

Development of Fischer Tropsch Reactors

B. JAGER
Sasol Technology Netherlands BV
PO Box 217
7500 AE Enschede
The Netherlands

INTRODUCTION

In converting coal or natural gas to petroleum products, they are first gasified or reformed with oxygen and steam to syngas, a mixture of H_2 and CO, which after purification is converted to a syncrude by means of the Fischer-Tropsch (FT) process. This syncrude is then worked up in a relatively simple refinery to liquid fuels and/or chemicals. Depending on the final products required, either low temperature Fischer-Tropsch (LTFT) is used to produce a syncrude with a large fraction of heavy, waxy hydrocarbons or high temperature Fischer-Tropsch (HTFT) is used to produce a light syncrude and olefins. In both cases some oxygenates are produced as well.

Worldwide, there is considerable interest in LTFT, mainly for the conversion of stranded or remote natural gas for the production of superior diesel. Several projects to build such plants are under consideration, some of which are well advanced as for instance the Oryx-GTL plant being built by Sasol and Qatar Petroleum in Qatar. This has only become possible because the total cost of the project could be reduced to as low as close to \$ 25 000 per daily barrel.

There is less interest in HTFT applications. HTFT plants are considerably more complex than LTFT plants in terms of the product slate. This makes techno-economic feasibility studies more difficult and initial investments higher but HTFT also provides interesting opportunities. The HTFT complex operated by Sasol contributes significantly to Sasol's profitability.

FISCHER-TROPSCH PROCESS SYNTHESIS

The products from the FT synthesis vary depending on the catalyst formulation and process conditions. Typical product distributions obtained with iron based catalyst for LTFT and HTFT are shown in Table 1. The product slates follow the Schulz-Flory distributions with, for LTFT, alpha values ranging up to 0,95 or higher.

The reactor design has to take into account the conditions needed for the FT catalytic conversion, the properties of the syngas used and those of the syncrude produced which, as can be inferred from the table below, may exist in either the gas phase (HTFT) or liquid and gas phase (LTFT). The FT reaction is highly exothermic and the removal of heat is an important consideration for the design of the FT reactors.

Table 1: Selectivity (carbon basis) of Sasol processes

Product	LTFT	HTFT
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	48	9
Water soluble oxygenates	3	6

FISCHER - TROPSCH REACTORS

Fischer Tropsch reactors have shown considerable development since the first reactors were used even before the Second World War. Presently there are three types of reactors that are considered to meet the requirements for modern commercial applications.

Originally fixed bed reactors, later in the form of multi tubular fixed bed reactors, were used, all for LTFT operations [1]. In the multi tubular form these reactors are commercially used by Sasol in South Africa and by Shell in Malaysia. They typically operate between 180 and 250°C at pressures ranging from 10 - 45 bar. Under these conditions the reactor operates in the three phase gas-liquid-solid trickle bed mode. A new development is the slurry bubble column or Slurry Phase reactor which is under development by several companies but at this stage is only used commercially by Sasol [2].

There is also the high temperature Fischer-Tropsch (HTFT) process which has been operated by Sasol in South Africa since 1955. The HTFT process, called Synthol, up to a few years ago used a circulating fluidised bed reactor operating at a pressure of about 25 bar and temperatures of about 330 - 350°C. At these conditions the reactor is operated in the two phase gas-solid mode. The circulating fluidised bed reactors have now all been replaced by Sasol Advanced Synthol (SAS) reactors which make use of conventional solid-gas fluidisation.

LOW TEMPERATURE FISCHER – TROPSCH REACTORS

Multi Tubular Fixed Bed Reactors

The multi tubular fixed bed reactors (MTFBRs) which have been used since WW 2 are still used by Sasol in their Arge Process and by Shell in the Shell Middle Distillate Synthesis (SMDS) process. The FT reaction takes place over an iron based catalyst (Sasol) or over a cobalt based catalyst (SMDS) in a reactor which resembles a tubular heat exchanger, as shown in figure 1, with the catalyst packed in the tubes. The heat is removed through the tube walls to generate steam on the shell side of the reactor. The interaction between the generation of heat and heat removal through the walls gives rise to axial and radial temperature profiles. The axial temperature peaks are associated with the highest conversion rates. In effect this means that in the first few metres of the

10 to 12 metre long bed, most of the reaction takes place and that after the peak relatively little conversion is achieved and the catalyst is under utilised. It is possible to distribute the conversion more evenly over the tube length by either reducing the activity of the catalyst or by reducing the average temperature or by a combination of the two.

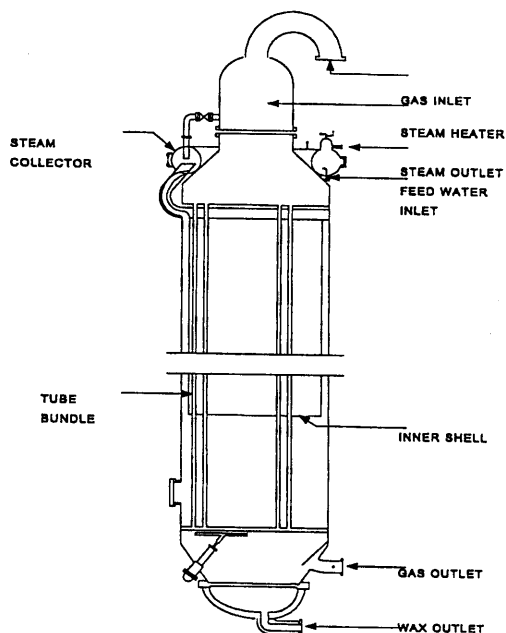


Figure 1: Multi tubular fixed bed reactor (Arge)

In order to obtain good conversions, a high average temperature is required but this is subject to a maximum temperature for the peaks above which selectivities are negatively affected and the catalyst may be damaged especially in the extreme case of temperature run-aways.

Efficient heat removal and effective temperature control at higher levels of temperature is therefore very important. Heat transfer in the bed and through the tube walls is much improved by increasing the gas and liquid flows in the bed. In the case where this is achieved by gas recycle, the conversion per pass is decreased but the overall conversion benefits in a large way by the recycle of reagents and the higher reaction rates possible at the higher average tube temperatures. This comes at the cost of recompression of the recycle gas. Recycle of liquid products also helps in improving the heat transfer and hence the heat removal processes. For this an effective liquid distribution is a prerequisite as uneven distribution can readily cause temperature run-aways and blockages in "dry" tubes.

The effective control of temperatures and prevention of unstable conditions becomes more critical with increasing activity of the catalyst. When the contributions to improved heat transfer possible through recycles of gas and liquids have been exhausted, further improvements can only be achieved by decreasing the tube diameters. This comes at increased reactor costs but makes it possible to make higher pressure steam.

The pressure drop over the tube tends to be high compared to those obtained in fluidised systems. With relatively high recycle flows, this gives rise to increased recompression costs.

In a tubular fixed bed, plug flow conditions are obtained which allow for optimal use of reagent concentrations. This benefit is however to a significant extent lost by recycle of the tail gas which has a diluting effect on the fresh feed.

The reactor is complex and expensive. The scale-up of the reactor is mechanically difficult and is complicated by the fact that the iron-based catalyst has to be replaced periodically and the design of the reactor has to provide for this. This replacement is cumbersome and maintenance and labour intensive. Cobalt-based catalyst has a long life and replacement is a less important factor.

Slurry Phase Reactors

The Slurry Phase reactor, as shown in figure 2, consists of a vessel containing a slurry consisting of process derived wax with catalyst dispersed in it. Syngas is bubbled through this slurry bed and is converted to hydrocarbons [2]. The heat generated is passed from the slurry to the cooling coils inside the reactor to generate steam. The light hydrocarbons in the vapour phase are removed from the freeboard in the top of the Slurry Phase reactor with the unconverted reactants and are condensed in the downstream condensing train. The heavier liquid hydrocarbons are mixed into the slurry from which they must be removed by means of a solid separation process. In the case of Sasol this is achieved by internal devices, in a proprietary separation process developed by Sasol. The successful development of an effective and a relatively cheap liquid-solid separation step was crucial to the development of the Slurry Phase reactor [3]. Precipitated catalyst, especially iron based catalyst, tends to be weak. It is important that the catalyst is strong enough to prevent break up which would make the liquid/solid separation more difficult and in the extreme, impossible.

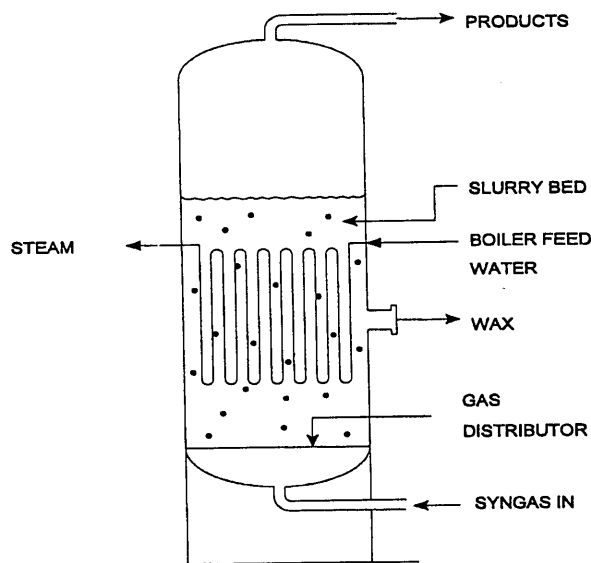


Figure 2: Sasol Slurry Phase Distillate Reactor

A most significant process characteristic of the Slurry Phase reactor is that it is well mixed and can operate virtually isothermally. The absence of axial and radial temperature gradients as in a MTFB

reactor, allows for much higher average operating temperatures in the Slurry Phase reactor and therefore higher reaction rates. As all the catalyst is at more optimal process conditions, the yields per reactor volume are high even though the catalyst concentration in the Slurry Phase reactor is lower than that for the MTFB reactor. Because the reactor is well mixed, the catalyst tends to see outlet gas concentrations. This has a disadvantage in terms of conversions in a once through system. Through staging inside the reactor and operating reactors in series, the disadvantages of well mixed reactor behaviour can be reduced to a large extent. The pressure drop across the Slurry Phase reactor is less than 1 bar.

The Slurry Phase reactor allows for on-line catalyst withdrawal and addition which is not feasible with the MTFB reactor. This is especially important for FT reactors that use iron based catalyst which must be replaced periodically. On line catalyst renewal also reduces maintenance costs. Where use is made of cobalt catalyst which has a longer life, this is obviously less important, but in principle the addition and withdrawal features can also be used for reactivation of cobalt catalyst if required.

Because of the isothermal nature of the reactor and the much smaller pressure drops across the reactor, the control of the reactor is much simpler and operating costs are much reduced. The easier control of average catalyst life through regular catalyst renewal, allows for easier control of the process selectivities and hence the quality of the primary products. This is especially important for processes using iron based catalyst.

LTFT Catalyst

For LTFT either an iron or a cobalt based catalyst can be used. Cobalt based catalyst has a longer life than the iron based catalyst. It has higher activity than the iron based catalyst when high conversions per pass are required because with the iron based catalyst, the water produced by the FT reaction has an inhibiting effect on the reaction rates. When high conversions per pass are required, cobalt based catalyst is preferred. The position is less clear in a series of reactors configuration where per pass conversion can be reduced. Under those conditions iron based catalyst can have higher activities. Iron based catalyst also has considerable water gas shift activity which complicates the FT plant design. However, this can be an advantage when syngas with a low H_2/CO ratio is used. This can readily be handled by an iron based catalyst. This is true for both the MTFB and Slurry Phase reactors.

The effect of process conditions on the behaviour of these catalysts is dealt with extensively in the literature [3, 4]. Both cobalt and iron based catalysts are oxidised by water, the product of the FT reaction. Cobalt based catalyst is however more resistant to re-oxidation and hence its longer life. Still, even in the case of cobalt based catalyst there is a maximum water vapour pressure to which the catalyst can be exposed. Above this partial pressure its economic life is affected. This has to be taken into account in the design of the FT reactors and associated gas loops.

As indicated by the relevant reaction rate expressions [3], in the case of iron based catalyst the conversion benefits from higher partial pressures of H_2 and CO . In the case of cobalt based catalyst, conversion depends on the H_2/CO ratio rather than on the partial pressures. Both catalysts produce heavier product slates (higher Schulz-Flory α values) with lower H_2/CO values. In the case of cobalt based catalysts higher α values are also obtained with increasing pressures.

To obtain the maximum conversion of the combined H_2 and CO , the reaction should take place at the stoichiometric H_2/CO ratio of about 2. For cobalt this ratio is not ideal for the required

selectivities. As shown below this negative effect tends to be enhanced by diffusion limitations which are more pronounced in the larger catalyst particles used in MTFB reactors. For the same selectivities the operating pressures for MTFB reactors will therefore be substantially higher than for Slurry Phase reactors. For iron based catalyst the same holds but to a lesser extent because with iron based catalyst the selectivities are less sensitive to syngas pressure and H₂/CO ratios. This also compensates for the effect of the water gas shift reaction which tends to increase the H₂/CO ratio.

Effect of catalyst particle size and reactivity

The two reactor types behave quite differently to changes in catalyst reactivity and also because of differences in catalyst particle size. In a fixed bed reactor, particles will be 1 mm in diameter, or bigger, to prevent excessive pressure drops across the bed. In the case of slurry bubble columns the catalyst particles are preferably small and the lower particle size is typically determined by the solid separation process used to recover the liquid products from the slurry. In practise this means that the lower diameter should not be below, say, 20 microns. The maximum size does not need to be bigger than this but is typically in the range of 100 to 200 microns. Smaller size particles are preferred for purposes of keeping the particles in suspension in the slurry bed. With the proper design of slurry bed reactors, settling of catalyst particles can be prevented and if need be a small recycle of slurry from the top to the bottom of the bed can be considered.

With the particle sizes pertaining to MTFB reactors, present day catalysts have effectiveness factors well below unity. This indicates that increases in catalyst activities only give limited advantages in these reactors. Because H₂ has a higher rate of diffusion than CO, the concentration gradients of H₂ and CO in the particles tend to increase the H₂/CO ratio with negative consequences for the selectivities of the FT reactions. Although this can be counteracted by adjustments in the H₂/CO ratio in the gas phase, moves away from the stoichiometric value may affect the conversion rate and require increased gas recycles and more complex gas circuits. Alternatively, the negative effects of diffusion limitations can be reduced by operating at higher pressures.

For Slurry Phase reactors the situation is more favourable. For the cobalt catalyst activities used in the Qatar design and the particle sizes mentioned above, the catalyst effectiveness factors are very close to unity and particle size has no or little effect on selectivities. Already catalysts of higher activities have been developed and even higher activities appear possible. With 1mm particles this would have limited benefits whereas with the particle sizes associated with Slurry Phase reactors the full benefits of the higher activities can be realised and there is an important incentive to develop more active catalysts.

Reactor capacities

Originally the MTFB reactors used for SMDS had average capacities reported of about 3 000 bbl/day. These reactors are configured in series where three primary reactors feed into a single secondary reactor. Shell has recently indicated reactor capacities of 9 000 bbl/day and that future generations of these reactors could achieve up to between 10 000 and 15 000 bbl/day [5]. Apparently this is the result of improvements in the catalyst used and optimisation of the way the reactors are operated and the process configuration and conditions. The size of these MTFB reactors is probably determined by limitations imposed by the shop manufacturing process and transport limitations. It seems unlikely that these reactors can readily be made much bigger and important capacity increases are unlikely.

The largest Slurry Phase reactor build to date, has a capacity of about 3 000 bbl/day. The Slurry Phase reactor is simpler in construction than the MTFB reactor. The suspended cooling coils and a gas distributor give a cheaper arrangement than the tube and tube sheet arrangement in the MTFB reactor. Because of this the Slurry Phase reactor lends itself much better to scale up. These differences make it possible to design, at an operating pressure of 25 bar, single Slurry Phase reactors with high capacities. For the Oryx-GTL plant being built by Sasol and Qatar Petroleum, two reactors each with a capacity of 17 000 bbl/day will be operated in parallel. Like the MTFB reactors these will be shop fabricated and delivered to the plant location as complete units.

Slurry Phase reactor capacities larger than those mentioned above may be possible at higher pressures due to more favourable hydrodynamic interaction between gas and liquid. Even at the present operating pressures considerable higher capacities are possible. Higher activity catalysts are being developed which will allow for considerably higher conversion rates. By staging inside the reactors, operations can approach plug flow more closely which has beneficial effects on reaction rates, especially with iron catalyst, and it also benefit selectivities.

Gas flows decrease with conversion. By having interstage fresh feed addition more optimal use is made of the reactor volume as the gas flow reduces in subsequent stages. Reactors can also be configured in series with condensing trains between the different reactor stages. By removing condensable vapours, especially water, from the feed to secondary or subsequent reactors, higher reaction rates can be maintained for better conversions and/ or improved selectivities. As with interstage fresh feed, inter-reactor addition of fresh feed can make use of any gas flow capacities that may exist in lower order reactors. Making full use of all these opportunities it is expected that the presently sized but somewhat modified reactors can have on average capacities well in excess of 30 000 bbl/day. At the same time gas recycle is considerably reduced or eliminated which allows for savings on both capital and operating costs. These opportunities are especially valid for larger sized plants with a multiplicity of reactors.

On the whole it appears that the use and application of slurry bed reactors is still relatively early on the learning curve.

HIGH TEMPERATURE FISCHER – TROPSCH

The Sasol Advanced Synthol (SAS) Reactor

Nineteen Synthol-Circulating Fluidised Bed (CFB) reactors were used commercially by Sasol in the period from 1955 to 2000. The reactor system was complex and needed a complex support system to cope with the circulating catalyst loads and temperature differences especially during start up. This made it expensive. The large tonnages of catalyst circulated, caused relatively high pressure drops across the reactor system. At any time only a small fraction of the catalyst in the system was used for conversion purposes. The reactor systems were prone to erosion due to the high gas velocities in the reactor which operated in the transport bed mode. These and other disadvantages are eliminated when using a Sasol Advanced Synthol (SAS) reactor that makes use of conventional solid-gas fluidisation. For that reason between 1998 and 2000 the 16 Synthol-CFB reactors with capacities of 6 500 bbl/day, still in use, were replaced by eight SAS reactors, four 8 m diameter reactors with capacities of 11 000 bbl/day each and four 10,5 m diameter reactors with capacities of 20 000 bbl/day. Two different capacity reactors were used to fit in with the train configuration used with the then existing CFB reactors. The capital cost of these reactors is about 40% of that of equivalent CFB reactor systems.

The SAS reactor, as shown in figure 3, is a vessel containing a fluidised bed consisting of reduced, fused iron oxide catalyst [6]. Syngas is bubbled through the bed where it is catalytically converted to hydrocarbons that are in the vapour phase at the process conditions of about 340°C and 25 bar. The products and unconverted gases leave the reactor through internal cyclones. The SAS reactor is operated in such a way that the cyclones very effectively retain the catalyst. With the CFB reactors, scrubber towers were needed downstream of the cyclones to remove the last traces of catalyst before the product stream is passed to the condensing train. Although these scrubbers have been retained in the plant they can probably be eliminated in future plants using SAS reactors.

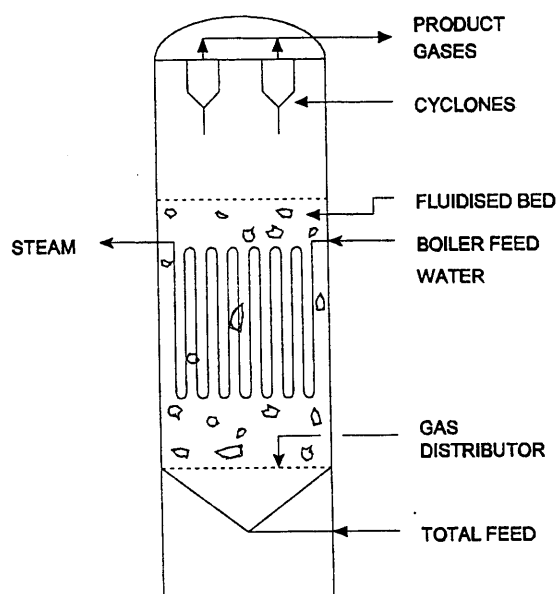


Figure 3: Advanced High Temperature Fischer- Tropsch Synthol reactor.

The major advantages of the SAS reactor over the CFB reactor are its simplicity, ease of operation and low operating cost due to elimination of the catalyst recycle. Catalyst consumption is reduced to about 40% and maintenance costs to about 15% of that of the CFB systems. In general, higher conversions are obtained at higher gas loads. The latter together with the fact that more cooling coils can be installed in the SAS reactor and more heat can be removed, allows for larger capacity equipment, which translates into advantages of economy of scale. Capacities are presently up to 20 000 bbl/day. They also have thermal efficiencies four percentage points higher than CFB reactor systems.

The design of the present SAS reactors was geared towards the need to retrofit them into an existing plant where they had to replace the circulating fluidised bed reactors. Although the catalyst consumption with these reactors is much lower than with the circulating bed reactors, it appears that the catalyst is even now not used with maximal effectiveness. The reactors are operated in parallel mode. In the case of HTFT only iron based catalyst can be used to give reasonable product selectivities. As with the LTFT process, the water which is a product of reaction, has an inhibiting effect on the conversion rates. Also here, high conversions per pass cannot therefore be obtained and considerable recycle of unconverted gas has to be used to achieve a reasonable overall conversion. Series operation of the SAS reactors with intermediate removal of water allows

for lower conversions per pass which reduces the need for gas recycles. Based on these and other considerations, it appears that there is considerable scope to increase the average capacity of the present reactors to well beyond the present capacities of 20 000 bbl/day. As in the case of LTFT reactors, with higher activity catalyst or in this case with better use of the present catalyst, other mechanisms become limiting with respect to the maximum average capacities that can be achieved of which the most important may be heat removal.

CONCLUSION

New reactors have been available for both LTFT and HTFT for some time. In recent years, the developments around Gas-to-Liquid project have stimulated the developments of these and the older MTFB reactors and the optimisation of the gas loops around. This has led to considerable increases in reactor capacities and reduction of their costs. As catalyst activities increase different mechanisms become limiting, for instance heat removal. Heat removal is closely associated with the heat management in a plant and affects the utilities. The optimal design of the FT reactors can not be determined or done in isolation but must be done within the philosophy of the overall plant design.

It is clear that the development of the LTFT Slurry Phase reactor and the use of the HTFT SAS reactors are still early on the learning curves and considerably higher capacities and cost reductions can be realised for these reactors and the gas loops associated with them.

LITERATURE CITED

- 1 Sie, S.T. and Krishna, R.: Fundamentals and Selection of advanced Fischer-Tropsch reactors, Applied Catalysis a: General 186, 1999, 55-70.
- 2 Jager, B., Kelfkens, R.K. and Steynberg, A.P.: A Slurry Bed Reactor for Low Temperature Fischer-Tropsch, Third International Natural Gas Conversion Symposium, Sydney, July 1993, Elsevier Science B.V., 1994, 419-425.
- 3 Jager, B. and Espinoza, R.: Advances in Low Temperature Fischer-Tropsch Synthesis, Catalysis Today 23, 1995, 17-28.
- 4 Espinoza, R.L., Steynberg, A.P., Jager, B. and Vosloo, A.C.: Low temperature Fischer-Tropsch synthesis from a Sasol perspective, Applied Catalysis A: General 186, 1999, 13-26.
- 5 De Graaf, W. and Schrauwen, F.: World Scale GTL, Hydrocarbon Engineering, May 2002, 55-58.
- 6 Jager, B., Dry, M.E., Shingles, T. and Steynberg, A.P.: Experience with a New Type of Reactor for Fischer-Tropsch Synthesis, Catalysis Letters 7, 1990, 293-302.

