

FISCHER-TROPSCH SYNTHESIS OVER IRON CATALYSTS

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Because of the decreased profitability of making synthetic fuels, Sasol intends expanding its production of the higher valued chemicals, in particular waxes and olefins. The advantages and disadvantages of using Fe, Co and Ru catalysts are discussed from the point of view of costs, availability, product selectivity, activity and sensitivity to poisons.

The loss of activity and selectivity of iron based catalysts in both fixed and fluidized bed reactors is discussed. The main contributing factors are sulfur poisoning, oxidation and coke fouling. In fixed bed reactors sulfur poisoning and “coke” laydown deactivates the front end of the bed while hydrothermal sintering/oxidation deactivates the back end. In fluidized beds the deposition of large amounts of Boudouard carbon does *not* markedly lower the activity. The smaller catalyst particles end up consisting of small iron carbide entities embedded in a matrix of carbon. The larger catalyst particles consist of cores of inert magnetite surrounded by the carbide/carbon matrix.

FT reactor development at Sasol is briefly reviewed.

1. Expanding chemicals production at Sasol

The Sasol One plant which commenced operating in 1955 has always produced both hydrocarbon fuels and a variety of chemicals [1]. The very much larger Sasol Two and Three plants which came on stream in 1980 and 1982 respectively were built in response to the oil crisis of the time and hence were geared predominantly at fuel production although ethylene recovery plants were also incorporated. Because of their large scale the Sasol Two and Three plants have remained profitable operations despite the current relatively low price of crude oil. This is not so, however, for the older and much smaller Sasol One plant and presently it is being considered whether to cut back fuel production there and to expand the production of chemicals.

Sasol's existing high temperature Synthol FT units (see section 4) already produce large amounts of ethylene, ethane and propylene. As already mentioned, ethylene is being recovered and the production has been increased further by increasing the ethane cracking capacity. The most abundant single hydrocarbon produced in the Synthol process is propylene which until recently has been

oligomerised to gasoline and diesel fuels. A new polypropylene plant is now in operation and produces 120 000 tpa polypropylene.

2. Metals suitable for FT catalysts

In both the fixed and fluidized bed Sasol FT reactors only iron based catalysts have been used to date. The four metals known to be most active for CO hydrogenation to hydrocarbons are Fe, Ni, Co and Ru. It is generally agreed that nickel is not a good choice. Of the four metals Ni is the most active for hydrogenations and consequently at high temperatures it has a very high selectivity for methane and the olefin selectivity is very low. Ni is also an active hydrogenolysis catalyst and so higher hydrocarbons can subsequently be “hydro-cracked”. At lower temperatures volatile nickel carbonyls are formed and so the catalyst is lost from the reactors.

The choice between the remaining metals, Ru, Co and Fe is not a simple one as it is influenced by several factors, e.g., cost, availability, desired product spectrum and required catalyst life-time and/or activity. Sasol uses iron oxide ores as the starting material for the fused promoted catalyst used in its Synthol process [2] while scrap iron metal is used in the preparation of the precipitated extrudates used in the fixed bed reactors [2]. If the cost of the iron used is equated to unity the cost of cobalt is then about 230 while that of Ru is about 31 000.

Besides its very high price the availability of Ru could be a problem if large capacity FT plants are required. It has been estimated that the entire available world stock of Ru would be needed to produce enough catalyst (with only 0.5% Ru on a support) for a FT plant with the same production capacity as the Sasol plants. If on the other hand a relatively small capacity plant is required for the production of high quality and high priced FT waxes, Ru may well be viable. Workers at Johnson Matthey [3] have shown that a 0.3% Ru on Al_2O_3 gives a wax selectivity of 88% (with a feed gas H_2/CO ratio of 2.0) which is considerably higher than the 60% obtained with the iron based Sasol catalyst under similar conditions.

Suitably promoted cobalt catalysts can also produce high yields of wax. As for Ru, the raw wax usually contains less olefins and oxygenated products than the equivalent wax produced by iron based catalysts. The activity of supported cobalt catalyst increases with Co loading and so some compromise between cost and activity is required. By way of example, should a 10% cobalt on Al_2O_3 be such a compromise, it could still be more than 10 times as expensive as the equivalent iron based catalyst. A much longer life, or higher activity would be required to justify its use.

Should olefins be the desired products (e.g. C_2 to C_6 for polymer, or C_{12} to C_{16} for detergent production) then promoted iron catalysts would be the best choice. Table 1 compares the light olefin selectivities obtained with Fe, Co and Ru

Table 1
Selectivity comparison (C atom basis)

	Fe	Co	Ru/Al ₂ O ₃
C ₂ H ₄	4.0	0.3	0.1
C ₂ H ₆	3.0	0.8	0.5
C ₃ H ₆	10.7	2.3	1.1
C ₃ H ₈	1.7	0.7	1.8
C ₄ H ₈	9.4	2.3	1.1
C ₄ H ₁₀	1.1	0.9	2.1
% i C ₄	10		

catalysts. Both Co and Ru have the advantage over Fe based catalysts, that under normal FT synthesis conditions they do not oxidise or deposit carbon. Iron oxide is inactive in the FT process and hence oxidation results in a loss of active surface area. (This aspect will be dealt with in more detail in section 3). The deposition of carbon results in catalyst particle swelling which results in complete plugging of fixed bed reactors. This precludes the use of iron catalysts in fixed bed reactors at temperatures above about 270°C [2]. The Arge reactors which are geared at wax production operate at around 230°C [2]. In the higher temperature fluidized bed Synthol reactors carbon deposition and the resultant swelling does *not* adversely affect the activity of the catalyst but as the result of mechanical breakage/erosion the very fine particles which are generated are lost from the reactors and so inevitably results in loss in overall activity. (More detail is given in section 3.)

The kinetics of the FT reaction over iron catalysts is described by

$$r = mP_{\text{CO}} \cdot P_{\text{H}_2} / (P_{\text{CO}} + aP_{\text{H}_2}).$$

Water vapour, which is a primary product in the FT reaction has a strong negative effect on the kinetics which inevitably means that the rate of the reaction declines markedly as the gas proceeds through the reactor. Fig. 1 illustrates a typical reaction conversion profile. This means that in the case of Fe catalysts considerably more FT work occurs in the first half than in the second half of the catalyst bed.

Sarup and Wojciechowski [4] report that the kinetics over a cobalt catalyst can be described by

$$r = aP_{\text{CO}}P_{\text{H}_2}^{0.5} / (1 + bP_{\text{CO}} + cP_{\text{H}_2}^{0.5})^2.$$

Note the absence of a water vapour pressure term in the equation. This could mean that a cobalt catalyst with an intrinsic activity equivalent to an iron catalyst could result in a higher overall conversion in commercial reactors. Fig. 1 illustrates the possible difference.

For commercial iron catalysts promotion with a strong alkali is absolutely essential in order to obtain a satisfactory selectivity. The “basicity” of an iron

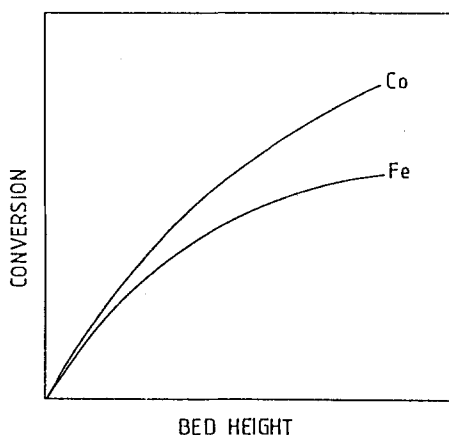


Fig. 1. Relative reaction profiles assuming Co FT kinetics to be less depressed by H_2O than is the case for Fe.

catalyst is determined by the alkali level and also by its interaction with other compounds present. Thus, while successful catalysts can be made by using Al_2O_3 as a support for Co or Ru, this is not the case for iron because of the “acidic” nature of the Al_2O_3 . To neutralize this “acidity” a relatively large amount of alkali has to be added in order to achieve the desired selectivity and then it is found that the activity has been negatively affected.

Whether the catalysts are Fe, Co or Ru based, they are all permanently poisoned by sulfur compounds. At Sasol the coal derived synthesis gas is purified by the Rectisol process [2] which lowers the S content to below 0.05 ppm. It is however an unfortunate “fact of life” that in commercial operation occasional upsets do result in S break-throughs. One such occurrence would wipe out the higher activity and longer life advantage a cobalt catalyst is expected to have over an iron based catalyst. The expensive Co or Ru catalysts would therefore require the additional expense of extra guard beds (or the like) to protect their potential advantages.

3. Aging of iron catalysts

3.1. LOW TEMPERATURE FIXED BED CATALYSTS

The operation of the multi-tubular reactors are entirely geared at producing high quality waxes. The overall conversion as well as the wax selectivity of the presently used precipitated iron catalyst decreases with time on stream and because of the high value of the wax it is the wax yield which determines the economic life cycle of the catalyst. Although the catalyst itself is cheap there is nevertheless an incentive to prolong its high performance period as this would mean less down time of the reactors and thus improve the overall efficiency.

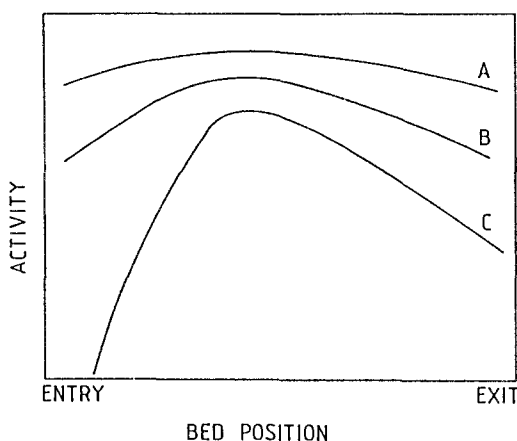


Fig. 2. FT activity profiles of catalysts along the length of the bed. The time on stream increases from A to B to C.

In order to evaluate how the catalyst properties changed with time on stream, full length commercial tube units were run for different times and then carefully unloaded to produce about twenty samples in each test. The samples were individually analysed and the FT syntheses activity and wax selectivity also determined in laboratory units under fixed test conditions.

X-ray line-broadening studies were done on the samples as received to estimate the average crystallite size of the magnetite present. The crystallinity of the active iron carbide phase changed in the same direction as the magnetite phase but the carbide peaks were in general more diffuse. With young catalyst no peaks were discernable indicating that only very small crystallites were present. BET surface areas were done on the samples after exhaustive solvent extraction treatments (decalin, xylene and MEK) to remove all wax. The “carbon/coke” contents of the used catalysts were also “measured”, being taken as that material remaining after exhaustive wax extraction, followed by HCl extraction, followed by HF extraction.

The activity and wax selectivity profiles are depicted in figs. 2 and 3 respectively. From figs. 2 and 3 it can be seen that the activities and selectivities of the young catalyst from the different bed positions were all much the same. This indicates that the “conditioning” procedure used did not damage the catalyst. (“Conditioning” is the procedure followed taking the H_2 pre-reduced catalyst up to full synthesis conditions.) From fig. 2 it can be seen that as time on line increases the activity of the catalyst at the bed entrance decreases. At the reactor exit the activity also declines but less so. There is a “peak” in the activity profile, approximately a third of the way into the reactor. The activity decline in this peak area is considerably lower than elsewhere and this then also indicates that intrinsically iron catalyst can be relatively stable.

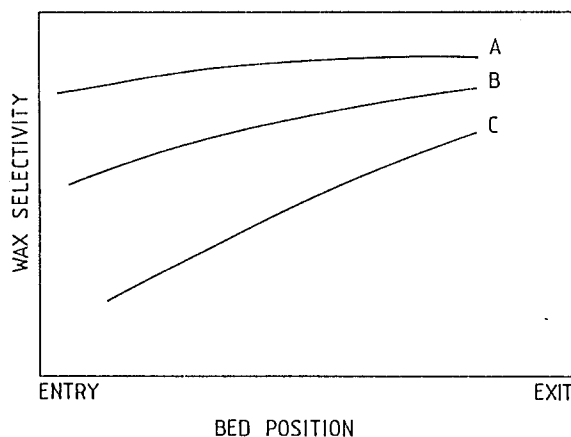


Fig. 3. Wax selectivity of catalysts sampled from different bed positions. The age of catalysts increase from A to B to C.

The BET area of the used catalysts declined progressively from the entry to the exit of the reactor (see fig. 4). In agreement with this trend it was also observed that the average crystallite sizes increased from entry to exit. Also the extent of oxidation increased in the same direction. In line with these observations the amount of pore volume present in pores greater than 35 Nm increased progressively from entry to exit (see fig. 3) which confirms that more sintering/area loss had occurred at the exit than at the entrance. The loss of activity at the bed entrance hence was clearly not due to loss of surface area. Chemical analysis of the samples showed that the levels of sulfur were much higher at the bed entrance than elsewhere and so S-poisoning is the likely cause of activity loss. Iron catalysts are of course excellent “S-getters” and so the above observations are not surprising. It was also found that the “carbon/coke” content of the entry samples

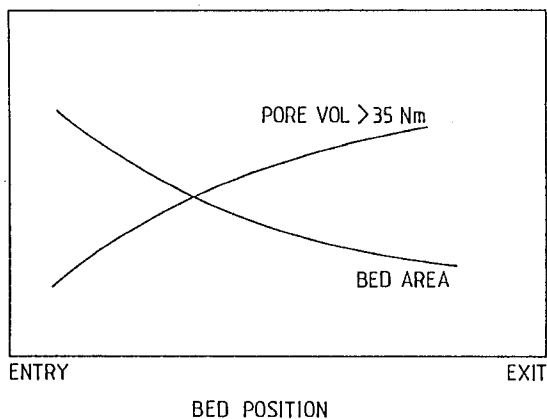


Fig. 4. The changes in surface areas and pore volume of an aged catalyst taken from different bed positions.

were about 35% higher than elsewhere in the bed. This difference too probably contributed to the lower activity of the entry zone samples. Note that despite the higher “coke” laydown at the entry the total areas of these samples were higher than elsewhere. The H/C ratio of the “coke” was found to be about 1.0 but infrared analysis showed that aromatic structures were absent and the only groups present were methylene and carbonyls. So it is presumed that this “coke” consists of a mixture of Boudouard carbon and insoluble high molecular weight waxes. If there really is Boudouard carbon present then this could also contribute to the higher BET areas of the entry samples.

The progressive loss of activity in the reactor exit zone is presumed to be due to the loss of active surface area as evidenced by the decrease in BET area, increase in crystallite sizes and increase in extent of oxidation of the active carbide phase to inactive magnetite. This hydrothermal sintering and oxidation is only to be expected as the partial pressure of H_2O (the main single product of the FT reaction) obviously progressively increases as the FT reaction proceeds down the catalyst bed.

Detailed X-ray analysis of the catalyst extrudates showed that the cores of the extrudates were more oxidised than the outside “skin”. This is as expected and is discussed again in section 3.2.

Fig. 3 illustrates that the trends for changes in wax selectivity differ from the activity changes. While there also are large decreases in the selectivity of the catalyst at the entrance, the selectivity of the catalyst at the exit does not change much with time. For low temperature fixed bed iron catalysts the parameters influencing selectivity are the H_2/CO ratio inside the reactor, the temperature and the catalyst’s “basicity” [2]. As in these *laboratory tests* the first two parameters were fixed for all the samples it is presumed that the selectivity differences must be due to catalyst “basicity” changes. Analysis of all the samples showed that the alkali (and all other promoter) contents were all the same and unchanged from the originally charged catalyst. These alkali analyses of course reflect the *bulk* analysis and it is possible that the actual dispersions of potassium on the catalyst surfaces may differ. Alkali is known to migrate over the iron catalyst surface (see section 3.2) and the presence of water vapour, the pressure of which increases down the catalyst bed, is likely to have an influence on this migration. As the BET area decreases down the bed the K_2O coverage and hence the surface basicity, may well increase. Note, however, that the wax selectivities do not actually exceed the wax selectivity of the fresh catalyst and hence this K_2O migration concept can at best only be compensating for some other factor which depresses the basicity.

An alternative factor may be the influence of S poisoning. The sulfide ion being highly electronegative is likely to be preferentially adsorbed at electron-rich, i.e. the basic, sites. This is the most likely explanation for the low wax selectivity of the reactor entrance samples where the S-contents *are* higher than elsewhere. This selectivity poisoning concept suggests that possibly the S-bearing contami-

nants in the feed gas penetrate much deeper into the catalyst bed than the bulk S analysis imply. Previous experiments carried out did indicate that while H_2S was rapidly adsorbed by the catalyst at the reactor inlet other S-compounds like COS and CH_3SH are less strongly adsorbed and so could penetrate deeper into the catalyst bed [2]. The observed activity profiles do not clash with the above concepts as the peak in activity could be the combined result of S-poisoning of the “entry half” of the bed and steam sintering/oxidation of the “exit half” of the bed.

Another factor that may depress “basicity” is the laydown of “carbon/coke”. As alkali is known to enhance carbon laydown [2] more carbon laydown should occur at the more basic sites and should this result in the effective blanketing (i.e. “loss”) of these sites then the “average basicity” of the catalyst will decrease and hence the wax selectivity would decrease. Note that the laydown of carbon was higher at the bed entrance zone and so this concept does fit the finding of lower wax selectivity of the front end catalyst.

3.2. HIGH TEMPERATURE FLUIDIZED BED CATALYSTS

In the Synthol reactors the general performance shift with time is similar to that observed in the fixed bed reactors, namely a drop in activity and a shift in the selectivity towards lower molecular weight products. There are, however, several major operational differences which impact on performance decline.

As the catalyst is fluidized, contaminants such as H_2S entering with the fresh feed gas would uniformly affect *all* of the catalyst particles, i.e., decrease both activity and selectivity, as discussed in section 3.1.

Whereas at low temperatures (in the wax producing mode) iron catalysts do not produce any aromatics, these are formed at the higher temperatures at which fluidized bed reactors are used [2]. Successive extraction of used fluidized bed catalyst with progressively stronger solvents showed that the extracted hydrocarbons became progressively more aromatic in character [2]. It was therefore deduced that aromatic coke deposits are probably present which are expected to cover active surface sites and so contribute to loss of activity. It was found [2] that H_2 re-reduction of the solvent-extracted catalyst did result in the formation of light hydrocarbons (from “coke residue” hydrocracking?) and also resulted in an increase in FT activity. Since H_2 reduction at 400°C is known to be incapable of removing sulfur or graphite from iron catalysts the reactivation is likely, in part at least, to be due to the removal of heavy carbonaceous residues.

During the FT process at high temperatures the Boudouard CO decomposition reaction occurs readily and after several weeks there is, on an atomic basis, twice as much carbon as iron present on the catalyst. In spite of this massive deposition of carbon the drop in conversion is relatively small. If the reactor system used is such that no fines are lost from the reactor the carbon deposition results in an expansion of the catalyst bed volume which actually results in an increase in

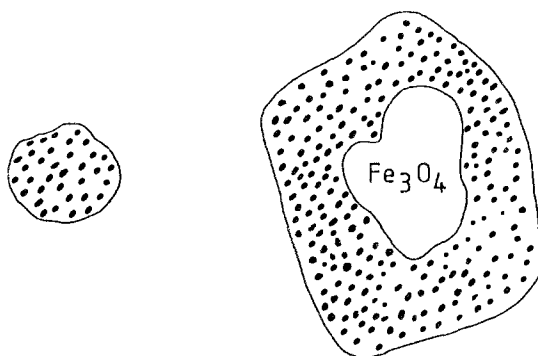


Fig. 5. Illustration of polished cross sections of small and large aged catalyst particles taken from a high temperature FT reactor. The black dots represent iron carbide particles embedded in a matrix of carbon. The core of the large particle consists only of magnetite.

conversion. Overall these results imply that the deposition of Boudouard carbon is not a major factor in performance decline.

It has long been known [2] that the finer particles present in used Synthol catalyst contain more Boudouard carbon, more iron carbide and less iron oxide than the courser particles and from this it was deduced that the larger particles probably consist of inert cores of inactive magnetite surrounded by an active iron/carbon layer. Recent investigations of polished used catalyst with a scanning electron microscope coupled with EDX detector showed that the finer particles consisted solely of small iron carbide particles embedded in a matrix of carbon whereas the larger particles consisted of cores of magnetite surrounded by the iron carbide and carbon mixture. Fig. 5 illustrates these observations. The formation of the magnetite core results from the fact that as the synthesis gas enters the porous particles the FT reaction occurs, which consumes H_2 and CO and produces H_2O . So the deeper the gas penetrates into the particle, the more oxidising the residual gas becomes and so the cores of the larger particles will be oxidised while the outer layers will remain in a “reducing” atmosphere.

As previously mentioned, promotion of iron by K_2O is a key factor determining the selectivity of the catalyst and hence the distribution of the potassium over the active iron surface is obviously of importance. Previous studies on fused Synthol catalyst [2] as well as studies by others on the closely related NH_3 -synthesis catalyst [5] have shown that in the unreduced catalyst the alkali is concentrated in silicate occlusions. In the milled catalyst many of these silicates are present as completely separate particles [2]. Overall, hence the distribution of the potassium promoter is very inhomogeneous. During H_2 reduction, however, it has been shown that the potassium migrates from the inclusions and spreads itself over the reduced iron catalyst [5]. On subsequent synthesis this migration continues [6] and the K also apparently creeps onto the Boudouard carbon formed. While the K migration over the iron surface appears to account for the *initial*

improvement in heavy hydrocarbon selectivity [6] its further migration onto the Boudouard carbon later could constitute an effective “loss” of potassium and so contributes to the decline in selectivity overserved in practice. This would of course be in addition to the “poisoning” of the potassium by sulfur as already discussed in section 3.1.

In commercial fluidized catalyst reactors there is the additional complication of loss of the ultra-fine and ultra-light catalyst particles from the reactors despite the use of highly efficient cyclones. In this way some of the light alkali-rich silicate particles are lost from the system and hence result in a shift in the selectivity spectrum. In addition, as the Boudouard carbon builds up (see fig. 5) the particles become lighter and also break up as the result of scowering in the high gas velocity system. Thus the low density ultra fines, containing active catalyst, are blown through the cyclones and so constitute a loss of catalyst from the reactor, thus contributing to the steady decline in activity.

4. Sasol FT reactor developments

Sasol commercially uses two types of FT reactors. The fixed bed multi-tubular Arge reactors (see fig. 6A) operate at “low” temperatures and produce waxes while the fluidized catalyst bed reactors (see figs. 6B and C) operate at “high” temperatures to produce essentially low molecular weight olefins and gasoline [2]. The original Sasol One Arge reactors operate at 2.7 MPa. Research had previously shown [2] that the production capacity of FT reactors should increase linearly with increasing pressure and two years ago a new 4.5 MPa multi-tubular fixed bed reactor was put into commercial operation. As predicted, the wax production per tube (i.e., per unit catalyst volume) increased in proportion with the pressure increase while the wax selectivity and quality remained unchanged.

The original Synthol CFB (Circulating Fluidized Bed) reactors operate at 2.0 MPa. When the new Sasol Two and Three plants were constructed, the capacity of the CFB reactors were increased three fold by increasing both their diameters and the operating pressure. Several years ago Sasol built and operated a demonstration unit of a much simpler type of fluidized bed reactor, the Synthol FFB, Fixed Fluidized Bed, (see fig. 6C). A commercial unit has now been successfully operated at Sasolburg. (This subject is dealt with in a separate paper at this conference.)

The only remaining type of reactor that requires demonstration is the slurry reactor [7]. The Sasolburg demonstration unit used to develop the FFB is now being converted to operate in the slurry mode. The objective is to operate it as a wax producer, i.e., as an alternative to the multi-tubular fixed bed reactor. The incentive is that the reactor capital cost should be about halved, the operating costs should be lower (because of a lower differential pressure) and the on-line

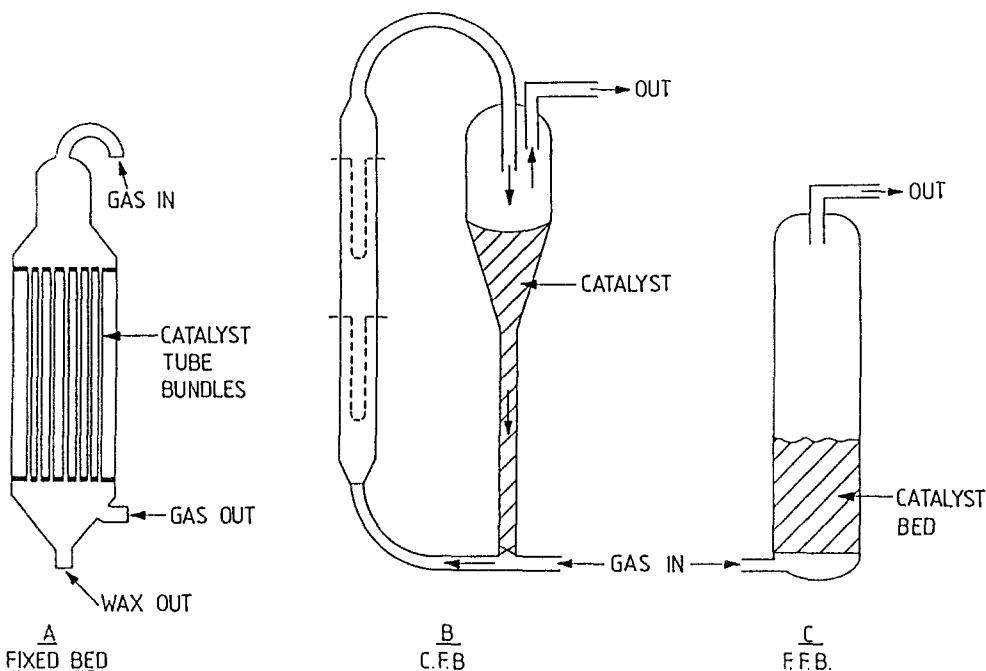
SASOL FT REACTORS

Fig. 6. Commercial Sasol reactors: A, Arge reactor (28 or 45 bar); B, circulating fluidized bed reactor; C, fixed fluidized bed reactor.

time should be higher because catalyst addition and removal can be carried out on-line [7].

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