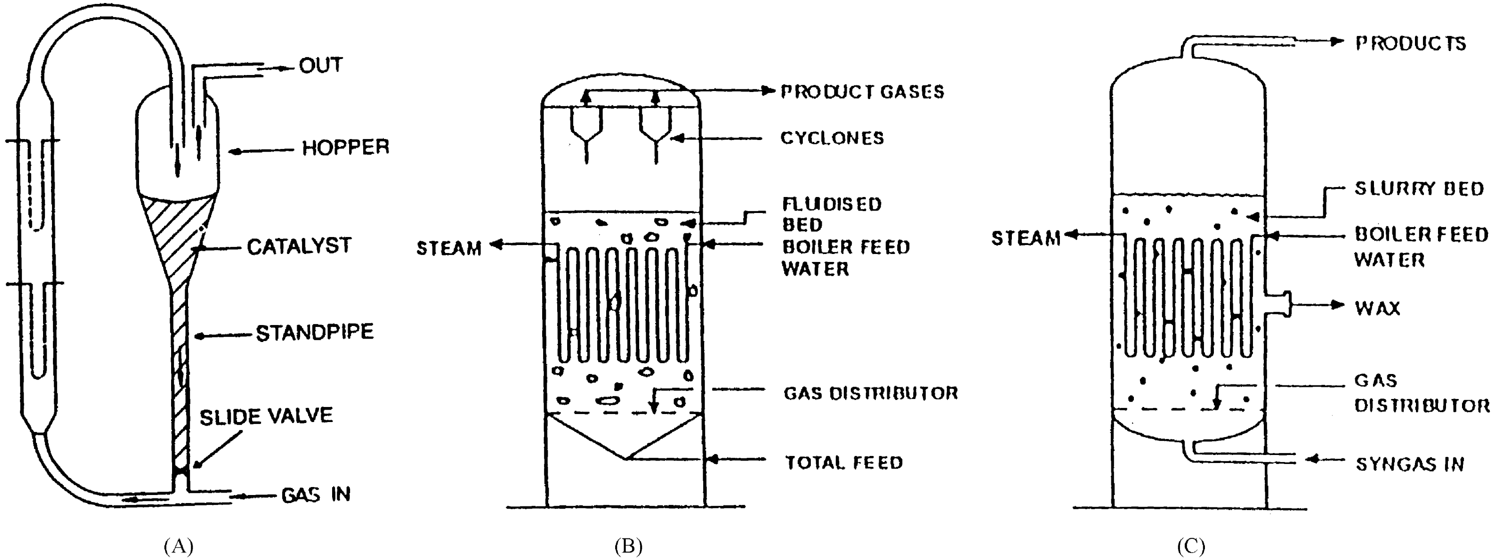

Fig. 3. Fluidised bed FT reactors: (A) CFB reactor; (B) ebulating or FFB reactor; (C) slurry phase bubbling bed reactor. Types (A) and (B) are two phase systems (gas and solid catalyst), while type (C) has three phases present, gas passing through a liquid in which the solid catalyst particles are suspended. Note the diagrams are not drawn to the same scale. The CFB reactors are about three times higher than the FFB or slurry reactors.

and thus the differential pressure over the standpipe. It is therefore not possible to raise the catalyst loading in the reaction section in order to compensate for the normal decline of catalyst activity with time-on-stream.

Although the original commercial HTFT reactors at Sasolburg were CFB units, the Sasol R&D department's HTFT pilot plants used to develop improved catalysts and to study various process variables were FFB units [2]. Under apparently similar process conditions the pilot plant units appeared to outperform the commercial units and so in the late 1970s it was decided to investigate the feasibility of commercial sized FFB units. Because rumour had it that the commercial units at the Brownsville, TX, plant had experienced fluidisation problems an exhaustive study of the fluidisation behaviour of the Sasol HTFT catalyst was undertaken using large Plexiglas units. In 1984 a 1 m i.d. FFB demonstration reactor, designed by Badger, was brought on-line at the Sasolburg plant. In 1989 a 5 m i.d., 22 m high commercial unit came on stream and it met all expectations [8]. From 1995 to 1999 the 16 second generation CFB reactors at Secunda were replaced by eight FFB reactors, four of 8 m i.d. with capacities of 470×10^3 t per year each and four of 10.7 m i.d. each with a capacity of 850×10^3 t per year. These reactors were named Sasol Advanced Synthol (SAS). It is of interest to note that about 35 years after the shut down of the Brownsville, TX, FT plant which used FFB reactors improved versions of the same type of reactor are operating at Sasol.

The main advantages of FFB over CFB reactors are as follows:

- The construction cost is 40% lower. For the same capacity the FFB reactor is much smaller overall.
- Because of the wider reaction section more cooling coils can be installed increasing its capacity. (More fresh gas can be fed by either increasing the volumetric flow or by increasing operating pressure. Pressures up to 4 MPa are feasible.)
- At any moment all of the catalyst charge participates in the reaction, whereas in the CFB only a portion of it does.
- For the reasons previously discussed the lowering of the bulk density by carbon deposition is of less significance in the FFB and thus a lower rate of on-line catalyst removal and replacement with fresh catalyst is required to maintain high conversions. This lowers the overall catalyst consumption.
- Because the iron carbide catalyst is very abrasive and the gas/catalyst linear velocities in the narrower sections of the CFB reactors is very high these sections are ceramic lined and regular maintenance is essential. This problem is absent in the lower linear velocities FFB reactors and this allows longer on-stream times between maintenance inspections.

3.2. Low-temperature operation

Under the operating conditions used the large amount of wax produced is in the liquid phase in the FT reactors and so three phases are present, liquid, solid (catalyst) and gas. In top-fed multitubular reactors (Fig. 2) the wax produced trickles down and out of the catalyst bed. In slurry reactors (Fig. 3C) the wax produced accumulates inside the reactors and so the net wax produced needs to be continuously removed from the reactor.

For the Sasolburg FT plant which came on stream in 1955 five multitubular ARGE reactors (designed by Lurgi and Ruhrchemie) were installed for wax productions [2]. These reactors are currently still in operation. Each reactor contained 2050 tubes, 5 cm i.d. and 12 m long. They operate at 2.7 MPa and 230 °C. The production capacity of each is about 21×10^3 t per year. Based on Sasol R&D pilot plant studies an additional high capacity reactor operating at 4.5 MPa was installed in 1987 [9].

In the Shell Bintuli plant which came on stream in 1993 there are four large multitubular reactors each with a capacity of about 125×10^3 t per year. There are probably about 10 000 tubes per reactor. As cobalt-based catalysts are used, which are much more reactive than the iron-based catalysts used in the Sasolburg reactors, the tube diameters of the Shell reactors are narrower in order to cope with the higher rate of reaction heat released.

The use of slurry bed reactors for FT synthesis was studied by several investigators in the 1950s, e.g. Kölbel developed and operated a 1.5 m i.d. unit [10]. In the late 1970s Sasol R&D compared the performance of fixed and slurry bed systems in their 5 cm i.d. pilot plants and found the conversions and selectivities to be similar [2]. Further development was delayed because a reliable system was required to separate the net liquid wax produced from the fine friable precipitated iron-based catalyst used. In 1990 an efficient filtration device was tested in a 1 m i.d. demonstration slurry bed reactor. In 1993 a 5 m i.d. commercial unit was commissioned and has been in operation ever since [11]. Its capacity is about 100×10^3 t per year which equals that of the combined production of the original five ARGE reactors. Note again that only about 40 years after Kölbel's pioneering work did the first commercial slurry reactor come on-line. Using a cobalt-based catalyst Exxon successfully operated a 1.2 m i.d. slurry bed reactor for wax production [5]. The unit's capacity was 8.5×10^3 t per year.

The advantages of slurry over multitubular reactors are as follows:

- The cost of a reactor train is only 25% of that of a multitubular system.
- The differential pressure over the reactor is about four times lower which results in lower gas compression costs.
- The lower catalyst loading translates to a four-fold lower catalyst consumption per tonne of product.
- The slurry bed is more isothermal and so can operate at a higher average temperature resulting in higher conversions.
- On-line removal/addition of catalyst allows longer reactor runs.

The disadvantage of a fluidised system is that should any catalyst poison such has H_2S enter the reactor all of the catalyst is deactivated, whereas in a fixed bed reactor all the H_2S is adsorbed by the top layers of catalyst, leaving the balance of the bed essentially unscathed.

4. FT catalysts, preparation and activity decline

Only the metals Fe, Ni, Co and Ru have the required FT activity for commercial application. On a relative basis taking the price of scrap iron as 1.0 the approximate cost of Ni is 250, of Co is 1000 and of Ru is 50 000. Under practical operating conditions Ni produces too much CH_4. Besides the very high price of Ru the available amount is insufficient for large scale application. This leaves only Fe and Co as viable catalysts.

Iron-based catalysts used for wax production (LTFT process) are currently prepared by precipitation techniques, promoted with Cu and K_2O and bound with SiO_2. The iron content is high, typically the composition is 5 g K_2O, 5 g Cu and 25 g SiO_2 per 100 g Fe [2]. Prior to FT application the catalysts are usually partially pre-reduced with either H_2 or mixtures of H_2 and CO. The iron catalysts used in the high-temperature application is prepared by fusing magnetite together with the required chemical (usually K_2O) and structural promoters such as Al_2O_3 or MgO [2]. The catalyst is pre-reduced with H_2 at about 400 °C.

Cobalt-based catalysts are only used in the LTFT process as at the higher temperatures excess CH_4 is produced. Because of the high price of Co it is desirable to minimise the amount used but to maximise the available surface area of the metal. To achieve this the Co is dispersed on high area stable supports such as Al_2O_3, SiO_2 or TiO_2 [12]. Typically the cobalt metal loadings vary from 10 to 30 g per 100 g of support. The catalysts are also usually promoted with a small amount of noble metal, e.g. Pt, Ru, Re which is claimed to enhance the reduction process and also keep the Co metal surface "clean" during FT [13]. It has been found that there is a clear correlation between activity and Co metal area irrespective of the nature of the support, i.e. the support has no chemical effect on the turn over frequency of Co sites [14].

In order to minimise reactor down-time and catalyst consumption it is vital that the FT catalysts maintain high activity for long times. Both Co and Fe catalysts are permanently poisoned by sulphur compounds and thus the sulphur content of the syngas should be kept below about 0.02 mg/m^3 (STP). The exact detail of the chemical steps occurring during FT remains a contentious topic but because the carbon–oxygen bond in CO has to be broken during the process it is very probable that both carbon species such as elemental C, CH_x, etc. and oxygenated species such as O, OH, H_2O, etc. are chemisorbed on the surface of the metal catalyst. The former represent "carbided" metal sites and the latter "oxidised" metal sites. The process of course involves rapid cycling, i.e. at any instant a particular surface metal atom could be in the oxidised, carbided or reduced state. This chemical cycling should enhance sintering and so loss of active surface area. The metal in the oxidised state can also chemically interact with the support forming inert aluminates, silicates, etc. The smaller the supported metal particles, i.e. the higher the proportion of exposed surface metal atoms, the higher the likelihood of these processes occurring. This could mean that a very highly dispersed metal may well have a high initial FT activity but could rapidly decline with time-on-stream. For similar reasons high H_2O/H_2 ratios within the reactor should not exceed some critical value. High conversions can nevertheless be achieved by recycling a portion of the tailgas after water and heavy product knock-out. This is common practice in FT operations.

For iron-based catalysts bulk phase oxidation occurs in addition to the above factors [15]. At high temperatures aromatics are formed which lead to fouling of the surface by aromatic coke [2,15]. Large amounts of elemental carbon is also formed which results in catalyst break up and subsequent physical loss of the low density carbide and alkali rich fines from the fluidised bed reactors. The deposition rate of elemental carbon increases with the alkali promoter content of the catalysts and correlates with the value of $p_{CO}/p_{H_2}^2$ at the reactor entrance [2]. The latter factor means that if the syngas pressure is increased then despite the higher FT production rate the rate of carbon deposition is lower.

5. FT selectivity

Irrespective of operating conditions the FT synthesis always produces a wide range of olefins, paraffins and oxygenated products (alcohols, aldehydes, acids and ketones). The variables that influence the spread of the products are temperature, feed gas composition, pressure, catalyst type and promoters. There is, however, always a fixed interrelation between the individual products irrespective of what variables were altered. Fig. 4 illustrates the relationship between the CH_4 selectivity and that of some selected hydrocarbon cuts. The explanation of these interrelationships lies in the stepwise growth process occurring on the catalyst surface. Fig. 5 illustrates the concept of the process. The CH_2 units, formed by the hydrogenation of CO are taken as the "monomers" in a stepwise oligomerization process. At each stage of growth the adsorbed hydrocarbon species has the option of desorbing or being hydrogenated to form the primary FT products or of adding another monomer to continue the chain growth. If it is assumed that the probability of chain growth (α) is independent of the chain length then it

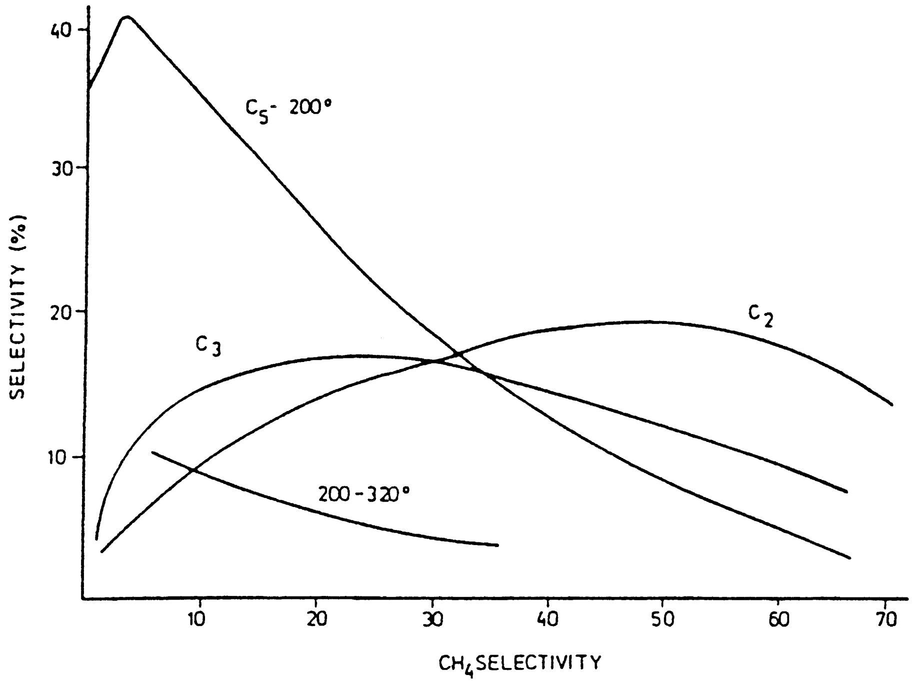

Fig. 4. The relation between the selectivity of CH_4 and that of various hydrocarbon cuts (on a carbon atom basis) for the HTFT process.

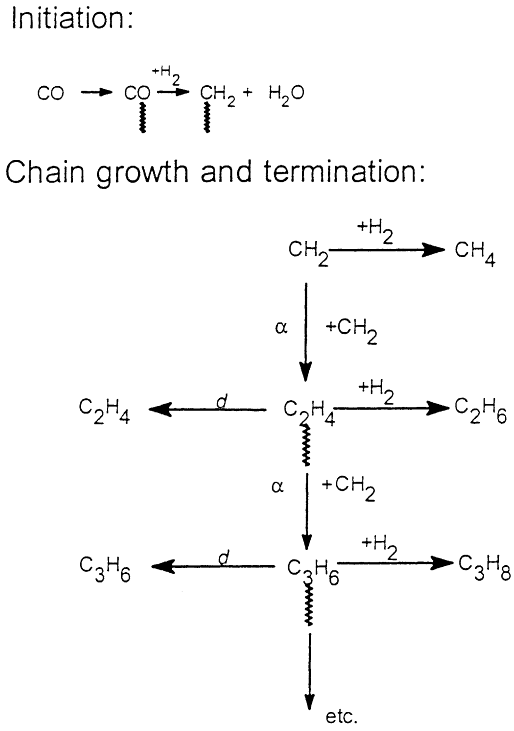

Fig. 5. FT stepwise growth process. Note that no specific chemical mechanism is implied in the sequence presented.

is a simple matter to calculate the product distribution for various values of α. The agreement between the calculated and observed results, with the exception of the C_1 and C_2 products [2,9], is good and this supports the concept of a stepwise growth process.

It must be stressed that it is not proposed that Fig. 5 represents the actual FT mechanism. Various detailed mechanisms have been proposed over the last 50 years and this matter still remains controversial [1,2,9,16]. Some of the questions that arise are: does the chemisorbed CO molecule first dissociate into C and O atoms and the C is then hydrogenated to CH_2 monomers; or is CO hydrogenated to "CHO" or "HCOH" species which insert into the growing chain; or does CO insert directly and is then subsequently hydrogenated. Since large amounts of alcohols and aldehydes are formed in the FT synthesis and appear to be primary products insertion of some form of oxygenated species is required to account for these products. The linear α-olefins which also are formed in large amounts must be primary products as at the partial pressures of hydrogen present in the reactors virtually all olefins should, according to thermodynamics, be hydrogenated to paraffins [9]. The viability of the FT process depends on three key factors, the life, the activity and the product selectivity of the catalyst. The question is asked whether detailed knowledge of the chemical reaction sequences occurring will in fact result in improvements in these three key factors. Better catalyst formulations and synthesis process conditions are more likely to result in improvements.

5.1. Effect of temperature

For all FT catalysts an increase in operating temperature results in a shift in selectivity towards lower carbon number products and to more hydrogenated products. The degree of branching increases and the amount of secondary products formed such as ketones and aromatics also increases as the temperature is raised [2]. These shifts are in line with thermodynamic expectations and the relative stability of the products. As Co is a more active hydrogenating catalyst the products in general are more hydrogenated and also the CH_4 selectivity rises more rapidly with increasing temperature than it does with Fe catalysts.

5.2. Effect of chemical and structural promoters

For iron-based catalysts the "basicity" of the surface is of vital importance. The probability of chain growth increases with alkali promotion in the order Li, Na, K and Rb [2]. Because of the high price of Rb potassium salts are used in practice. The basicity of the catalyst does not only depend on the amount of K added but also on the anion used as well as on the presence and amount of oxides such as SiO_2, Al_2O_3, etc. with which the alkali can chemically react to form less basic compounds [2]. These oxides may either be impurities present or deliberately added as supports, binders or spacers. In general cobalt-based catalysts are much less influenced by the presence of chemical or structural promoters. While it has been found by various investigators that the addition of low levels of noble metals such as Ru, Re or Pt enhance the FT activity of the Co catalysts it is not clear if the selectivities are influenced [12].

5.3. Feedgas composition and pressure

Taking the scheme shown in Fig. 5 as a guide it can be argued that the lower the partial pressure of CO the lower the surface coverage by the CH_2 species, the lower the probability of chain growth and the higher the probability of desorption of the $n(CH_2)$ species. The higher the H_2 partial pressure the more likely the termination of the surface species to paraffins. Thus, one could expect that as the H_2/CO ratio increases the selectivity would shift to lighter and more saturated hydrocarbons. This could, however, be an oversimplification as the presence of CO_2 and of H_2O could complicate matters. For example, since the chemisorption of CO is much stronger than that of H_2 the presence of CO_2 and H_2O could have a greater negative effect on H_2 than on CO chemisorption. Thus, the selectivity may possibly correlate better with a more complex ratio such as

$$\frac{p_{H_2}^a}{xp_{CO}^b + yp_{CO_2}^c + zp_{H_2O}^d}$$

Commercial FT reactors operate at high gas linear velocities and so there is likely to be a high degree of plug flow through the units. This means that the composition and partial pressures change along the length of the reactor and so possibly the FT selectivities as well. For both design and control purposes it should be useful to establish a relatively simple relationship between the total feed gas composition (that of the sum of the fresh feed and recycle flows) and the overall product selectivity. To this end 5 cm i.d. pilot plant studies were carried out using various pressures, gas compositions and recycle ratios with standard commercial iron catalysts at fixed temperatures [2]. Typical results for the low-temperature fixed bed process are shown in Fig. 6. As high wax production is the key objective of LTFT the hard wax selectivity was used as the indicator of selectivity. In the runs the total pressures, the partial pressures of CO_2 and the H_2/CO ratios were varied over wide ranges. As can be seen from Fig. 6 the simple H_2/CO ratio adequately reflects the wax selectivity.

A similar series of experiments was carried out for the HTFT fluidised process [2]. The details of the entry partial pressures are shown in Table 1. Since there is

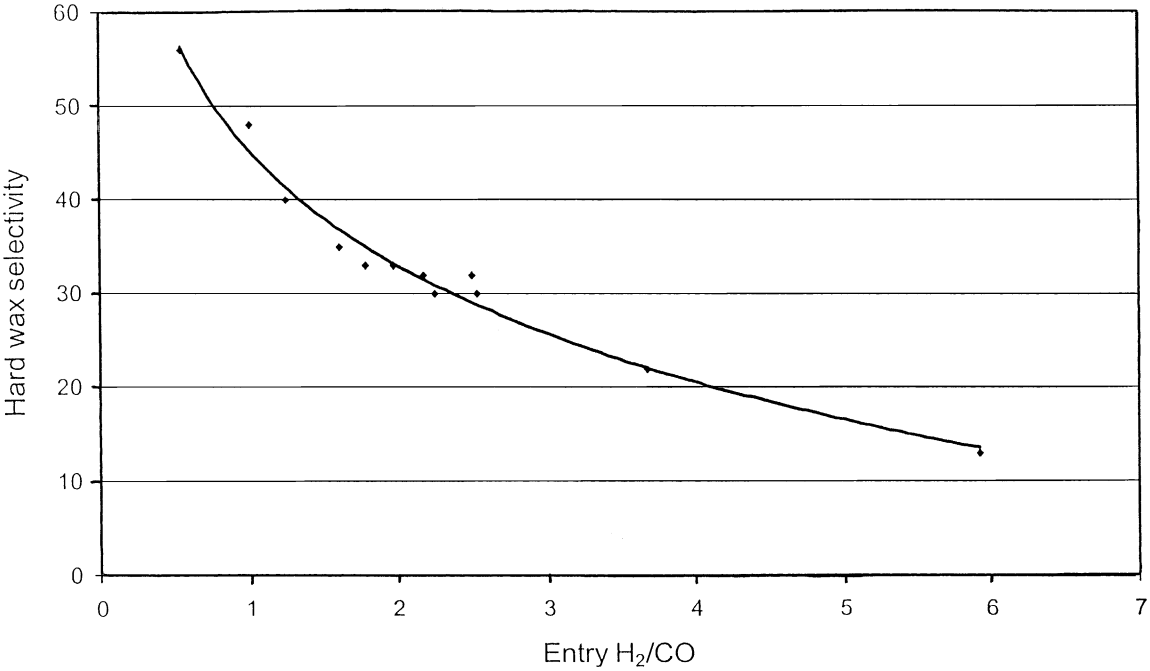

Fig. 6. The selectivity of hard wax (bp > 500 °C) as a function of the H_2/CO ratio at the reactor entrance for the fixed bed LTFT process using precipitated iron catalyst.

Table 1
Relation between entry gas partial pressures and CH_4 selectivity[a]

CH_4 selectivity (%)	Entrance partial pressures (MPa)				H_2/CO ratio	$p_{H_2}^{0.25}/(p_{CO}+0.7p_{CO_2})$
	p_{H_2}	p_{CO}	p_{CO_2}	p_{H_2O}		
22.1	1.15	0.147	0.004	0.004	7.8	1.23
20.8	0.49	0.094	0.053	0.004	5.3	1.14
17.7	1.16	0.162	0.025	0.004	7.2	1.03
15.0	1.41	0.014	0.297	0.004	100	0.87
14.5	0.94	0.178	0.057	0.004	5.3	0.80
13.7	0.97	0.184	0.062	0.004	5.3	0.78
13.5	1.44	0.016	0.33	0.004	90	0.79
11.7	0.98	0.186	0.078	0.004	5.3	0.74
11.4	1.03	0.184	0.157	0.279	5.6	0.61
10.8	1.15	0.22	0.183	0.004	5.2	0.53
9.8	0.71	0.201	0.134	0.004	3.5	0.55
8.0	0.69	0.215	0.181	0.004	3.2	0.47
7.1	1.04	0.041	0.802	0.004	25	0.30
6.8	2.52	0.469	0.436	0.004	5.3	0.29
6.5	0.89	0.063	1.023	0.004	14	0.22
5.5	3.14	0.603	0.522	0.004	5.2	0.24

[a] HTFT conditions; iron catalyst.

a good correlation between CH_4 selectivity and that of all of the other products in the HTFT process (see Fig. 4) the CH_4 selectivity is used here to reflect the overall selectivity. As can be seen from Table 1 there is no correlation with the simple H_2/CO ratio. The factor

$$\frac{p_{H_2}^{0.25}}{p_{CO}+0.7p_{CO_2}}$$

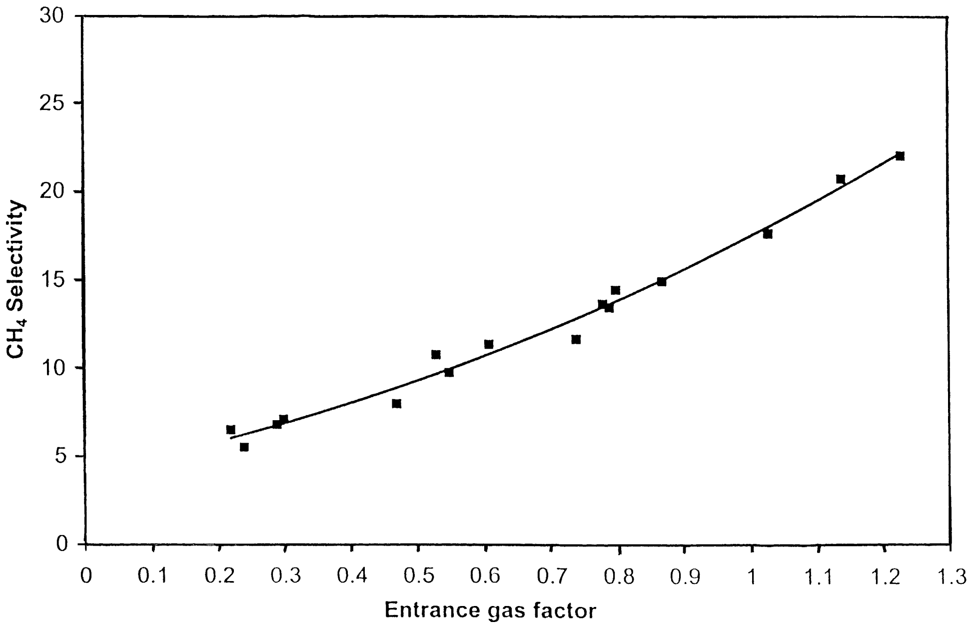

Fig. 7. The selectivity of CH_4 as a function of entrance gas factor ($p_{H_2}^{0.25}/(p_{CO}+0.7p_{CO_2})$) at the reactor entrance for the HTFT process with iron catalysts.

at the reactor entrance appears to correlate well (see Fig. 7). Note that, unlike the LTFT case, changes in the total and in the CO_2 partial pressures were found to influence the selectivity and this is accounted for in the above factor. As an alternative approach the average partial pressures in the reactor were used for correlation and then it was found that the factor

$$\frac{p_{H_2}^{0.25}}{p_{CO} + 0.7p_{CO_2} + 0.6p_{H_2O}}$$

also correlated.

In recent years there has been a lot of work done on cobalt-based catalysts but detailed results of pilot and demonstration plant tests have not been published. From the pre-war fixed bed studies in Germany [1] and in later laboratory scale studies [17] the FT wax selectivity correlated with the H_2/CO ratio of the gas as is the case for iron catalysts in the same temperature range, namely 200–240 °C. With regard to the effect of total pressure, however, cobalt catalysts behaved differently in that as the pressure was increased the wax selectivity increased [18].

6. Kinetics of the FT reaction

For the purpose of comparing the FT kinetics of iron-based as against cobalt-based catalysts the following two kinetic equations are used:

- for iron [9],

$$r = \frac{m p_{H_2} p_{CO}}{p_{CO} + a p_{H_2O}}$$

- for cobalt [19],

$$r = \frac{k p_{H_2} p_{CO}}{(1 + b p_{CO})^2}$$

The equation for iron was based on extensive studies carried out with the commercially used iron catalysts in the fixed and fluidised pilot plant units at Sasol R&D. Thus, total pressures varied from 0.8 to 7.6 MPa and the effects of varying individually the partial pressures of H_2, CO, CO_2 and H_2O were investigated [2]. Residence times were varied by using different catalyst charges and thus the reaction profiles through the reactors were determined. Some of the key findings were as follows:

- The partial pressure of H_2O had a strong negative effect, whereas that of CO_2 had no influence on the FT rate.
- The rate increased with hydrogen pressure and at low conversion levels the rate was solely dependent on p_{H_2}.
- The percent conversion remained constant when the total pressure was increased while keeping all other variables constant, such as feedgas composition, residence time, etc.

The equation also described the reaction profiles in the commercial FT reactors. It is of interest to note that the equation based on all the above investigations turned out to be the same as that published about 25 years earlier [1].

For cobalt catalysts no kinetic information appears to have been published for the industrial fixed bed reactors of the Shell plant or for the demonstration slurry bed units operated by Exxon and Sasol but laboratory investigations have confirmed that the Satterfield equation is satisfactory. The most significant difference between the iron and cobalt equations is the absence of a water vapour pressure term in the latter equation. Chemically it is well known that iron is oxidised at much lower H_2O/H_2 ratios than is cobalt metal and so it can be argued that under FT conditions a much larger fraction of the exposed iron surface will be occupied by oxygen atoms/ions at any instant resulting in a loss of actives FT sites as the conversion, i.e. the H_2O/H_2 ratio, increases along the reactor length. This gives cobalt a big activity advantage over iron catalysts.

The percent conversion profiles for various cases were calculated for the LTFT process using the two presented equations. The results are shown in Fig. 8. For this particular set of calculations the constants m and k were deliberately chosen so that at 3.15 MPa a conversion of 4% was achieved at the same catalyst bed length, i.e. the “initial” activities of the Fe and Co catalysts were the same. The H_2/CO ratios of the feedgases were taken as equal to the respective usage ratios of the two catalysts. Once through operation is assumed (i.e. no tailgas is recycled). The calculations show that the cobalt catalyst is superior in that much higher conversions per pass can be achieved. If the iron catalyst was made to have an “intrinsic”, i.e. initial, activity five times higher than that of the cobalt catalyst the iron catalyst would be superior up to about 50%

conversion but beyond this level it would again drop well below that of cobalt.

The calculations indicate that high conversions can be achieved with cobalt catalysts in single stage reactors without the need to recycle part of the tailgas or to run two stages with water knock-out between stages. For iron-based catalysts high conversions, e.g. 90%, can be achieved but this requires two stage operation together with gas recycling and this increases both capital and running costs. It should, however, be borne in mind that because of the high price of cobalt, the metal needs to be highly dispersed, i.e. very small Co crystals will be present on the oxide support. As discussed in Section 4 these very small Co particles could deactivate at high H_2O/H_2 ratios, i.e. high conversions. To avoid this it may nevertheless be advisable to operate with two stages with water knock-out between, or alternatively, to recycle a portion of the tailgas after water knock-out.

As observed in practice, the calculations (Fig. 8) also show that for iron-based catalyst the conversion profile does not change with an increase in total pressure if the residence time and other variables are constant. Thus, doubling the pressure and the gas feed rate results in doubling the reactor's production rate. The calculations indicate similar results can be expected for cobalt catalyst. Thus operating at low pressures as proposed by Syntroleum [6], may well give high percent conversions but the actual production rates will be low and so either more or much larger reactors will be required.

7. Versatility of the FT process

The FT reaction inevitably produces a wide range of products but by applying various downstream work-up processes the yields of the desired products can be markedly increased.

7.1. Gasoline

For maximum gasoline production the best option is using the high capacity FFB reactors at about 340 °C with iron catalyst. This produces about 40% straight run gasoline. Twenty percent of the FT product is propene and butene. These can be oligomerised to gasoline and because the oligomers are highly branched it has a high octane value. The straight run gasoline, however, has a low octane value because of its high linearity and low aromatic content. The C_5/C_6 cut needs to be hydrogenated and isomerised

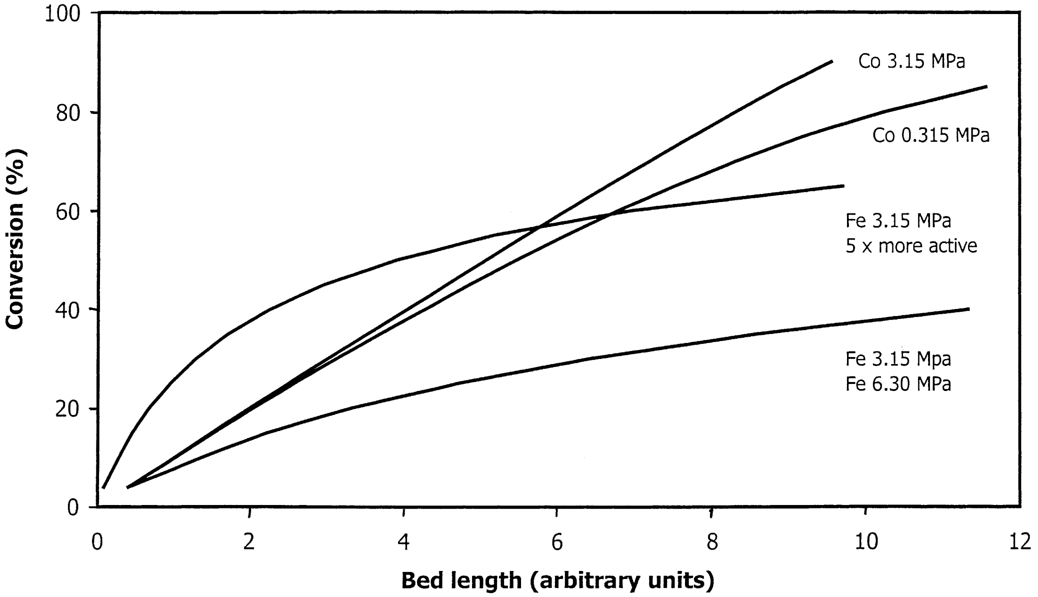

Fig. 8. The calculated conversion profiles for LTFT operation with cobalt- and iron-based catalysts.

and the C_7–C_{10} cut needs severe platinum reforming to increase the octane value of these two cuts. Di-isopropyl ether can be produced from propene and water and this will further boost the octane number of the gasoline pool. The overall complexity of gasoline production, however, make it less attractive than the diesel fuel option.

7.2. Diesel fuel

The very factors that count against the production of high quality gasoline, namely high linearity and low aromatic content are very positive factors for producing high cetane diesel fuel. The recommended process option is the use of the high capacity slurry bed reactors with cobalt catalysts and operated to maximise wax production. The straight run diesel selectivity is about 20% and after hydrotreatment its cetane number is about 75. The heavier than diesel products accounts for about 45–50% of the total and mild hydrocracking produces a large proportion of high quality diesel, virtually free of aromatics. The final diesel pool has a cetane number of about 70. As the market normally requires a cetane number of 45 the FT diesel can either be used in areas where there are very tight constraints on diesel quality or it can be used as blending stock to upgrade lower quality diesel fuel. The naptha produced would need severe reforming to convert it to high octane gasoline. Preferably it could be steam cracked as it would produce a high yield of ethylene.

The mild hydrocracking of wax was investigated at the Sasol R&D division during the 1970s [2,20]. The product heavier than diesel was recycled to extinction. The overall yields were about 80% diesel, 15% naphtha and 5% C_1–C_4 gas. When the decision to construct the third Sasol plant was made the wax hydrocracking proposal was rejected because at that time making gasoline was the more economic option and the straight duplication of the second plant resulted in huge savings in time and capital. Also at that stage, the FT slurry reactors had not yet been developed. About 20 years later the same concept of wax hydrocracking was implemented at the Shell Bintuli plant where multitubular FT reactors are used and currently Sasol/Chevron are designing a slurry FT plant with wax hydrocracking in Nigeria. A similar plant at Qatar is in the pipeline.

7.3. Chemicals

The high-temperature fluidised bed FT reactors with iron catalyst are ideal for the production of large amounts of linear α-olefins. As petrochemicals they sell at much higher prices than fuels. The olefin content of the C_3, C_5–C_{12} and C_{13}–C_{18} cuts are typically 85, 70 and 60%, respectively. Ethylene goes to the production of polyethylene, polyvinylchloride, etc. and propylene to polypropylene, acrylonitrile, etc. The extracted and purified C_5–C_8 linear α-olefins are used as comonomers in polyethylene production. The longer chain olefins can be converted to linear alcohols by hydroformylation. The only required purification of the narrow feed cuts is the removal of the acids. The hydroformylation was investigated at the Sasol R&D laboratories in the early 1990s. The alcohols are used in the production of biodegradable detergents. Their selling prices are about six times higher than that of fuel.

The LTFT processes produce predominantly longer chain linear paraffins. After mild hydrotreatment to convert olefins and oxygenates to paraffins the linear oils and various grades of linear waxes are sold at high prices.

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