SECTION 3 - DISCUSSION OF THE FOUR REACTOR SYSTEMS

3.1 GENERAL

Task Order No. 15 required the comparison of the commercially operating entrained bed Synthol process with three other processes that have not been commercialized. This in itself created a difficulty, because processes frequently appear more attractive in the conceptual stage than after a process is put into final form following commercial experience. This study was conducted to determine if any of the three conceptual reactors appear to offer significant advantages over the commercial process. If a reactor is not attractive as a conceptual design, it probably should be dropped from further consideration. If any appears to have a significant advantage over the commercial process, the system in question deserves some further development effort prior to commercialization. Only after the process has been commercialized can a true comparison with the entrained bed process be made.

A review of the four reactor systems, prepared from data available in the literature, is presented in this section. Upon completion of this literature review, it was clear that there are many complications to preparing a comparison between these reactor systems. Although all of the reactors employed iron catalyst, results changed considerably depending on the presence of other metals or contaminants. Experiments on the various reactors were invariably carried out at widely different operating conditions (summarized in Table 3.1-1), at different conversion levels, and on different feed compositions. It was impossible to determine whether the different results reported in the literature were caused by differences between reactor systems or the choice of catalyst or operating conditions.

The problem presented by Task Order No. 15 was, therefore, approached on two fronts:

<u>First</u>: Carry out a fundamental kinetic study of each reactor system to sort out which of the claims in the literature with respect to yields are due to fundamental differences in the reactor systems.

Second: Make physical comparisons between the reactors, with operating conditions and yields selected in the light of the kinetic study, to determine the approximate differences in investment costs and operating efficiencies.

The results of the above two studies are presented in Sections 4 and 5, respectively, of this report.

3.2 ENTRAINED BED REACTOR

This reactor was originally developed and designed by M. W. Kellogg Company. Sasol has operated the process in Sasol I since 1955. The designs for the newer Sasol II and III projects were based on improvements developed by Sasol during operation of the first plant. Since Kellogg has published much more descriptive information on their version of the process (4), this study is largely based on the process as offered by Kellogg. Sasol has also published many papers, and these were used to supplement the Kellogg data.

There are many descriptions of the process in the literature (4, 5, 12, 14). The reactor system typically consists of three vessels in series with intercoolers. A separate vessel is required to recover the catalyst from the product vapor for recycle to the reactor. It is a vapor phase process, operated with about 75% CO conversion per pass. The process operates with considerable recycle gas (2.3/1 molar recycle/feed), consisting of 40 mol-% H_2, unconverted CO, large amounts of CO_2 and methane, and other light hydrocarbons. The feed syngas has a H_2/CO ratio of 2.4/1, and the combined feed has a H_2/CO ratio of 4.7/1. Preheated feed is introduced to the reactor at about 600°F and 365 psig. The catalyst separator runs at 635°F and 285 psig (4).

This is the only one of the reactor systems under consideration that is in commercial operation. However, no information on the performance of the commercial unit was available for the preparation of this study. Both Kellogg and Sasol regard such information as proprietary. While there is no detailed publication of Sasol's operating experience with the process, Rousseau (5) mentions that there were considerable difficulties when the plant was started up in 1955. Both conversion and selectivity were much lower than predicted by pilot plant data. Fouling of reactors was experienced, and frequent shutdowns were required for removal of deposits. Also, catalyst activity declined rapidly. A third reactor was added to the two originally built to maintain output when one reactor was down for cleaning and catalyst changing. The plant was substantially revamped in 1960 to correct deficiencies in the original design, but no details of the changes are revealed. Hoogendoorn (12) indicates that improvement of the catalyst contributed to achieving "reasonably continuous operation". Although Kellogg designed the process for continuous catalyst addition and withdrawal, Sasol shuts down and replaces the entire load of catalyst after 50 days operation (12). In another publication, Hoogendoorn (13) also states that "It is necessary to limit the production of high boiling hydrocarbons, as a too high production of such material results in agglomeration of catalyst particles and loss of fluidization properties". There is also an indication (9) that some of the original loss of on-stream efficiency was due to mechanical problems with compressors. Perhaps the most significant information in the literature with respect to the operability of the Sasol plants is Sasol's decision to proceed with the Sasol II and III projects, which is a clear statement of their confidence that they have solved the operating problems. Sasol II was starting-up at the time of the writing this report. Publication of the start-up results is awaited with interest.

Dry (14, 15) has published interesting insights into the kinetics of the entrained bed system, particularly with respect to the effect of H_2/CO ratio on the degree of polymerization, and methane and free carbon formation. He indicates that the temperature used for the entrained bed system is above that where free carbon formation due to the Boudouard reaction ($2\ CO \rightarrow CO_2 + C$) occurs. The rate of free carbon formation can be reduced by increasing the hydrogen partial pressure, but Dry's mechanism indicates that this will result in additional methane formation in place of free carbon.

From the literature review, it can be concluded that Sasol's entrained bed system is a commercial process that can be operated successfully. The operating conditions require a high hydrogen partial pressure in the reactor in order to hold free carbon formation to a reasonable level. Free carbon formation results in loss of catalyst activity and in catalyst fracture, requiring the replacement of the catalyst inventory after 50 days operation. The operating conditions result in high methane formation, considerably above that predicted by a Schulz-Flory distribution (discussed in Section 4).

3.3 TUBE-WALL REACTOR

The concept of the tube-wall reactor originated at the U.S. Bureau of Mines. The first bench-scale studies were on methanation reactors (16) and the technique was later adapted for Fischer-Tropsch synthesis (1). In 1977 the R. M. Parsons Company published a Fischer-Tropsch Complex Conceptual Design/Economic Analysis (17), in which tube-wall reactors were to be used for the shift conversion, Fischer-Tropsch synthesis, and methanation. This study indicated the use of tube-wall reactors would result in an overall thermal efficiency for the plant of 69.7% and, in general, in a very attractive process.

The tube-wall reactor is illustrated in Figure 1-1. The concept is very simple and involves coating catalyst by a flame-spraying technique onto the surface of heat exchanger tubes. In the flame-spraying technique a high temperature flame is used to melt powdered catalyst onto a metal surface. Designs differ in the placement of catalyst either on the inside or the outside tube surface. In 1971 the C. E. Lummus Company undertook the design of a tube-wall methanator with catalyst applied to the inside of 2-inch diameter tubes (18). Parsons, in their conceptual design, chose to apply the catalyst to external fins.

In the Parsons-type design, the vapor phase reactants and products flow through the shell side of the reactor. Boiling water or oil inside the tubes carries away the heat released by the reaction. "Typical" operating conditions in a tube-wall reactor, as shown in Table 3.1-1, are a catalyst temperature of 580-640°F, pressure of 400 psig, and H_2/CO ratio in combined feed greater than 2.0. Some recycle gas is generally used, although this is not necessary for temperature control.

The major advantages claimed for the tube-wall reactor are excellent temperature control and near-isothermal operation (17). The high rate of heat transfer from the catalyst surface eliminates the possibility of hot spots forming on the catalyst surface. The catalyst surface temperature is very near the coolant temperature and thus very nearly isothermal. It is believed that excellent temperature control will contribute to maintaining catalyst activity.

The main difficulty in applying the tube-wall reactor to Fischer-Tropsch synthesis is getting enough catalyst surface area into the reactor. Fischer-Tropsch catalysts generally show low activity and very little internal surface area; therefore, a large geometric surface area is required. At the same time, this surface area must be achieved within a configuration which allows recoating with new catalyst when the activity of the old catalyst declines.

3.4 SLURRY REACTOR

The concept of the slurry Fischer-Tropsch reactor was originated in 1951 by Koelbel and Ackermann (20). This early laboratory-scale work showed great potential when compared to existing fixed-bed technology and eventually became the performance target for subsequent research. In 1953, as part of a joint venture between Rheinpreussen and Koppers Company, a semiindustrial demonstration plant with a 5 foot diameter by 28 foot tall reactor began operation (7). Dr. H. Koelbel was also involved in this project, and the plant operated successfully until 1955.

During the postwar period other countries also began work on the slurry Fischer-Tropsch reactor. Farley and Ray operated a bench-scale reactor at the British Fuel Research Station in 1952 (21), and in 1964, a pilot plant-scale unit at Warren Spring Laboratory in Stevenage (8). From 1948 to 1953 the U.S. Bureau of Mines investigated the slurry reactor as part of a larger program investigating synthesis gas conversion (22, 23, 24). The last group to become involved was the Japanese (25). The incentive for their work, which was supported by the iron and steel industry, was to utilize the large quantities of CO-rich gas which are by-products of steel production.

In all of these investigations the basic slurry reactor concept has remained unchanged. It is illustrated in Figure 1-1. A synthesis gas feed is sparged into a reactor containing a liquid catalyst slurry. The liquid is largely paraffinic and generally inert to reaction. The reactor diameter is sized for a gas superficial velocity of 0.2 to 0.3 feet per second. This gas rate maintains the catalyst in suspension within the slurry. Since the Fischer-Tropsch reaction is highly exothermic, temperature control is maintained by heat removal through steam cooling coils located within the reactor. The major portion of products is removed overhead as vapor, with heavier products remaining in the slurry. The split between vapor and liquid depends upon the degree of polymerization of the product. If a heavy product is produced, net liquid must be removed through a filtering system in order to maintain a constant fluid level in the reactor. Liquid is added to the reactor if there is a net decrease of liquid through evaporation.

General agreement exists among the investigators on certain advantages claimed for the slurry system. These include:

1. Reactor design is simple.
2. Catalyst (usually between 1 and 40 microns in size) is easily added to or removed from the reactor without shutdown.
3. Temperature control is superior to other reactor systems.
4. Product flexibility and selectivity is superior to other reactor systems.
5. There are no erosion problems.

Koelbel's work (7) includes the following additional claims:

1. Feed gas H_2/CO ratios as low as 0.7 can be used without significant free carbon formation.
2. Single pass $CO + H_2$ conversions as high as 90% are attainable.
3. Gasoline yields in excess of those predicted by a Schulz-Flory distribution are attainable.
4. Methane yields are lower than from other types of reactors.

Although the Japanese work by Sakai and Kunugi (25) reportedly substantiate some of these claims, no other investigators have been successful in duplicating Koelbel's work. In particular, Farley and Ray (8) attempted to operate at Koelbel's operating conditions and found they could only attain 50% conversion. To maintain conversion, temperature increases were required which led to build up of free carbon followed by increased slurry viscosity and eventual gelation of the reactor contents. Schlesinger and coworkers (23, 24) at the Bureau of Mines did not have the gelation problems of Farley and Ray but did show substantially lower conversion (70%) with product yields which closely approximated a Schulz-Flory distribution. Attempts have been made to clarify these discrepancies by suggesting that different catalysts were used (10), and that Farley and Ray were producing a much heavier product which led to the increased viscosity. It is apparent that while the Fischer-Tropsch slurry reactor may offer some significant advantages, it still requires further investigation.

3.5 EBULLATING BED REACTOR

The original oil circulation reactor contained a fixed bed of catalyst. Oil trickling down through the bed removed the heat of reaction, allowing reasonable temperature control. However, agglomeration of the catalyst particles caused a rapid increase in pressure drop across the reactor and continuous operation was not possible (19). In the 1940's the U.S. Bureau of Mines (26) revised the process to incorporate upward-flowing oil at a velocity to expand the catalyst bed by about 30%. This was the jiggling bed, later known as the ebullating bed, reactor.

Operation with an expanded catalyst bed eliminated the pressure drop problem. The new system looked sufficiently promising in bench-scale tests to justify building, in 1949, a 50 BPSD demonstration plant at Louisiana, Missouri (27). The demonstration reactor was 3 feet diameter by 30 feet tall and operated at a temperature of 500 to 524°F, a pressure of 300 to 350 psig, and a syngas H_2/CO ratio of 0.76. Methane yield was only half that of a fixed-bed reactor, and 86% of the hydrocarbon product was in the C_3+ fraction. The plant operated successfully, though only at half capacity, until 1953. At this time, due to the abundance of cheap petroleum, the synthesis of fuels from coal was no longer interesting, and the demonstration unit was shut down.

Bench-scale work on the ebullating bed reactor continued. The fused iron catalysts used at the Louisiana, Missouri facility broke up rapidly due to the constant motion in the reactor. In the search for a physically stable catalyst massive iron catalysts, including steel shot and steel lathe turnings, were tried (28). These catalysts, though better able to withstand the agitation in an ebullating bed reactor, were also less active.

Chem Systems (29) has also done considerable development work on the ebullating bed reactor, but not for Fischer-Tropsch synthesis. They have used ebullating bed reactors on a pilot plant-scale to produce methane and methanol from syngas. They also have a Department of Energy contract to build a liquid-phase reactor to demonstrate methanation.

A survey of the literature reveals that operating advantages similar to the slurry reactor can be claimed for the ebullating bed reactor. These advantages include superior temperature control, superior product flexibility and selectivity, and the use of low H_2/CO syngas. It also shares with the slurry reactor the potential problems of oil degradation and increasing viscosity, leading to reduced conversion. The unique and recurring problem in operating an ebullating bed reactor operation is that of physical stability of the catalyst. For Fischer-Tropsch synthesis, it is not clear that the problem has been solved.

TABLE 3.1-1

	Entrained Bed Reactor	Tube-Wall Reactor	Slurry Reactor	Ebullating Bed Reactor
Pressure, psig	300-400	400	150-175	300-400
Temperature, °F	600-635	580-640	500-540	500-540
GHSV, hr^{-1}	1000	20-1000	200-300	200-300
H_2/CO (fresh feed)	2.4	1.0-2.0	0.6-1.2	0.6-1.2
Recycle/Fresh Feed	2.3	1.5	0	0-1.5
Catalyst Size, microns	40	-	1-40	2000-4000