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Advances in low temperature Fischer-Tropsch synthesis

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Abstract

Recent developments in the Fischer–Tropsch process are reviewed and discussed. Particular attention is given to the commercial slurry-bed reactor which was commissioned by Sasol in May 1993.

1. Introduction

This paper is intended as an update of previous reviews of the Fischer-Tropsch process [1–5] with the emphasis on the commercial Slurry Bed Reactor, which was commissioned by Sasol in May 1993.

In 1989 Sasol commissioned a new High Temperature Fischer-Tropsch (HTFT) reactor, called the Sasol Advanced Synthol reactor [6,7]. This has now been followed by an equally significant development for the Low Temperature Fischer-Tropsch (LTFT) processes.

LTFT was originally performed in tubular fixed bed reactors (TFBR). To replace them, the Sasol Slurry Bed reactor (SSBR) was developed and commissioned. The reactor is much simpler; it is easy to operate; it has on-line catalyst renewal facilities and it is capable of much higher capacities.

The catalyst used for both LTFT processes is a precipitated and promoted Fe-catalyst, the preparation of which is outlined. Shell's TFBR Fischer-Tropsch plant in Malaysia uses a cobalt based catalyst.

Some catalyst development was needed for the SSBR. The catalyst usage for the SSBR is about a third of that for the TFBR with a promise of even better. A wider range of selectivities is possible with the SSBR and the product is more olefinic.

2. Tubular fixed bed reactor

Fischer-Tropsch synthesis in the LTFT mode was originally practised in pre-war Germany in packed beds. This developed into the tubular fixed bed, Arge reactors which were commissioned at Sasol in 1955.

The Arge reactor consists of a shell containing 2050 tubes, 12 m long, 5 cm in diameter, packed with iron based catalyst. Heat removal for the highly exothermic synthesis reaction is achieved by generation of steam on the shell side of the reactor. Earlier reactors operate at a shell side temperature of about 220°C, and a reactor pressure of 25 bar. A reactor commissioned in 1987 operates at 45 bar. The respective capacities are about 600 and 900 bbl/day per reactor. The general arrangement of the reactor is shown in Figure 1. A detailed design for a 5 000 tube reactor was also produced for use at the Sasolburg factory but eventually not

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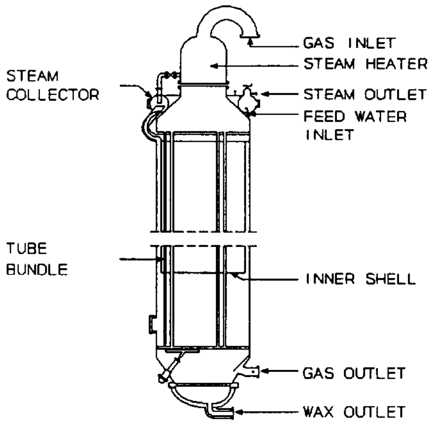

Fig. 1. The Arge reactor (TFBR).

Table 1
Selectivity of Sasol processes (carbon basis)

Product	TFBR	Synthol (fluidised bed)
CH_4	4	7
C_2 to C_4 olefins	4	24
C_2 to C_4 paraffins	4	6
Gasoline	18	36
Middle distillate	19	12
Heavy oils and waxes	148	9
Water soluble oxygenates	3	6

used because of the development of the SSBR.

The products from the LTFT as obtained from the TFBR using Fe-based catalyst vary depending on the catalyst formulation and process conditions. A typical LTFT product distribution as obtained for a TFBR and that typically obtained for high temperature Fischer-Tropsch synthesis, is given in Table 1. The LTFT product slate follows the Schulz-Flory distribution with a typical alpha value of 0,95.

The reactor is complex and expensive. The scale-up of the reactor is mechanically difficult. The mechanical design is complicated by the fact that the iron based catalyst has to be replaced periodically and the design has to provide for this. The replacement is cumbersome and maintenance and labour intensive. It causes considerable downtime and disturbances in plant operations. The product selectivities also change with ageing of the catalyst. With a number of reactors the total selectivities can, however, be evened out by staggering the catalyst age in the reactors.

Because of the exothermic nature of the Fischer-Tropsch reaction, axial and radial temperature profiles exist in the tubes. Maximum average temperature is required for maximum conversion. This is, however, limited by the maximum allowable temperature peak that may not be exceeded in order to prevent carbon formation on the catalyst and the effect temperature has on product selectivities. Carbon formation causes breakup of the catalyst that in turn causes blockages and a need to replace the catalyst.

Product selectivities are temperature dependant and flexibility with respect to temperature control would be advantageous. The choice of temperature level is however severely curtailed by the need to avoid exceeding the maximum peak temperature.

Pressure drops across the TFBR's are high and may very from 3 to 7 bar depending on the operating pressure. With relatively high recycle flows, this gives rise to considerable recompression costs.

3. Development of the sasol slurry bed reactor (SSBR)

Most of the difficulties associated with the TFBR can be eliminated in a Slurry Bed Reactor. This idea was first tried out during the Second World War and up to the late 1970's by Kölbel and co-workers [8]. Sasol's own experiments on small scale started in the early 1980's. Although they could not repeat Kölbel's results, and it was difficult to obtain consistent results in the 5 cm diameter reactor used, they did show promise for the concept. It was realised that the hydrodynamics obtained from these small tubes is quite different from those expected from larger diameter reactors.

In 1990 a slurry bed with a diameter of about 1 m was commissioned which confirmed the original expectations. In June 1991, although the design issues had not all been resolved in detail,

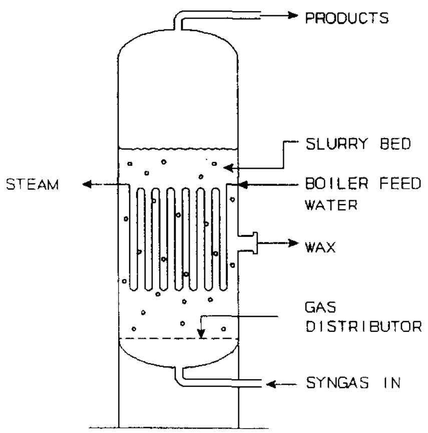

Fig. 2. The Sasol slurry bed reactor (SSBR).

Sasol decided not to use existing designs for two 5 000 tube TFBR's but rather use the slurry bed concept for its planned expansion of LTFT capacity. A single slurry bed reactor, 5 m in diameter, 22 m high, was commissioned in May 1993 and the process was called the Sasol Slurry Bed Process (SSBP).

The SSBR is much simpler than a TFBR, it is much easier to fabricate and is much cheaper. It consists of a shell with cooling coils in which steam is generated (Figure 2). Syngas is distributed in the bottom and rises through the slurry that consists of liquid reaction products, predominantly wax, with Fe-based catalyst particles suspended in it. The reagent gases diffuse from the gas bubbles through the liquid phase to the suspended catalyst where they react to produce hydrocarbons and water. The heavy hydrocarbons form part of the slurry phase whereas the lighter gaseous products and water diffuse through the liquid to the gas bubbles. The gaseous products with unreacted syngas pass through the freeboard above the bed and then to the gas outlet.

4. Advantages of the slurry bed reactor

Because of the churning nature of the slurry-gas bubble interaction, the slurry phase is well mixed and tends to be isothermal. This gives much better and more flexible temperature control. Temperatures on average can be much higher than in a TFBR without the danger of carbon formation and break-up of catalyst. Better control of product selectivities becomes possible at higher average conversions. This makes it ideal for use with high activity catalysts where the problems with excessive radial and axial temperature gradients are much more pronounced.

The pressure drop across the bed is practically that of the static hydraulic head and is much lower than that for the TFBR. This translates to considerable savings in compression costs.

On-line catalyst removal and additions can be done without difficulty. This is an important improvement on the TFBR where catalyst has to be replaced from time to time. Losses due to down-time and labour intensive turn-arounds are eliminated.

For iron catalyst, the product slate is considerably affected by the age of the catalyst, with wax selectivities decreasing with time. By proper scheduling of catalyst renewal, it is possible to maintain a steady selectivity profile for a single reactor while minimising the catalyst consumption.

Although scale-up of TFBR's is possible, it is not easy from a mechanical point of view. Scale up is achieved by increasing the shell diameter and increasing the number of tubes. The largest Arge TFBR was designed for about 1 500 bbl/day. With the SBR, capacity can be increased by increasing both diameter and height of the reactor. It is thought feasible that a single SBR with a capacity of about 10 000 bbl/day can be built. Full advantage is then taken of the potential for economy of scale.

A study was done, comparing the capital cost of the TFBR with that of the SSBR. Two cases were considered; one using an iron based catalyst as in our present operations and the other using the preliminary results of a higher activity cobalt catalyst. In both cases the study showed that the capital required for a large scale SBR train was less than 40% of that needed for an equivalent TFBR plant.

5. Operating experience with the commercial SSBR

In the development of the SSBR several areas needed special attention. Foam build up was experienced under certain conditions. It was found that it could easily be prevented by modifying operating procedures. Separation of the gas from the entrained slurry was another development area that was easily resolved.

The major challenge was that of solid separation from the net liquid products and considerable work was done to solve problems associated with this step. Attention was given both to the production of catalyst and its physical characteristics and the separation processes themselves. Several techniques were evaluated, the information of which is considered proprietary information. Stringent specifications for solids in the final wax cut, are now very easily met.

At present the SSBR is operated in such a way that its product slate closely matches that of the existing TFBR's. This is achieved as far as carbon distribution in the products is concerned. However, as shown in Table 2, the SSBR products are much more olefinic than products obtained from the TFBR. Presently the olefines are hydrogenated to straight chain paraffins. Potentially the lighter hydrocarbon streams are excellent sources for alpha olefines.

The experience with the SSBR has been very good. The first run lasted 7 months when it was terminated for a planned factory shutdown. An availability of 99% was obtained during this run. The reactor is easy to operate and catalyst renewals can be done without any problems. Capacities of over 120% of design were achieved. The catalyst usage of the SSBR is about a third of that of the TFBR with a promise of even better.

Table 2
Typical product spectra for LTFT and HTFT reactors

Product	TFBR		SSBR		Synthol	
	C_5–C_{12}	C_{13}–C_{18}	C_5–C_{12}	C_{13}–C_{18}	C_5–C_{10}	C_{11}–C_{14}
Paraffins (%)	53	65	29	44	13	15
Olefins (%)	40	28	64	50	70	60
Aromatic (%)	0	0	0	0	5	15
Oxygenates (%)	7	7	7	6	12	10
Paraffin (%)	95	93	96	95	55	60

6. Catalysts preparation

6.1. *Iron based catalyst*

The precipitated iron based catalyst used in the FT Slurry Bed Reactor process is similar to that used in the TFBR's or Arge reactors.

The preparation of the catalyst starts with its precipitation from an iron nitrate solution by an alkaline solution. This step determines the surface area and the pore structure of the final catalyst. These can be varied to a large extent by controlling variables like temperature, order of addition, rate of precipitation, nature of the precipitating agent, concentration of the solutions, etc [4]. The precipitate thus obtained is washed, reslurried and the chemical and structural promoters added.

Up to this point, the mechanical procedure for preparation is the same for fixed bed and slurry bed reactors. With fixed bed catalyst, the slurry obtained is filtered, extruded and dried.

For the SBR, the catalyst slurry is spray dried, as a much finer particle size distribution is required. The products from the spray drier go to a cyclone/screening/scrubbing system where the catalyst proper is separated from the catalyst fines and any oversize that may be present.

In the slurry bed application the production of catalyst fines due to abrasion or breakage should be prevented to a minimum as fines could possibly affect the efficiency of the separation of solids from the liquid products.

It was found that while the breakage of the catalyst particles is inversely proportional to the mechanical strength of the particles, the formation of ultra fine particles due to abrasion does not necessarily follows this trend.

Figure 3.1 is a SEM picture of a typical SBR catalyst. The sphericity and particle size distribu-

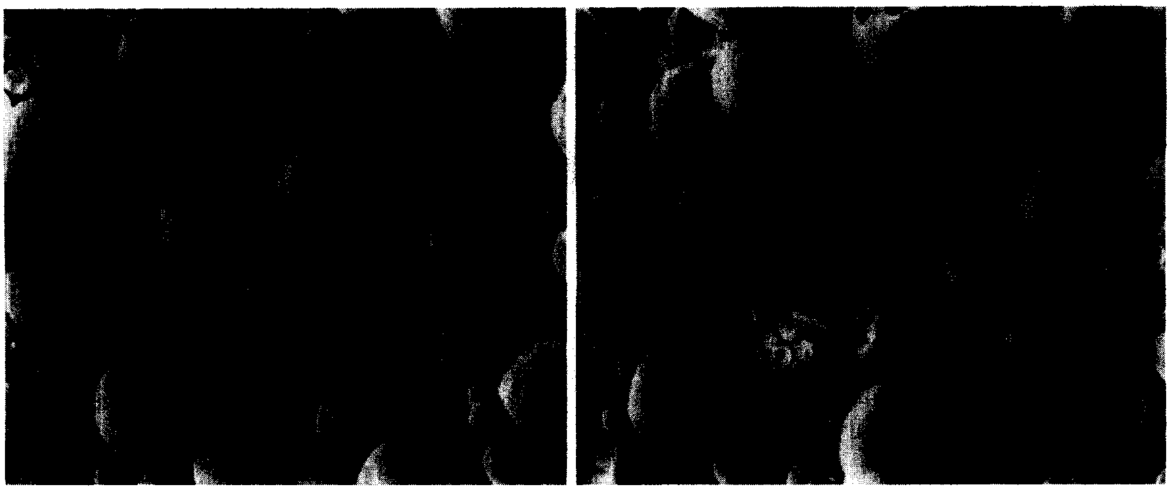

Fig. 3. SEM photographs of spray-dried iron catalysts. (a) Typical Sasol spray-dried catalyst. (b) Catalyst with 'dimpled' particles.

tion of the catalyst is controlled through the spray drying procedures. Should the spray drier operate outside a range of parameters identified for the catalyst, the sphericity is lost and "dimple" shaped particles begin to predominate. An explanation for this effect is offered by Shaw [9]. The mechanical integrity of the dimple shaped particles is much lower than that of the spherical particles, and they break easily. A high incidence of broken particles is evident in Figure 3.2.

6.2. Cobalt based catalyst

There were many early attempts to prepare cobalt based catalysts suitable for the production of liquid fuels. The early catalysts typically used unsupported oxides, like pure cobalt oxide, cobalt-chromium oxide, cobalt-zinc oxide [10], cobalt chromate, cobalt-copper oxide [11], cobalt-copper containing alumina, cerium oxide and zinc oxide [12]. Thoria and magnesia were found to increase the activity [13,14]. Storch et al. [15] is a good source for the early history of cobalt catalysts. An important development was the support of the metal on a silica carrier.

Fischer realized that reduction, at temperatures higher than 350°C caused extensive loss of surface area due to sintering. In 1931 he precipitated nickel-thoria on kieselguhr [16] and in 1932 cobalt-thoria on kieselguhr [17]. This preparation procedure was optimized, more readily available raw materials (kieselguhr) were identified and part of the thoria replaced by magnesia [15]. This was the catalyst used in the first commercial Fischer-Tropsch plant.

In the past two decades, interest in cobalt FT catalysts increased, mainly due to the sharp increase in the price of crude oil towards the early 70's. The modern cobalt catalysts are similar to the one prepared by Fischer in 1932, i.e. promoted cobalt on a metal oxide support.

There are many patents in this field and a few examples will be mentioned. As supports, silica, alumina, titania, zirconia, magnesia, silica-aluminas, gallia, ceria, carbon, molecular sieves, zeolites, etc. are mentioned [18–26].

Promoters like the noble metals from the Group VIII have a beneficial effect on the activity, probably because it facilitates the reduction of cobalt [23,24,27,28].

Cobalt catalyst may deactivate due to gradual oxidation or surface condensation of heavy hydrocarbons. Reactivation may be obtained by hydrogen treatment to re-reduce the catalyst and to remove the carbon (and oxygen) species on the surface. Metals like Ru, Re, Hf, Ce, Th and U help this process [29,30] and also increase the activity [19,29].

Other promoters that increase the activity and/or selectivity towards heavier hydrocarbons products are Zr, V, Ti, Mg, Mn, Cr, Th, Ce, La, Ni, Fe, Mo, W, Pr, Nd, U, elements from groups Ia, IIa, and Ib, etc. [19,20,22,24,26,28,31].

Some patents for the preparation techniques deal with the order of impregnation for the cobalt and the promoter [32], the kneading technique compared with impregnation [31], and the impregnation of cobalt in the external portion of the support particle ("egg-shell" type) [18] to improve the selectivity towards the C5 + fraction. Others deal with small catalyst particles "encapsulated" in permeable meshes to allow the use of small particles in fixed bed reactors to improve the heat transfer and diffusion while avoiding high pressure drops [33].

Some patents for the reduction step include a gradual increase in the partial pressure of hydrogen [34] or a gradual increase in the reduction temperature [35]. This is done to minimise the well-known negative effect of the partial pressure of water on the reduction of the catalyst.

On the whole, these relatively recent patents deal with the effect of promoters on cobalt supported on a metal oxide. They cover a wide range of promoters and there is a high degree of interlinkage between them.

7. Kinetics of the FT synthesis

7.1. *Iron based catalyst*

Literature proposes several kinetic expressions to describe the effect of the partial pressures of reactants and products on the Fischer-Tropsch rate of reaction, both for iron and for cobalt based catalysts.

For iron based catalysts it is well known that the partial pressure of water has a negative effect on the rate of reaction, while the partial pressure of hydrogen has a positive influence.

The Anderson equation [4] is widely used for fitting experimental data from micro to commercial scale reactors.

Anderson FT rate equation:

$$r_{FT}\ \alpha\ \frac{\mathrm{P_{H_2}\,P_{CO}}}{\mathrm{P_{CO}\ +\ aP_{H_2O}}} \tag{1}$$

The value for the constant "a" has to be found for each specific iron based catalyst. When doing macro kinetic studies it is common to assume that the results obtained with a specific catalyst are valid for all the different "families" of catalyst based on the same metal. The value of "a" differs for different iron based catalysts. Even the same catalyst but conditioned differently, may have different values.

An interesting example of the problems with generalised use of kinetic expressions is given by Ledakowicz [36]. His catalyst has a very high water-gas-shift activity and practically no water is observed in the products. Clearly Anderson's equation will not fit his experimental data, and a CO_2 term has to be included. It is therefore safer to start with a more general FT equation like

$$r_{FT}\ \alpha\ \frac{\mathrm{P_{H_2}\,P_{CO}}}{\mathrm{P_{CO}+\acute{a}P_{H_2O}+bP_{CO_2}}} \tag{3}$$

and test it against the experimental data to determine the value and statistical significance of both constants rather than selecting a particular, published, rate equation.

Water-gas-shift reaction

The WGS reaction is described by:

$$\mathrm{CO+H_2O} \rightleftharpoons \mathrm{CO_2+H_2} \tag{4}$$

A typically kinetic expression for the WGS reaction [37] is:

$$r_{WGS}\ \alpha\ \frac{P_{H_2O}P_{CO}-K^{-1}P_{CO_2}P_{H_2}}{a\,P_{H_2O}+P_{CO_2}} \tag{5}$$

where

$$K=0{,}0132\ \mathrm{e}^{4578/T} \tag{6}$$

The water-gas-shift reaction has a large influence on the activity and selectivity obtained from FT catalysts as the partial pressures of the H_2O, H_2, CO and CO_2 are affected by the extent of the

WGS reaction. This influence will be discussed in more detail in the catalyst deactivation section.

7.2. *Cobalt based catalyst*

For cobalt based catalysts the literature also proposes several rate expressions:

Yates and Satt [38]

$$r_{FT} \,\alpha\, \frac{P_{H_2}P_{CO}}{(1+aP_{CO})^2} \quad (7)$$

Brotz [39]

$$r_{FT} \,\alpha\, \frac{aP_{H_2}^2}{P_{CO}} \quad (8)$$

Sarup and Wojchiechowski [40]

$$r_{FT} \,\alpha\, \frac{aP_{CO}P_{H_2}^{0,5}}{(1+bP_{CO}+eP_{H_2}^{0,5})^2} \quad (9)$$

$$r_{FT} \,\alpha\, \frac{aP_{CO}^{0,5}P_{H_2}^{0,5}}{(1+bP_{CO}^{0,5}+eP_{H_2}^{0,5})^2} \quad (9a)$$

Anderson [1]

$$r_{FT} \,\alpha\, \frac{aP_{CO}P_{H_2}^2}{l+bP_{CO}P_{H_2}^2} \quad (10)$$

Yang et al. [41]

$$r_{FT} \,\alpha\, aP_{H_2}P_{CO}^{0,5} \quad (11)$$

Pannell et al. [42]

$$r_{FT} \,\alpha\, aP_{H_2}^{0,55}P_{CO}^{-0,33} \quad (12)$$

Of particular interest is the response of these equations to a change in operating pressure while keeping all other variables constant. Table 3 shows the predicted increase in conversion solely due to an increase in operating pressure. For a feed H_2/CO ratio of 2,0 as a reference, a conversion of 35% is assumed at 20 Bar. The equations shown above are then used to predict the conversion at 50 Bar. The calculations were performed using a simplified general kinetic model in which the effects of variables like mass transfer, diffusion, etc. are neglected.

The large range of predictions makes it difficult to believe that there is a "best" equation. Most probably, the different equations are valid for the specific catalysts used to develop the specific kinetic expressions. This is an area for further investigation. As for iron based catalysts, it is not "safe" to simply select a priori any given equation proposed in the literature. The experimental data should be used to select the more suitable kinetic expression for the catalyst under consideration.

Table 3
Effect of operating pressure by some kinetic equations for cobalt

(H_2 + CO) Conversion (%)

Equation tested	20 bar	50 bar
Yates and Sattersfield	35	37.3
Brotz	35	69.1
Sarup and Wojciechowski (Eq.9)	35	75.5
Sarup and Wojciechowski (Eq.9a)	35	44.1
Anderson	35	35.1
Yang et al.	35	49.1
Pannell et al.	35	39.0

There is consensus on the absence of a negative effect of the partial pressure of water on the FT reaction rate. It is therefore easier to obtain a high per pass conversions with a cobalt based catalyst, than with an iron based catalyst. Because of this, a cobalt based low temperature FT reactor would be cheaper than an iron based one. The reactor height would be lower and/or a lower recycle ratio could be used as there is no need to remove the reaction water that suppresses the reaction rate with iron based catalyst. Compression costs will therefore be reduced considerably.

For fixed bed reactors, high per pass conversion leads to reduced gas flows that create a heat removal problem due to reduced heat transfer coefficients. To offset this effect, some recycle can be used which, however, reduces the savings in compression costs.

8. Product selectivity

The effects of the type or reactor and catalyst used on the hydrocarbon product selectivities, will be discussed.

8.1. Selectivity: cobalt vs iron catalysts

In general, cobalt based low temperature FT catalysts produce more methane and less olefins than iron based catalysts.

Considerable effort has been devoted to increase the wax selectivity of cobalt based catalysts as shown in the section on catalyst preparation. Other approaches include the recycle of olefins [43] or liquid products [44].

While for iron based catalysts pressure has very little effect on products selectivity [4], its effect on cobalt based catalysts is pronounced. The beneficial effect of pressure on the wax selectivity for cobalt based catalysts has been known for a long time and is discussed in other FT reviews [4].

Shell [45,46] indicates Schulz-Flory alpha values for "classical" cobalt based catalysts between 0,78 and 0,82, while for new cobalt based catalysts, the alpha value ranges between 0,8 and about 0,93-0,94. The same source shows an alpha value range for "classical" iron based catalysts from 0,75 to about 0,89. Since 1955 Sasol, using iron based catalyst in their tubular fixed bed Arge reactors, have been producing a product slate with an alpha value of about 0,95.

8.2. Selectivity: slurry vs fixed bed reactor

The following discussion deals with a comparison between the fixed and slurry bed reactors, in particular for iron based FT catalysts.

Important for low temperature FT product selectivities are the chain growth probability (alpha value), and the olefins and oxygenates selectivities. The main parameters affecting these selectivities are the operating conditions, the catalyst composition and the catalyst structure.

Carbon number selectivity for the low temperature FT products is often expressed in terms of the alpha value from the Schulz-Flory (SF) distribution. This has been explained in detail in the literature [4].

This approach, however, is an over simplification of the real product distribution. Typically, the methane fraction is above the SF line, the C2 fraction is below the line and the alpha value increases at the C7-C10 carbon number, until it stabilizes at a higher value as shown in Figure 4.

The reason for the higher methane is thought to be the presence of hydrogenation sites that favour the production of methane. The lower C2 value is thought to be due to the readsorption of ethylene and its further incorporation into the growing

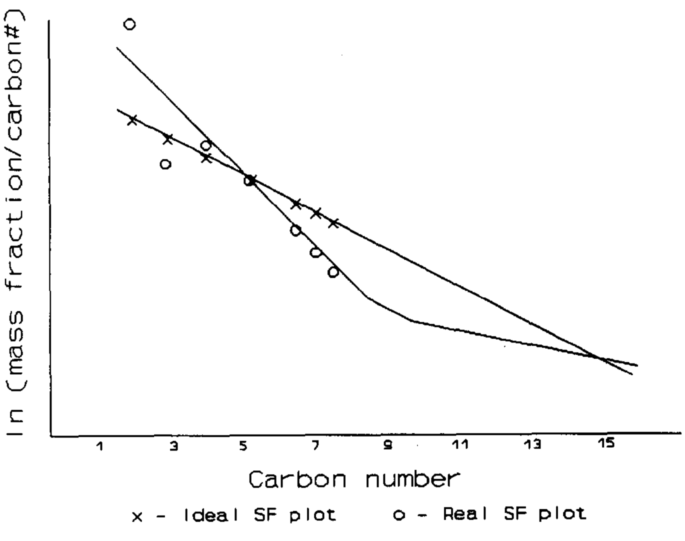

Fig. 4. Ideal vs. real low-temperature FT product spectra.

chain [47,48]. The results differ in the extent of this reincorporation, which is likely to be due to the different catalysts used.

The change in the slope of the SF line can be explained by either the presence of sites that produce preferentially heavier hydrocarbons [49] or by the readsorption of the lighter olefins with their further reincorporation into the growing chain. The carbon number where the slope changes, is typically C7-C10 which can be related to the change in phase from gas to liquid. At this point there is a drastic increase in the residence time of the species to be readsorbed.

At similar operating conditions, using iron based catalysts, the slurry reactor tends to produce products heavier than those obtained for the fixed bed reactor. While the fixed bed reactor typically produces between 50 and 55% reactor wax (C20+), the selectivity for the slurry reactor is between 55 and 60%.

It was reported [4] that the selectivity towards heavier hydrocarbons increases with a decrease of the H_2/CO ratio in the feed, with a decrease in temperature and with an increase in the potassium level. While the SBR still follows the same trends, the response is less than for the fixed bed reactor.

The lower response of the reactor wax selectivity of the slurry reactor to operating variables, provides greater freedom for the optimization of the operating conditions for the commercial slurry bed reactor when compared to the fixed bed reactor.

9. Catalyst deactivation

The deactivation of the precipitated iron based Fischer-Tropsch catalysts has been dealt with in the literature [4,50].

For cobalt based catalysts it is well known that they are more resistant to oxidation although they are also poisoned by sulphur. Some promoters enhance the catalyst regeneration [29,30]. Cobalt catalyst in Shell's plant in Malaysia will have a useful life of up to 5 years, and will be regenerated several times during that period [46].

The deactivation of the iron based FT catalyst is due to oxidation, sintering (loss of surface area), poisoning and formation of carbonaceous deposits.

Sintering is related to the partial pressure of water, while the formation of carbonaceous species has been shown to play only a minor role in the deactivation process [50].

Sulphur is the main poison agent for FT reactions. While care is taken to remove it from the feed, there is always a small amount that find its way to the catalyst. Fischer [51] recommended a maximum sulphur content in the feed gas of between 2 to 4 ppm. From commercial considerations Dry [4] recommends a maximum sulphur content of about 0,2 ppm. When cobalt is used instead of iron, catalyst life should be measured in years instead of months, because of its high cost. The removal of sulphur from the feed has therefore to be more efficient for cobalt. Shell recommends that for a cobalt catalyst in a fixed bed reactor, the feed gas should essentially be sulphur free and a zinc oxide bed is included in their plant in Malaysia for effective sulphur removal [45,52].

For the tubular fixed bed FT reactor, end of the run catalyst analyses have shown that sulphur is preferentially found in the top section of the reactor [50]. That is, the upper section of the reactor acts as a guard filter for the low levels of sulphur that remain in the feed.

The slurry bed reactor behaves as a continuously stirred reactor and all the catalyst is exposed to feed gas. Sulphur poisoning studies comparing the effect of sulphur on fixed and slurry bed reactors showed that for the same conditions the loss in conversion due to sulphur poisoning in a slurry bed reactor is between 1,5 and 2 times higher. Although not as high as expected, it shows the need for more thorough sulphur removal for slurry applications.

Sulphur poisoning does not have an effect on the products selectivities for iron based catalysts, except with severe poisoning which produces increased acid selectivity.

Table 4
Change in the FT and WGS rates with time on line

Time on line	0.17	0.33	0.50	0.67	0.83	1
Ratio FT/WGS	1	0.89	0.79	0.73	0.69	0.66

Oxidation of the reduced catalyst is one of the main deactivation mechanisms for precipitated iron based catalysts. This is accompanied by a general loss in surface area and possible changes in the selectivity.

It is known that the WGS reaction takes place (although not exclusively) on oxides [52,53]. For precipitated iron based FT catalysts, it is thought that WGS takes place on the magnetite [52]. In a fixed bed reactor the level of magnetite increases with time. It also increases along the axis of the reactor due to the higher partial pressures of water towards the outlet of the reactor [50]. This increase in magnetite level is thought to be the main reason for the increase in the rate of WGS with time on line, while the rate of FT decreases. The effect is illustrated in Table 4. The combined effects of loss in FT activity and gain in WGS activity results in a continuous asymptotic decrease of the FT/WGS ratio.

This ratio may be used to follow the deactivation caused by catalyst oxidation during an experimental test without having to interrupt the specific run.

The change in the FT/WGS ratio alters the concentration of reactants and products and therefore affects the selectivity and rate of the FT reactions. It shows the intimate relationship between the FT and WGS reactions and the difficulties in the macro kinetic studies of the FT reaction for iron catalysts.

It may occur during macro kinetic studies, that the wide experimental range - statistically necessary - of concentration of the reactants used, leads to surface changes in the catalyst, converting it practically into a different catalyst. In that case the selection of the "best" rate of reaction based upon the least squares criterium becomes merely a statistical exercise.

10. Catalysts consumption: slurry versus fixed bed

Experimental and commercial results show that for the same catalyst the slurry bed reactor has a much larger yield per unit mass of catalyst than the fixed bed reactor. Slurry bed reactors produce the same amount of hydrocarbon products as fixed bed reactors, using only about 30%, or less, of the mass of catalyst.

The explanation proposed is in terms of the catalysts effectiveness and the higher average temperature used in the slurry bed reactor. Because of the much smaller size of the catalyst particles used in the slurry bed reactors as compared to the fixed bed FT reactors, the effectiveness factor approaches unity and the size of the slurry catalyst particle is no longer a matter of concern from the viewpoint of diffusion limitations [54,55].

It has been suggested [54] that in slurry bed FT reactors, mass transfer limitations come into effect. In practise however, the combination of a higher effectiveness factor and a higher average operating temperature, gives higher conversions than possible in tubular fixed bed reactors.

11. Developmental challenges

The developments with the SBR are recent and are still early on the learning curve.

Where product slates are required, different from the present, operating temperatures can be adjusted for higher or lower Schulz-Flory alpha values. More and better hard waxes can be obtained with higher alpha values or higher conversions can be obtained at higher temperatures with a lighter product slate. In both cases, to maximise production of diesel a mild hydrocracking step can be used to convert waxes to an excellent quality diesel.

Because of the isothermal nature of the SBR, it is ideal for high activity catalyst which in a TFBR would cause excessive temperature gradients and peaks, leading to the need for smaller diameter tubes. For SBR's higher activity catalyst like that obtained with cobalt based catalysts can be considered. Per pass conversions with iron based catalysts are negatively affected by the water produced, which inhibits the reaction. Cobalt based catalyst does not have the same constraint and close to complete conversion is theoretically possible. Cobalt based catalyst has, however, the disadvantage that it has to operate at lower temperatures to get suitable selectivities. This leads to the production of steam of a quality inferior to that obtained from Iron based catalyst. With a cobalt based catalyst the olefinicity of the product would also be much lower. The cobalt based catalyst product selectivity is much more sensitive to the gas H_2/CO ratio, pressure and temperature than the iron based catalyst which is much more robust in use. It is more stable than iron based catalyst and has a longer life. Iron based catalyst behaviour can be more readily tuned by promoters and it is less sensitive to operating conditions. In general it has a shorter life and is less active compared with cobalt based catalyst.

Ideally a catalyst should be developed with the activity of a cobalt and the robustness of an iron based catalyst towards changing operating conditions.

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