

RECENT DEVELOPMENTS IN SASOL FISCHER-TROPSCH TECHNOLOGY

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When considering improvements in the Fischer-Tropsch (FT) route for producing liquid fuels from coal, it is important to bear in mind the relative costs of the various process steps. An approximate cost breakdown for a typical plant is as follows:

Synthesis gas production	58 %	(coal gasification 53 %; CH ₄ reforming 5 %)
FT synthesis	18 %	(plant 15 %; Catalyst 3 %)
Product separation	12 %	(cryogenic 4 %; Alcohols & ketones 4 %)
Refinery	10 %	(olefin oligomerization 4 %)
Diverse	2 %	

The advantage of a big improvement in the selectivity of the FT synthesis (an ideal case would be one which only produces gasoline and diesel fuel) is that this would lower the costs of both the product separation and the refinery sections, which, together account for 22 % of the total. Obvious provisos, however, are that the cost of the catalyst should not be markedly increased and that its conversion activity should remain high otherwise the gains in say the refinery would be negated by increased FT synthesis costs. Elimination of certain products do not necessarily improve the economics. If the FT process made no ethylene, the expensive cryogenic separation unit could be replaced by a cheaper process but this would not be a real gain as the market value of ethylene relative to that of liquid fuels justifies its recovery. A similar situation holds for the alcohols and ketones produced in the FT process. If these products were absent then the expensive process of first recovering them from the FT water and then refining them would significantly lower the overall costs. (Note that these products would have to be completely absent and not just lowered as the latter would have little impact on the economics of recovery as the volume of water to be processed would remain unchanged.) These low molecular mass alcohols and ketones, however, sell at high prices and furthermore the alcohols are valuable as gasoline octane boosters. Thus the production and recovery of these components are justified.

At Sasol the amount of methane produced far exceeds the need of the local fuel gas market and so the CH₄ is reformed with steam and oxygen to yield H₂ and CO which is recycled to the FT synthesis units. This reforming is of course thermally inefficient and results in a (about 14 %) loss of hydrocarbon produced from the reformed CH₄. In the Sasol process the bulk of the CH₄ comes not from Fischer-Tropsch but from the Lurgi coal gasification process and so to eliminate CH₄ reforming would require an alternative gasification process. Confining the issue to only the FT process, if a zero C₁ to C₂ selectivity could be achieved with only gasoline and diesel fuel being produced, it is estimated that the overall cost of the process could be cut by about 5 %. Because the capital outlay for a big commercial plant is huge, the 5 % saving is very significant.

To date, however, the attainment of a big improvement in the FT selectivity has been an elusive goal. All the proposed mechanisms of the reaction involve the concept of stepwise addition of single carbon entities to the growing hydrocarbon chains on the catalyst surface (1). This inevitably leads to a wide distribution of products. By manipulating the catalyst's formulation and/or the process conditions the probability of chaingrowth can be varied but the result is simply that if the production of C₁ to C₃ hydrocarbons is lowered the

production of the products heavier than diesel fuel increase. The maximum of the sum of gasoline plus diesel fuel lies in the vicinity of 60 % (1). To improve on this appears to require either a new kind of catalyst with a different mechanism or to superimpose some secondary catalytic action such as olefin oligomerization and/or wax cracking.

To date Sasol has exclusively used iron based catalysts in the FT process not only because iron is cheap but also because the products are richer in olefins than those normally produced by other metals active in the FT reaction. The lighter, C₂ to C₅, olefins are readily oligomerized to either gasoline or diesel thus giving the overall process a high degree of flexibility regarding the ratio of gasoline to diesel fuel produced. A major drawback of iron catalysts at temperatures above say 270 °C is that carbon deposition occurs. This, for mainly mechanical reasons (eg, disintegration of the particles) results in shorter reactor on-line times which means both a higher catalyst consumption rate and more reactors required per unit of gas converted. At the temperatures at which metals like cobalt or ruthenium are active in the FT synthesis, very little carbon is deposited and so these metals have attracted attention as alternative catalysts. On a unit mass basis the cost of cobalt is about 250 times that of the iron used at Sasol while that of ruthenium is about 20 000 times that of iron. To make cobalt competitive with iron, a much lower mass per volume of catalyst will have to be employed, the catalyst life will have to be longer (with its activity and selectivity as good or better than that of iron) and the spent catalyst will have to be regenerated for re-use. While these objectives may well be met with cobalt, the case for ruthenium is bleak. Putting aside the price, it can be shown that for only a single Sasol commercial plant one would require more than the entire available world stock of ruthenium to produce the needed catalyst charge which would only contain 0,5 mass % of Ru on a typical support. The production of Ru and other noble metals such as Rh, is entirely linked to the demand for Pt.

While Sasol remains committed to developing catalysts with longer lives and improved selectivities these objectives are seen as longer termed. In the short term investigations have concentrated on increasing the production per reactor, developing lower cost reactors and optimizing the product spectrum by improving the processes downstream of the FT reactors. Several of these new developments are in the process of being commercialized.

Kinetic investigations had indicated and pilot plant tests had confirmed that for both fixed bed tubular and fluidized bed reactors the production per unit volume of catalyst could be raised by simultaneously increasing the operating pressure and the volume of feed gas thus maintaining a fixed linear velocity, ie a fixed residence time in the reactors (1). Sasol recently decided to build an additional commercial fixed bed tubular reactor to increase the production of FT waxes. This reactor will operate at a pressure considerably higher than the reactors currently in use.

The Synthol reactors, which are the "work horses" of the Sasol FT process, are circulating fluidized bed (CFB) types with catalyst flowing down a standpipe on one side and up a riser on the other side (see Figure 1). These units are already very large and there are doubts whether they could be scaled up further by either increasing their diameter or raising the operating pressure. As an alternative Sasol has been investigating for some time the fixed fluidized bed (FFB) system. In this reactor the catalyst is not circulated but remains "stationary" as an ebulating bed with the gas entering at the bottom. This reactor is considerably smaller and so should be cheaper to construct, simpler to operate and increasing the operating pressure presents no mechanical problems. An additional advantage of higher pressure in the case of iron catalysts operating at high temperatures is that the rate of carbon deposition on the catalyst decreases (1) which for the reasons already mentioned, should result in longer life catalysts. A demonstration FFB unit has been operating at the Sasolburg plant for some time and various design aspects have been

investigated. The design of a large commercial size unit is currently underway for cost estimating purposes and hopefully for implementation in the near future.

Another reactor version being investigated is the slurry phase reactor. In concept this is similar to the FFB reactor but the finely divided catalyst is suspended in a suitable liquid, eg molten FT wax. Compared to the fixed bed reactor it is cheaper to construct and because of this it may be a viable alternative process for producing FT waxes. A potential advantage of the slurry phase system is that with iron catalysts it can operate in the temperature range 260 to 290 °C. In this temperature region a fixed bed would plug up due to carbon deposition while a "dry" fluidized bed would "defluidize" because of catalyst particle agglomeration due to wax formation. To date the experimental investigations at Sasol have been confined to 5 cm ID pilot plant reactors. The next planned phase is the construction of a larger pilot reactor in order to investigate the system at hydrodynamic conditions likely to exist in a commercial scale reactor.

With regards to process improvements downstream of the FT reactors two catalytic processes are being developed. FT waxes produced at low temperatures are essentially straight-chained containing no aromatics and are sulphur and nitrogen-free. Because of these factors the wax can be hydrocracked under relatively mild conditions to yield up to 80 % of high quality diesel fuel. These results have been independently verified by firms specializing in hydrocracking and no problems are foreseen in commercializing the process.

Light olefin oligomerization to gasoline and diesel fuel has been commercially practiced by Sasol for many years but the process which utilizes a supported phosphoric acid catalyst produces a light diesel fuel which has a lowish viscosity and a very poor cetane number, the latter being due to the high degree of skeletal branching. Because of this the amount of this fuel which can be added to the overall pool is limited and so restricts the full utilization of olefin oligomerization to maximise diesel fuel production. The new generation ZSM-5 type zeolites can completely remove the above-mentioned limitations. Because of the high strength of the zeolite acid sites, a higher degree of oligomerization occurs which results in a higher molecular mass product with a higher viscosity. Because of the unique size of the zeolite pores, it is physically impossible to produce highly branched oligomers and consequently the product diesel fuel has a high cetane number. This process has been thoroughly evaluated on pilot plant scale with FT feedstocks both at Sasolburg and abroad. The building of a full scale commercial plant is presently under consideration as part of a debottlenecking process at Sasol's Secunda complex. A new zeolite oligomerization plant would not only process additional olefins but should also be able to improve the yield and quality of the overall diesel fuel pool.

Table 1 illustrates the selectivities (on a carbon atom basis) typically obtained in the two types of commercial FT reactors used by Sasol, namely, the high temperature Synthol process (geared at making light olefins and gasoline) and the lower temperature fixed bed process (geared at making waxes). Applying to each of these product streams, the secondary processes previously discussed, namely, oligomerization of the C_3 to C_6 olefins to yield 75 % diesel fuel and hydrocracking of the wax to yield 80 % diesel fuel, the overall liquid fuel situation obtained is shown in Table 2. As can be seen high quality diesel fuel at high yields can be obtained in both processes. When both maximum liquid fuel yield and maximum diesel fuel to gasoline ratio is required, the low temperature Arge FT process has the greater potential.

REFERENCE

- (1) Catalysis Science and Technology, Vol 1, Ch. 4, Ed. by J R Anderson & M Boudart Springer Verlag 1981

TABLE 1
COMPARISON OF THE STRAIGHT-RUN FT PRODUCTS FROM THE SYNTHOL AND ARGE REACTORS

Cut	Synthol high temperature	Arge low temperature
C ₁ + C ₂	16.0	5.4
C ₃ to C ₆ paraffins	5.0	8.4
C ₃ to C ₆ olefins	33.5	7.6
C ₇ - 160 °C	17.2	8.0
160 - 350 °C	14.0	19.5
+350 °C	7.8	48.1
Water soluble oxygenated compounds	6.5	3.0

TABLE 2
COMPARISON OF THE TWO DIESEL PRODUCING SCHEMES

Cut	Synthol	Arge
Total final liquid product	80	87
% diesel of liquid fuel	55	75
Diesel source:		
- From oligomerization	58	9
- Straight run	31	30
Wax cracking	11	61
Cetane number of diesel pool	53	67

(All figures are percentages except for the cetane number)

