# SECTION 5 - PHYSICAL COMPARISON OF REACTORS

## 5.1 CRITICAL DESIGN REVIEW

### 5.1.1 Introduction

The physical comparison of the reactor systems consists of a general review of each system and a side-by-side comparison of the four systems on specific common points. In Section 5.1 each system is critically reviewed and unique features are discussed.

Section 5.2 is divided into five parts:

- 5.2.1 Basis of Comparison
- 5.2.2 Product Yield Comparison
- 5.2.3 Size and Cost Comparison
- 5.2.4 Thermal Efficiencies
- 5.2.5 Upstream/Downstream Considerations

Conceptual designs were prepared for each of the four reactor systems, with each system being sized to convert the same quantity of $CO + H_2$. This provides a fair basis for comparison of product yields, investment costs and thermal efficiencies.

### 5.1.2 Entrained Bed Reactor

For the purpose of this reactor comparison, the Pullman Kellogg (4) Synthol reactor has been used as representative of the entrained bed reactor system. The only substantial change made to the flow scheme is to use steam generation for reactor cooling rather than hot oil circulation. This was not done for the reactor modeling work described in Section 4, but was changed for the physical comparison of reactors because it is believed to be a practical change that would result in considerable investment cost savings. This system will be somewhat less flexible with regard to reactor temperature control, because heat removal can not be adjusted by changing the heat exchange fluid circulation rate; however, other variables, such as feed temperature, catalyst circulation rate, and the $H_2$ and CO concentrations in the combined feed gas stream should provide acceptable temperature control. The use of direct steam generation may result in a lower skin temperature in the coolers. Whether this can be used will depend on the product yield structure as discussed below.

The Synthol reactor consists of three reactors in series, with intercoolers between reactors. For the purpose of this study, all of the reactor systems were compared at 400 psia nominal operating pressure, which is about 100 psi higher than that used by Kellogg. Further details of the plant basis are presented in Section 5.2.3. The reactors were sized to give the same superficial velocity as the 300 psig design. The kinetic model indicates this increase in space velocity is justified by the increased reaction rate at higher pressure.

This reactor is the only one of the four reactors under consideration that has had commercial demonstration. (The other commercially proven system, the tubular packed bed Arge reactor, was not included in this study.) The Synthol plant designed by Kellogg has been operated by Sasol since 1955. From a design standpoint, the principal advantages of this reactor are:

- It is a commercially proven design
- It allows very high capacity from a single reactor train. (For the 28.05 MM SCFH of CO + $H_2$ conversion which has been set as the basis for this comparison, only two reactors are required.)

The configuration of this reactor does restrict the choice of operating conditions and this results in several disadvantages. It is a vapor phase reactor, and careful attention must be paid to the hydrocarbon dew point of the vapor flowing through the reactor. The vapor must not come into contact with surfaces below its dew point. The coldest surface in the reactor is the heat exchange surface in the heat removal sections. With direct generation of 600 psig steam, the tube skin temperature will be about 500°F. If oil circulation is used, the lowest skin temperature will depend on the oil inlet temperature, but with the 472°F inlet temperature suggested by Kellogg, the skin temperature will be very similar to the steam case at around 510°F. If the yield structure at the outlet of the reactor given by Kellogg is used as a basis for calculation, the dew point of the outlet vapor from the reactor is between 565 and 580°F, depending on the operating pressure selected. The dew point of the gas leaving the last heat exchanger will be lower, as about 15% of the overall conversion takes place in the last reactor. However, on the basis of this yield structure, it would appear that this design would result in liquid condensation on the cooling tubes, which would create operating problems for a fluidized catalyst system. The calculation of dew point is, however, very sensitive to the concentration of high molecular weight components. As discussed in section 5.2.2, the Kellogg yield structure does not fall on a Schulz-Flory distribution, and a yield structure was estimated for a product with $C_5$+ components falling on a Schulz-Flory distribution with a degree of polymerization corresponding to 3.3 (see Table 5.2-3). If the dew point of the reactor effluent is calculated with this net product composition, the dew point of the product is reduced to the range of 445 to 455°F, depending on whether the operation is at the 300 psig nominal pressure used by Kellogg, or the 400 psia used for this study. The dew point of this product is safely below the skin temperature of the heat exchanger tubes.

The yield structure published by Sasol also shows a larger amount of $C_{26}$+ than would correspond to a Schulz-Flory distribution. Kellogg has confirmed that this is the yield structure that they expect to achieve, and indicates that the departure from the Schulz-Flory distribution is due to a number of factors including "the nature of the catalyst" and "polymerization of light components in the recycle". Kellogg also offers the explanation that any liquid film produced at the heat exchanger surface will be removed by the very large flow of catalyst, and that this deposition of product on the catalyst contributes to the need for catalyst replacement.

Any vapor phase fluidized reactor must, therefore, be operated to ensure that no operating problems result from liquid deposition on the heat removal surface. This will impose many restrictions on the operating conditions chosen and the yield structure that can be tolerated. For example, the degree of polymerization of the product must be lower than would be required for the other systems under consideration in this study. The liquid phase systems can tolerate cooling surfaces below the product dew point, and the tube-wall design selected for this study has a much higher tube-wall temperature (640°F nominal) because it is virtually equal to the vapor temperature. The actual degree of polymerization that can be tolerated by the entrained bed system is unlikely to be any higher than indicated by the yield structure published by Kellogg and Sasol, falling in the range of 3 to 3.5, which is significantly below that required to give the maximum gasoline yield.

While inherently lower gasoline yield is in itself a significant disadvantage of this reactor for the U.S. market, the operating conditions used to hold down the degree of polymerization cause further problems. The degree of polymerization is held down by two principal factors, high temperature and low CO concentration. High temperature causes a very large and undesirable increase in methane production, by a mechanism that appears to be related to free carbon formation at the selected high operating temperature [Dry (6)]. The free carbon also causes rapid catalyst deterioration. Holding down the free carbon formation requires high hydrogen partial pressure, and the combination of high hydrogen partial pressure and low CO concentration results in the process requiring a feed gas with a high $H_2/CO$ ratio.

Dry (15) has shown that high $CO_2$ partial pressure and high catalyst basicity will hold down methane formation to some degree. Unfortunately, the presence of significant quantities of $CO_2$ shuts off the shift reaction, requiring all of the hydrogen to be produced in external shift, and high basicity of the catalyst will tend to increase the degree of polymerization.

The required hydrogen partial pressure is obtained by a combination of syngas feed with a high $H_2/CO$ ratio, and a high recycle gas to fresh feed ratio, requiring a low conversion of $CO + H_2$ per pass. The high recycle gas ratio is beneficial in reducing the temperature rise across the reactor, as the recycle gas is a significant heat sink. Operation with a reduced recycle gas ratio would, therefore, require more, smaller reactors in series. A reduced recycle gas ratio would also tend to increase the dew point temperature of the reactor effluent and thus reduce the tolerable degree of polymerization for the process. Fluidization characteristics of the entrained bed reactor are also very sensitive to changes in recycle gas ratio. A reduction in recycle gas ratio causes a lower velocity in the reactor that results in a higher catalyst concentration. A relatively small reduction in recycle gas rate can cause a significant change across a reactor because by simultaneously increasing CO and catalyst concentration, and reducing the amount of heat sink, it allows a larger temperature rise. This is a very complex system and it is difficult to take into account all of these simultaneous changes when searching for operating conditions that could give an improved yield structure. The kinetic model used in this study could be used for this purpose, but this was not included within the scope of the present study.

If we define the following as criteria for an idealized Fischer-Tropsch reactor:

- It should operate with a degree of polymerization of about 4, in order to maximize the gasoline yield
- It should operate at a low enough temperature to eliminate free carbon formation and give low methane yield
- It should preferably operate on low $H_2/CO$ ratio syngas feed
- It should have a high conversion per pass,

it is apparent that the present design proposed for the entrained bed Fischer-Tropsch reactor cannot satisfy any of these criteria.

If the dew point problem can be eliminated, it seems likely that many of the other faults of this system could be solved. The temperature could be lowered, high conversion could be achieved by increasing the CO partial pressure, and the catalyst basicity could be adjusted to give the desired degree of polymerization. The use of multifunctional catalysts (36, 60) could provide the answer to this problem, as it would cut off the high boiling point "tail" in the Fischer-Tropsch product. However, such a catalyst is not presently available. There is also some reason to doubt whether such a catalyst could be used in the entrained bed system. This system has high velocity transport heat exchangers. The present iron catalyst is not very erosive and this probably accounts for the successful operation of this type of heat exchanger. A supported iron multifunctional catalyst would probably be much more erosive and dilute phase heat exchangers are unlikely to be practical. A dense bed fluidized reactor with cooling coils would almost certainly be a preferred system for a vapor phase reactor utilizing a multifunctional catalyst.

### 5.1.3 Tube-Wall Reactor

The conceptual design prepared by the R. M. Parsons Company (17) for a Fischer-Tropsch complex was used as a starting point for the tube-wall reactor design used in this comparison. The Parsons yield structure and reactor design were modified to be consistent with information from the kinetic model, and also to reflect changes considered necessary from an operations standpoint.

The Parsons tube-wall reactor design incorporates flame-sprayed iron catalyst on external extended-surface heat exchanger tubes. The reactor was designed for operation at 606°F and 400 psig, with a recycle ratio of 1.5 and a space velocity "J" factor of 10. Based on these conditions, Parsons predicted a very attractive process. However the predicted yield structure was based on an experiment (54) using potassium-promoted steel lathe turnings catalyst at a gas recycle ratio of 27 and a J factor of 1.5. It is doubtful that a flame-sprayed catalyst could be produced with the activity of magnetite (Parsons activity basis) and at the same time with the yield structure of the potassium-promoted lathe turnings. In addition, a critical review of the reactor design reveals other shortcomings.

The chief advantages claimed for the tube-wall reactor are isothermal operation, high thermal efficiency, and efficient utilization of a small amount of catalyst. The kinetic model for the tube-wall reactor supports the claim of good temperature control and isothermal operation, predicting catalyst temperatures never exceeding the coolant temperature by more than two degrees. Removal of the heat of reaction by steam generation in the reactor does give a good thermal efficiency for the reactor. This can be done in all the reactors included in this study, so the thermal efficiency is mainly dependent on the recycle-to-fresh feed ratio, as discussed elsewhere in this report. Catalyst activity is related to surface area, and compared to pelleted catalyst the flame-sprayed catalyst does have more surface area per pound; therefore, less is required. Compared to the finely divided catalyst used in the slurry and entrained bed reactors, however, our computer modeling work shows no advantage in activity per pound of catalyst.

When the kinetic model was run at conditions simulating those used for the Parsons reactor design, but with a catalyst considered to be more representative, it showed only 35% CO conversion compared to the 89% used in their basis. In order to get predicted CO conversion back up to 90%, it was necessary to raise reactor temperature to 640°F and almost double the catalyst surface area. With the excellent temperature control possible in the tube-wall reactor, recycle gas is not needed for temperature control. By operating without recycle the catalyst requirement is reduced. The present reactor is, therefore, intended to operate at 640°F at 400 psia, with no recycle gas and a J factor of 9. However, there are some doubts about the ability to operate for an extended time at this high temperature due to free carbon formation. Reducing the temperature would, of course, require more catalyst. The reactor could also require a higher $H_2/CO$ ratio for extended operation.

While the Parsons reactor utilized catalyst on external extended-surface heat exchanger tubes, the reactor used for this comparison has the flame-sprayed catalyst on the inside of the heat exchanger tubes. This is done in order to make in-situ catalyst replacement feasible. In-situ flame-spraying was demonstrated in the tube-wall reactor process development unit (16). Circulation of coolant during the flame-spraying prevented warping of the reactor. For the case of catalyst on external fins, catalyst replacement would require complete dismantling of the reactor. This would be prohibitively expensive and time-consuming. Applying the catalyst on the inside of 2-inch tubes (the minimum diameter for internal flame-spraying) does result in less surface area per reactor volume. The present conceptual design requires five to six times as many reactors as does the Parsons design, for a given amount of catalyst, or 42 reactors for 28.05 MM SCFH of CO + $H_2$ conversion.

For the purpose of this study, the yield structure was based on Hot-Gas-Recycle Experiment 26C (54), as was the yield structure in the Parsons conceptual design. As discussed in a later section of this report, this yield structure, modified to reflect higher methane yield due to the higher operating temperature, appears to be reasonable for the present reactor design. The assumption implicit in this choice of data base is the ability to flame-spray a promoted taconite catalyst and retain the properties associated with the lathe turnings catalyst used in Experiment 26C. To date, this ability has not been proven. Typical tube-wall reactor experiments (61) have shown a very low degree of polymerization, yielding only 10 to 15 wt-% gasoline compared to the 48 wt-% theoretical maximum. This yield structure is not attractive if liquid fuels are the objective.

As one might expect from the relative reactor size and the number required, the tube-wall reactor system is quite expensive, costing twice as much as the entrained bed reactor system. In addition, the flame-sprayed catalyst, due to the method of application, is much more expensive than the forms used in the other reactors. The development of a different catalyst, perhaps one which could be applied as a chemical wash on the inside of small-diameter tubes, could reduce the cost to an economically attractive range. However, for the tube-wall reactor as presently defined, the high cost, the lack of a proven flame-sprayed catalyst, and doubts about free carbon formation, all lead to the conclusion that the tube-wall reactor is not an attractive choice for the Fischer-Tropsch reaction.

### 5.1.4 Slurry Reactor

The slurry reactor described by Koelbel (2) was used as a basis for this reactor comparison. Since 400 psia operating pressure was selected for this study as compared to the 174 psia used by Koelbel, it was first necessary to check what effect this pressure change would have on space velocity requirements. The kinetic model described in Section 4 was used for this purpose. The model predicted that if the same linear velocity and catalyst concentration are used at 400 psia as at 174 psia, the conversion per pass will increase. Until further work has been done in fitting the kinetic model to slurry reactor data taken over a wide range of operating pressures, it is not believed justified to use the higher conversion predicted as a basis for this comparison. Therefore, it is assumed that the conversion will remain unchanged if the pressure is increased, providing the superficial gas velocity and gas feed composition are the same. Even with this assumption, the capacity of a given reactor is virtually proportional to the operating pressure and a given vessel can process more than twice the moles of syngas at 400 psia as at 174 psia. The kinetic model also indicates that if the same catalyst is used, the degree of polymerization will increase, but that this can be restored to the optimum degree of polymerization for gasoline by adjusting the hydrogenation rate constant. As this rate constant appears to be adjustable by changing the potassium concentration in the catalyst, it has been assumed that a suitable catalyst can be produced for the 400 psia operation.

A reactor superficial feed gas velocity of 0.3 ft/sec, and a reactor height of 27 feet (almost identical to Koelbel's demonstration unit) was selected for reactor sizing. With this superficial gas velocity, this type of reactor will require many reactors in parallel. Fourteen feet diameter was selected as the maximum diameter that will normally permit shop fabrication. With this diameter, 18 reactors in parallel are required to convert the 28.05 MM SCFH of syngas used as a basis for this study. The expanded liquid level was set at 21 feet, with 6 feet allowed for vapor disengagement. The gas hold up in the expanded liquid phase was taken as 30%, and the catalyst concentration in the liquid set at 10 wt-% of 30 μ catalyst.

The only internals included in the reactor design are a gas distributor and steam coils for the generation of 600 psig steam. No vertical baffles were included. There has been much discussion in the literature (2) on the possible scale-up problems of this type of reactor, but there is no documentation offered for the suggested channeling of bubbles. Scaling up from the 5 feet diameter used successfully in Koelbel's demonstration plant to the 14 feet diameter suggested in this study is not a large step. The cooling coils do provide vertical surfaces which reduce the hydraulic diameter of the system. Large diameter reactors are commonly used for bubbling slurry reactors without the need for internals to obtain good gas distribution (62).

With a gas velocity of 0.3 ft/sec, the degree of back-mixing of the liquid phase will be very high, and complete back-mixing of the liquid was assumed in the kinetic studies. With low viscosity liquids, there will be little gas back-mixing, and plug flow was, therefore, assumed in the kinetic studies. The superficial gas velocity is, however, in a region where some of the gas may travel through the reactor in slugs and, if this is the case, there will be some departure from plug flow; but more importantly, gas by-passing could result and conversion may suffer. The kinetic study did show that staging the slurry system will provide a significant increase in conversion from the same reactor volume. The use of baffles to reduce back-mixing and get some staging in the parallel reactors may be justified, but the utility of baffles to provide staging would need to be demonstrated. It is more likely that slurry reactors will be arranged with two or three reactors in series. The gas velocity in the first reactor will be higher, and the presence of some gas slugging will be tolerated. Subsequent reactors can be operated in the bubbling region and conversion could then be so high that recovery and recycling of residual CO and $H_2$, would not be justified. The potential of obtaining a conversion over 95% in one pass offers a considerable simplification of the Fischer-Tropsch process.

No means for temperature control beyond adjustment of steam pressure was provided in the reactor operated at Koppers. Most operators would probably prefer to keep the steam pressure constant, and an external, adjustable circulating trim cooler for temperature control of the reactor is included in the present design. This is a much smaller system than the very large circulation required for the ebullating bed system, and causes an increase in reactor cost of about 3%.

As the reactors are intended to maximize gasoline yield, there will be negligible production of liquid product at reactor conditions and virtually all of the product will leave in the vapor phase. No liquid product filtering system has been included in the design, although a small system will be required for removal of reactor liquid for the maintenance of the quality of the catalyst and the liquid phase.

The maintenance of the quality of the liquid phase appears to be an important factor in obtaining successful operation of this type of reactor. The liquid must have a low viscosity at reactor conditions if good hydrodynamic characteristics are to be achieved. The oil should also have good stability, and some further experimentation to determine the optimum material is probably justified.

The choice of the right catalyst and operating conditions is essential to the maintenance of oil quality. The operating temperature should be low enough that the formation of free carbon is not encountered. The combination of operating conditions and catalyst formulation should also ensure that the product is removed in the vapor phase in order to minimize contamination of the reactor oil with high molecular weight olefins which have poor stability. The correct selection of the oil, catalyst and operating conditions, combined with an appropriate oil withdrawal and replacement rate should ensure a high on-stream efficiency.

The slurry reactor appears to be the most promising for the Fischer-Tropsch reaction. It can operate on syngas with a low $H_2/CO$ ratio and provide high conversion per pass. Condensation of the high molecular weight "tail" of the product on cooling surfaces can be tolerated in this liquid phase system, which permits selection of the optimum degree of polymerization to fit the product needs. The use of high CO concentrations permits operation at low temperature while maintaining good conversion levels. Low temperature should avoid excessive methane production and free carbon formation. Operation in an essentially once-through mode is also a possibility that could greatly simplify the overall process.

The slurry reactor has never been operated for Fischer-Tropsch synthesis on a commercial scale. It has been operated up to 5 feet diameter, and the scale-up from there to the 14 feet diameter suggested for commercial production should not be difficult. The system will require a much lower investment if it is operated at 400 psia, but this will require some experimental work to demonstrate that a suitable catalyst can be developed for this operating pressure, and also to determine what operating temperature can be used at this operating pressure to avoid free carbon formation and obtain a suitable catalyst life.

### 5.1.5 Ebullating Bed Reactor

Operating conditions for the ebullating bed reactor were chosen primarily on the basis of work at the U.S. Bureau of Mines (26, 28). Chem Systems, Inc. was subcontracted under Task Order No. 15 to prepare an ebullating bed reactor conceptual design, using the specified operating conditions as a design basis. Chem Systems was chosen to do the design work because of their experience in the design and operation of ebullating bed reactors for production of methane and methanol (3, 29).

The ebullating bed reactor is a three-phase reactor in which the heat of reaction is removed by cooling oil circulated through an external heat exchanger, then returned to the reactor. Liquid and gas rise cocurrently through the reactor, at velocities sufficient to expand the bed of granular catalyst without carrying it out of the reactor. Liquid and vapor leave the reactor at the top and are separated in a disengaging vessel. Means for adding or withdrawing oil from the reactor can be incorporated in the liquid circulation loop.

The liquid phase provides excellent temperature control and eliminates concern over the formation of local hot spots in the reactor. The good temperature control and low temperature operation allow the use of a CO-rich syngas without excessive carbon formation. In turn, a high conversion per pass is made possible even at low temperature, by the use of CO-rich syngas. In addition, methane production is lower than in gas-phase reactors, as observed in work carried out at the Bureau of Mines (27).

The circulating oil method of heat removal is advantageous in several respects. In addition to the good temperature control discussed above, the method provides ease in adjustment of the amount of heat removal by varying the liquid circulation rate. While the range over which the liquid velocity can be varied is restricted by catalyst fluidization requirements, the maximum allowable velocity being approximately twice the minimum will allow good temperature control over a wide range of feed rates. By expanding the catalyst bed and providing some scrubbing action, the circulating oil prevents agglomeration of the catalyst particles. The expanded bed also makes more efficient use of catalyst than does a packed bed. (26)

As with the slurry reactor, stability of the cooling oil is critical to the operation of the ebullating bed reactor. An oil that becomes very viscous due to excessive free carbon or high molecular weight wax content does not allow adequate transport of gas-phase reactants and products to and from the liquid phase. The paraffins produced in the Fischer-Tropsch reactor have been used for this purpose and performed satisfactorily when used with the proper catalyst and in the correct temperature range. As with the slurry reactor, the selection and maintenance of the most suitable fluid will be an important part of the reactor development.

The ebullating bed reactor is very simple in design, containing no internals except for the gas distributor. This type of reactor does not present a scale-up problem as the flow behavior is expected to be the same in a 14-foot diameter commercial reactor as in a small pilot-scale reactor. The amount of oil circulation required to limit temperature rise in the reactor to about 20°F is very large, and the oil circulation pumps increase the cost of the reactors by almost 25% over that of the slurry system. Several reactors in parallel will be required for a large scale plant, and for the 28.05 MM SCFH of syngas conversion used as a basis in this study, twenty 14-foot diameter reactors in parallel would be required.

The liquid phase behavior in an ebullating bed reactor is nearer to plug flow than in a slurry reactor. As discussed elsewhere in this report, the kinetic model predicts that staging a three-phase reactor gives higher conversion for the same reactor volume and catalyst activity than a totally back-mixed system. This is not a great advantage over the slurry reactor, as the slurry reactor could be designed with two or three reactors in series. With either liquid system, one-pass conversion over 95% should be possible.

The largest obstacle to commercial development of the ebullating bed reactor is one of catalyst development. A granular catalyst (this study assumes 1/16-inch diameter) is required to allow liquid circulation without catalyst carryover, as well as the other operational advantages listed in preceding paragraphs. The only Fischer-Tropsch catalysts to have demonstrated the ability to withstand the constant agitation in an ebullating bed reactor over a reasonable period of operation are the massive iron catalysts developed by the U.S. Bureau of Mines. (28) These catalysts have no internal surface area and are, therefore, much less active than a typical ammonia synthesis catalyst. The use of these less active catalysts would require more catalyst and more reactors, and the system would be unattractive economically.

In order to keep the reactor size reasonable, use of the more active fused-iron catalysts has been assumed. In the Bureau of Mines experience (58), the fused-iron catalysts disintegrated within two to three months. Such frequent catalyst replacement could be very expensive. In addition, in the Bureau of Mines reactor, the catalyst fines settled out in the heat exchanger (27) and no doubt would eventually have caused a plant shutdown.

If a catalyst with high activity and good physical strength could be developed, this type of reactor could be considered for the Fischer-Tropsch reaction. The potential advantages over the slurry reactor are:

- Higher conversion for a given catalyst activity
- If high middle distillate yield is required, it would be easier to produce and separate a liquid product.

These are not very significant advantages. The second does not apply in a maximum gasoline case because operating conditions can be selected that allow the product to be removed as vapor. The first may not be significant because arranging slurry reactors in series would give the same result.

The lack of physical stability of the catalyst may be the result of changes in catalyst composition during operation, causing the particles to fracture. The use of a support that is stable in this reaction environment may be required to overcome this problem. A supported catalyst is likely to be expensive compared to the finely divided iron used in the slurry system. This combined with the expensive oil circulation system leads to the conclusion that the ebullating bed reactor is unlikely to be used for the Fischer-Tropsch reaction.

## 5.2. COMPARISON OF SYSTEMS

### 5.2.1 Basis of Comparison

### 5.2.1.1 General

In order to set a common basis for comparison of product yields, investment costs and thermal efficiencies, conceptual designs were prepared for criticial portions of each of the reactor systems. The basis used for the designs was conversion of 73,900 pound-moles per hour (28.05 MM SCFH) of CO + $H_2$. This quantity corresponds to approximately 25,000 barrels per day of hydrocarbon products, and is considered to be a typical size for an indirect liquefaction plant. The moles of CO + $H_2$ converted is thought to be a fair basis of comparison because it eliminates the effect of the water-gas shift reaction. In the shift reaction, one mole of CO reacts with water to form one mole of $H_2$, and the total moles of CO + $H_2$ remains constant.

The synthesis gases shown in Table 5.2-1 indicate the $H_2$/CO ratio considered optimum for each reactor type. As the compositions are based on work reported in the literature (4, 2, 54), they also reflect variations in minor components due to the different syngas sources. The quantities shown are those required to give the design conversion of CO + $H_2$, on a once-through basis for the tube-wall and slurry reactors, and in a recycle operation in the entrained bed reactor. In practice the CO and $H_2$ in the reactor effluent would presumably be recovered and recycled, resulting in conversions similar to that shown for the entrained bed reactor. (See Table 5.2-6). The effect of using some recycle gas is to reduce the quantity of fresh feed required, and to change the $H_2$/CO ratio in the feed gas. The resulting syngases and combined feeds are given in Table 5.2-2.

The operating pressure was set at 400 psia for all four reactor systems. This is a pressure at which syngas can be supplied from a modern gasifier without requiring additional compression. Other operating conditions were set according to the requirements of the individual systems, and are discussed separately.

A conceptual design and cost estimate were prepared for the ebullating bed reactor; however, there is no indication in the literature (27, 28) of a significant difference bewteen the ebullating bed and slurry reactors in fresh feed requirements or product yields. Both reactors are three-phase systems and as such are expected to produce similar yields under similar operating condtiions. In addition, thermal efficiencies will be similar. Therefore, when discussing syngas requirements, product yields and thermal efficiencies, references to the slurry reactor apply equally to the ebullating bed reactor, and the ebullating bed reactor is not discussed separately.

### 5.2.1.2 Entrained Bed Reactor

The Kellogg Synthol Feasibility Study (4) was the primary source used in the entrained bed reactor design. Where information given by Kellogg was insufficient for design purposes, it was supplemented by Sasol publications (9, 12, 63) and by standard engineering design practice.

With few modifications, the Kellogg design was scaled to the quantity of feed set for the conceptual design basis. The fresh feed shown in Table 5.2-1 is of a composition indicated by Kellogg, with the $CO_2$ content reduced to a level intermediate to that claimed by Kellogg and by Sasol (63). With the same exception, the product distribution given in Table 5.2-3 parallels that claimed by Kellogg. The ratio of recycle gas to fresh feed is the same as indicated in Kellogg. Although information published by Sasol is less specific, the ranges of feed composition, product distribution and recycle ratio they report are in general agreement with those used for this study.

The design pressure of 400 psia is higher than that used in the Kellogg design. In order to allow for the increased conversion attainable at higher pressure, gas hourly space velocity was increased in the same ratio as the pressure. The reactor diameter was set to give a superficial gas velocity of 8 feet per second, which is apparently in the range used by Sasol (12, 37). The operating tempearture of 600 to 635°F is the same as shown in the Kellogg design. It was decided, however, to use steam generation in the reactor cooling coils for heat removal instead of circulating oil. This decreases the length of the cooling section somewhat, and eliminates the need for a second heat transfer step from the oil to steam.

Very little information is available on the design used for the catalyst separator, quench tower and heat exchangers. These items were sized according to standard practices, and are included in the equipment list given in Appendix E.

### 5.2.1.3 Tube-Wall Reactor

In designing the tube-wall reactor consideration was given to the conceptual design prepared by R. M. Parsons (17) and data from the U.S. Bureau of Mines (1, 54) were also used. Due to apparent discrepancies (see Section 4.3.2) in the Parsons design, the reactor model developed in the kinetic modeling portion of this study was used to set the temperature and space velocity "J" factor to get the specified conversion of $CO + H_2$.

In order to predict a reasonable gasoline yield, it was necessary to run the reactor model with catalyst characteristics attributed to a hypothetical potassium-promoted flame-sprayed taconite catalyst. This catalyst would have the activity of flame-sprayed taconite, and a yield structure associated with potassium-promoted catalyst made from steel lathe turnings. With this catalyst, the model predicts that at a temperature of 640°F, pressure of 400 psia, and J factor of 9, a once-through $CO + H_2$ conversion of 90% will be achieved. The predicted yield structure is similar to that observed in Hot-Gas-Recycle Experiment 26C (54) and also claimed by Parsons (17).

The syngas shown in Table 5.2-1 for the tube-wall reactor has a composition typical of that used in tube-wall reactor experiments (28); however, it is not known with any degree of certainty what $H_2/CO$ ratio would be required to prevent free carbon formation at the temperature selected for this design. Operation with minimal recycle gas was selected because it decreases the size of reactor required.

The heat removal scheme uses boiling oil in the reactor instead of steam because, in the temperature range required for this operation, oil temperature is more easily controlled by pressure changes than is steam temperature.

The catalyst is applied to the inside of 2-inch diameter tubes. This results in a larger reactor section than shown in the Parsons design, where the catalyst was applied to external extended surfaces. The reason for this significant departure from previous practice is discussed in Section 5.1.3. The reactor sizes and other equipment details are listed in Appendix E.

### 5.2.1.4 Slurry Reactor

The conceptual design for the slurry reactor is based entirely on information published by Koelbel (2) on the Koppers-Rheinpreussen demonstration unit. The syngas shown in Table 5.2-1 has an average composition used in the demonstration unit. The product yield structure shown in Table 5.2-6 is that claimed by Koelbel. The demonstration unit was generally operated without recycle gas, and the conceptual design is also based on once-through operation. The one significant modification to the demonstration plant design consists in setting operating pressure at 400 psia instead of the 174 psia used in the demonstration unit. The operating temperature is also slightly higher at 527°F instead of 514°F. The effect of temperature and pressure on reaction rate is compensated by increased space velocity: the space velocity in the conceptual design is 772 $hr^{-1}$ while that used in the demonstration unit was 270 $hr^{-1}$. The catalyst concentration is that which Koelbel claims is optimum -- 10 wt-%. The total reactor cross-sectional area is set to give a superficial gas velocity of 0.3 feet per second, which is the same as typically run in the demonstration unit.

When the computer model of the slurry reactor was run at the operating conditions of the conceptual design, it predicted CO conversion of over 93%, and a high degree of polymerization. It is assumed the degree of polymerization could be corrected to give a maximum yield of gasoline, by using a catalyst with lower potassium content.

The surface area required for the cooling coils located in the reactor was calculated on the basis of the heat transfer coefficient claimed by Koelbel (2). Very little additional equipment is required for the reactor section of a slurry reactor Fischer-Tropsch plant. The complete equipment list is in Appendix E.

### 5.2.1.5 Ebullating Bed Reactor

As stated previously, the literature (26, 27, 28) indicates the ebullating bed and slurry reactors are very similar in terms of general operating conditions and yield patterns; therefore, the synthesis gas composition, average temperature and pressure for the ebullating bed reactor conceptual design are the same as those set for the slurry reactor. The yield structure is also expected to be similar.

The most significant difference between the two three-phase systems is in the size of the catalyst particles used. The slurry reactor uses a very finely divided catalyst, while the ebullating bed catalyst is large enough to remain in the reactor and not be carried overhead by the circulating oil. For the conceptual design, the catalyst diameter was set at 1/16 inch, typical of that used in U.S. Bureau of Mines work (26). The difference in size affects the activity of the catalyst, which in turn affects the amount required and the space velocity.

Based on their experience in the design and operation of ebullating bed reactors (3, 29), Chem Systems was requested to prepare a conceptual design for an ebullating bed Fischer-Tropsch reactor. The operating conditions specified for the design were 500°F, 315 psia, and fresh feed space velocity of 300 $hr^{-1}$, based on settled volume of catalyst. Two feed gas compositions were specified: one with a $H_2$:CO ratio of 2.0 and a second with $H_2$:CO ratio of 0.64. Their report is included as Appendix F.

As more information became available through more thorough literature review, new design specifications were set, and a new conceptual design was prepared based on information from Chem Systems. The final design specifications are based on U.S. Bureau of Mines oil-recycle Experiment

26A (26). In this experiment 90% conversion of CO + $H_2$ was achieved at a space velocity of 600 $hr^{-1}$, temperature of 492°F, and pressure of 415 psia. Syngas with 0.7 $H_2$:CO ratio was used and the recycle-to-fresh feed ratio was 1. A fused iron catalyst was used and over 2 months operation was achieved. For the conceptual design, the temperature was increased to 527°F, and space velocity (based on settled catalyst volume) was increased to 750 $hr^{-1}$. The resulting reactor and other equipment sizes are discussed in Section 5.2.3.5 and listed in Appendix E.

## 5.2.2 Product Yield Comparison

### 5.2.2.1 Introduction

Product yield structures for the entrained bed, tube-wall, slurry and ebullating bed reactor systems are given in this section along with a discussion of how each of the yield structures was determined.

In order to obtain as realistic a yield structure as possible for each of the systems, experimental data were used. The kinetic models were used as a guideline for determining the degree of shift activity and for making adjustments due to changes in operating conditions. The number of moles of $H_2$ + CO converted was held constant for all of the systems. The figures presented are net yields from the reactors based on a recycle operation of 2.3:1 for the entrained bed system, and once-through yields for the tube-wall and slurry systems. Moles of $H_2$ + CO converted is considered to be the best basis of comparison, because it eliminates the effect of internal versus external shift by giving yields per mole of syngas converted.

Synthesis gas feeds are shown in Table 5.2-1. Their compositions are based on those given in the literature pertaining to each particular reactor type (1, 2, 4). The feed shown for the slurry reactor is also applicable to an ebullating bed reactor. While initial design work for the tube-wall and liquid-phase reactors was based on once-through operation, it is presumed that the hydrogen and carbon monoxide in the effluent streams will in all cases be recovered and recycled, resulting in similar overall conversions. Syngas feeds, modified to reflect the effect of recycle operation in the tube-wall and slurry reactors, are shown in Table 5.2-2. The feed composition for the entrained bed reactor does not change and is shown only for comparison.

### 5.2.2.2 Entrained Bed Reactor

The product yield structure for the entrained bed reactor is shown in Table 5.2-3. The yield structure is based on data from Kellogg (4). The yield parallels that given in the Kellogg study with adjustments for a different $CO_2$ composition in the feed. The concentration of $CO_2$ in the synthesis gas was set at 4.0 mol-% which is intermediate to that used in the Kellogg study and concentrations reported by Sasol (63). Product properties were based on the hydrocarbon types given in the Kellogg study. For calculation purposes, the acid component was considered to be a mixture of acetic and propionic acid, and the non-acid chemical component was considered to be a mixture of ethanol and propanol, as reported by Sasol (11).

$C_8$ and heavier mixtures were broken down into individual alkanes and alkenes which were then regrouped to give the gasoline, diesel and heavy cuts as shown in the product yield in Table 5.2-3. The ratio of components within each cut was selected in such a way that the molecular weight of each cut was maintained after splitting into its individual components. Once the relative amounts of alkanes and alkenes were set, the product distribution was calculated so that gasoline contained $C_5$ to $C_{11}$, diesel $C_{12}$ to $C_{25}$, and heavies $C_{26}$ to $C_{40}$.

If the product yield is plotted, it shows that there are more high molecular weight materials (i.e., above $C_{26}$) than would be present if the $C_5$+ yield structure followed a Schulz-Flory distribution. This departure from Schulz-Flory not only increases the yield of heavy product but also increases the hydrocarbon dew point of the reactor effluent (see discussion in Section 5.1.2). An estimate was, therefore, made of what the yield structure would be if all of the $C_5$+ material fell on a Schulz-Flory line, with an overall degree of polymerization of 3.3 and an olefin-to-paraffin ratio of 2. This is shown as the modified yield structure in

Table 5.2-3. The degree of polymerization of 3.3 was determined by reference to Figure 4.3-3, using the method described in Section 4.3.1.2 of this report. The quantities of $H_2$, CO, $CO_2$ and $H_2O$ in this product structure were calculated by making an overall material balance and holding the molar ratio of $CO_2$ and $H_2$ to CO and $H_2O$ in the reactor effluent constant.

A product yield structure reported by Sasol (12) is also shown in Table 5.2-3, for comparison with the others.

#### 5.2.2.3 Tube-Wall Reactor

The basis for the yield structure from the tube-wall reactor is U.S. Bureau of Mines Experiment 26C (54). This yield structure was also the basis for the yield shown in the R. M. Parsons study, "Fischer-Tropsch Complex Conceptual Design/Economic Analysis" (17) and is shown in Table 5.2-4. Some modifications were made to this data in order to make it consistent with the particular catalyst and operating conditions selected for this reactor.

Experiment 26C was a Hot-Gas-Recycle experiment using potassium-promoted lathe turning catalyst operating at 586°F and a J factor of 1.5. The tube-wall reactor design uses a potassium-promoted taconite catalyst on the inside of 2-inch diameter tubes, having a J factor of 9, operating at 640°F, once-through mode of operation. When these conditions were used in the kinetic model, it predicted a degree of polymerization of 4.3 which is the same as Experiment 26C. This suggests that the yield structure for Experiment 26C is a reasonable estimate for the tube-wall reactor yield at 640°F.

One difference that can be expected and which the kinetic model does not account for is methane formation via the free carbon mechanism discussed previously. It is necessary to distinguish between the increase in methane due to the main Fischer-Tropsch mechanism and that due to the free carbon mechanism. When the kinetic model was run at 590 and 640°F, keeping the reactor configuration constant, the $C_1$ content, expressed as mol-%

of the hydrocarbon product, increased by 4.5%. However, when the yields from Experiment 26C at 586°F and 26H at 640°F are compared, the methane yield has increased by 5.9 mol-%. The difference of 1.4 percentage points was attributed to the free carbon mechanism, and the mole fraction of methane estimated for the tube-wall reactor product was increased by this amount. The quantities of $H_2$, CO, $CO_2$ and $H_2O$ in the product were determined from the tail gas analysis and adjusted as necessary to maintain an overall material balance. To make this adjustment, the molar ratio of $CO_2$ + $H_2$ to CO + $H_2O$ was kept equal to that shown by the kinetic model for the same operating conditions. The resulting product is shown as the modified yield structure in Table 5.2-4.

The syngas feed for the tube-wall reactor shown in Table 5.2-1 does not include nitrogen. This is because the experimental syngas composition did not contain $N_2$, and this was carried through the design. The effect of including $N_2$ in the feed would be to increase the size of reactors required. The modified yield structure for the tube-wall reactor is used for the yield comparison in Table 5.2-6 because it is believed to be more realistic.

#### 5.2.2.4 Slurry Reactor

The slurry reactor yield structure used for this study is based on data from Koelbel and Ralek (2). The hydrocarbon yield they report is shown in Table 5.2-5, scaled to a quantity consistent with the design basis of 28.05 MM SCFH CO + $H_2$ converted. For comparison with yields from the other reactors, the $C_5$+ material was broken into the individual components and then regrouped into the standard gasoline, diesel and heavy cuts shown. The $H_2$, CO, $CO_2$ and $H_2O$ in the reactor effluent were determined by making an overall material balance on the reactor, using the feed shown in Table 5.2-1. This syngas feed composition represents an average of the range of compositions reported by Koelbel (2). The kinetic model was used to determine the correct ratio of $CO_2$ + $H_2$ to CO + $H_2O$ in the reactor effluent at the operating conditions used in this study.

As the conceptual reactor operating pressure is 400 psia and the demonstration unit was operated at 174 psia, this could have a significant effect on yield structure. The kinetic model predicts that a given catalyst will produce a much higher degree of polymerization at 400 psia than at 174 psia. For the purpose of this comparison, it is assumed that the catalyst and operating conditions can be selected which will produce a yield structure similar to Koelbel's.

The slurry reactor yield structure reported by Koelbel shows a gasoline yield higher than the maximum of about 48 wt-% that is possible with a Schulz-Flory distribution of hydrocarbon products. A modified yield structure was, therefore, prepared in which the products follow a Schulz-Flory distribution with a degree of polymerization of 4 and an olefin-to-paraffin ratio of 2. The degree of polymerization of 4 was chosen by comparing Koelbel's yield structure with the plot in Figure 4.3-3, as discussed in Section 5.2.2.2. The olefin-to-paraffin ratio is the average ratio shown in Koelbel's slurry reactor product. This modified yield structure is shown in Table 5.2-5. The main differences between the two yield structures are the lower gasoline and higher diesel yield for the Schulz-Flory product, compared to the experimental data.

### 5.2.2.5 Ebullating Bed Reactor

It is expected that, due to the similarity of operating conditions in the two liquid-phase reactors, the product yield structures will also be very similar. The low $H_2/CO$ ratio syngas feed (shown in Table 5.2-1) as recommended for the slurry reactor, is also an appropriate feed for the ebullating bed reactor. The slurry reactor product yield structure shown in Table 5.2-5 also represents the product expected from an ebullating bed reactor.

The belief that slurry and ebullating bed reactors will give similar product yield structures is supported by work done at the U.S. Bureau of Mines (10). Under operating conditions similar to those used in Koelbel's demonstration unit, a similar product slate was achieved. During Experiment 37, Period 7, the reactor temperature was the same as reported for the slurry reactor. The effect of higher operating pressure and higher $H_2/CO$ ratio on degree of polymerization would tend to cancel each other, and, indeed, the observed degree of polymerization is very close to that observed in the slurry reactor.

The main differences between the slurry and ebullating bed reactors are catalyst particle size and method of heat removal. It is possible that pore diffusion effects in the larger catalyst particles could cause a shift in product distribution. This is not believed to be a significant effect with the type of catalysts used for ebullating bed Fischer-Tropsch synthesis.

The method of heat removal, by oil circulation in the ebullating bed reactor as compared to internal coils in the slurry reactor, is more likely to have an effect on product yield structure. The external oil circulation as well as the presence of larger catalyst particles results in a system in which the liquid phase is no longer totally back-mixed. The kinetic model, operated in a manner representing less back-mixing, showed a small effect on both conversion and degree of polymerization. While the understanding of the ebullating bed reactor is not sufficient to predict these effects with great precision, the differences appear to be of a magnitude that could easily be adjusted by changes in catalyst composition.

### 5.2.2.6 Yield Comparison

Yield structures for the entrained bed, tube-wall and slurry reactors are presented for comparison in Table 5.2-6. The entrained bed and slurry yields are those represented by Kellogg (4) and Koelbel (2), respectively.

In Tables 5.2-3 and 5.2-5, it has been shown that the gasoline yields would be 22% higher and 17% lower for the entrained bed and slurry reactors, respectively, if the yield structure followed Schulz-Flory distributions. However, there is no clear evidence that Schulz-Flory will be followed and, therefore, the published yields are used for comparison purposes. The tube-wall reactor design selected is so far from any experimental data with respect to operating conditions, recycle ratio and J factor, that an estimated yield has been used for comparison purposes.

Despite some remaining uncertainties with respect to yield structure, some broad conclusions can be drawn:

1. Yields should be compared on the basis of moles of hydrogen plus carbon monoxide converted.

2. The entrained bed and tube-wall reactors require high hydrogen content syngas feeds. The high operating temperatures require high hydrogen partial pressures to suppress carbon formation. The high hydrogen partial pressure reduces hydrogen production via internal shift. In the case of the entrained bed reactor, the high level of carbon dioxide in the recycle gas virtually eliminates the shift reaction. The slurry reactor operates with the lowest hydrogen partial pressures and can provide the internal shift reaction necessary to operate with a synthesis gas feed having a low hydrogen-to-carbon monoxide ratio, such as would be produced by the Texaco or Shell gasifiers.

3. The higher operating temperature of the tube-wall and entrained bed reactors will result in a considerably higher methane yield than with the slurry reactor.

4. The gasoline yield will be highest for the slurry reactor. The comparative yields in Table 5.2-6 show the slurry reactor to have almost twice the gasoline yield of the entrained bed reactor, with the tube-wall intermediate between the two. If all of the reactors produced a Schulz-Flory yield pattern, the slurry reactor would still produce the most gasoline, but the ratio would now be about 1.36 times the entrained bed. This higher gasoline yield is due to flexibility of the slurry system allowing the selection of operating conditions that minimize methane production and maximize gasoline production. This reflects a combination of high catalyst activity allowing lower temperature operation, and the inherent advantage of the liquid phase systems ability to tolerate the higher dew point product.

### 5.2.3 Investment Cost Comparison

#### 5.2.3.1 Introduction

This section compares sizes and investment costs of the four reactor systems. Since annual catalyst replacement costs proved to be significant, a comparison of catalyst costs is also included. The investment cost comparison is restricted to the reactor section of each Fischer-Tropsch plant. The impact of the reactors on upstream and downstream requirements is discussed in a separate section of this report.

A conceptual design for a reactor system capable of converting 28.05 MM SCFH of $CO + H_2$, was prepared for each reactor type under consideration. The complete design basis is included in Section 5.2.1 of this report. Based on the conceptual designs, in-house estimating procedures were applied in determining relative costs of the four reactor systems.

The items of equipment included in the designs are shown schematically in Figures 5.2-1 through 5.2-4. A complete list of equipment sizes is given in Appendix E. The decision as to which items to include in each design was based on items inherently a part of the particular reactor, plus additional heat exchange equipment required to recover usable heat from the reactor effluent. Due to the height of the entrained bed reactor, structural steel is a significant item. Thus the steelwork was included in the design and cost estimate for the entrained bed reactor but not for the other three.

The cost estimates include only major items of equipment, i.e., reactors and other vessels, heat exchangers, and pumps, plus labor for installation. Specifically excluded from the cost estimates are piping and instrumentation, foundations, insulation, painting, site preparation, land and buildings. As these are not complete cost estimates, actual dollar figures would be misleading and thus relative rather than absolute dollar amounts are presented in Table 5.2-7. The entrained bed reactor is the only commercial system and the cost of this operation is set at 100; all other items are compared against this figure.

The items in Table 5.2-7 are grouped into the following categories: reactor and receiver, other vessels, heat exchangers, and pumps. The reactor cost includes internals, if any are required. This category also includes, for the entrained bed reactor, the catalyst receiver and structural steelwork; for the tube-wall reactor, the hot oil receiver; and for the ebullating bed reactor, the product separator. The "heat exchange" category includes all heat exchangers external to the reactors.

Differences in reactor inventory and catalyst life contribute to significant differences in catalyst replacement costs. Based on available information, catalyst life for the entrained bed (4, 9) and ebullating bed (26) reactors is set at two months. Slurry reactor catalyst life is set at 38 days (10), and tube-wall reactor catalyst life is set at six months (64). There is some doubt about the ability to achieve a six month catalyst life in the tube-wall reactor for the reasons discussed in Section 5.2.3.4. Based on quotes from Kellogg and catalyst suppliers, it appears that catalyst for the entrained bed and ebullating bed reactors will cost about the same per pound. Koelbel used a precipitated iron catalyst for his slurry reactor which has been estimated to cost approximately 4.5 times the fused iron catalyst used in the entrained bed. The cost figures shown in Table 5.2-8 are based on on-site catalyst production. The cost of purchased catalyst is approximately three times this amount. The cost of application of the flame-sprayed catalyst for the tube-wall reactor was obtained from PETC.

While the investment and catalyst costs are only approximate, some definite trends can be observed. On the basis of initial investment and catalyst replacement costs, the slurry reactor is far superior to the other three.

### 5.2.3.2 Entrained Bed Reactor

The Synthol reactor design prepared by Kellogg (4) formed the basis for the conceptual design used in this comparison. While Sasol claims that 20 years experience has allowed them to improve on the design, published information indicates that the basic reactor design is still quite similar. Two modifications to the Kellogg design are the use of 400 psig operating pressure, and the use of direct steam generation instead of hot oil in the reactor cooling coils. Figure 5.2-1 illustrates the items included in the entrained bed reactor conceptual design and cost estimate.

For the design basis of 28 MM SCFH CO + $H_2$ conversion, two entrained bed reactor trains are required. The reactors themselves are 13-feet diameter by 111-feet overall height; each contains two sets of internal cooling coils. A 30-foot diameter by 40 foot tall catalyst receiver with cyclones is required to separate the catalyst from the product. A transfer line from reactor to catalyst receiver and a 50-inch standpipe with two slide valves are also included as part of the reactor. Due to the height and size of these vessels, extensive structural steelwork, amounting to about 10% of the cost of the reactor section, is required. As shown in Table 5.2-7, the reactor is about one-third of the cost of the entrained bed reactor system. The cost of two entrained bed reactors alone is comparable to the cost of 18 slurry or 20 ebullating bed reactors.

The "other vessels" in Table 5.2-7 include a quench tower and catalyst hoppers. The catalyst hoppers, one for fresh and one for spent catalyst, are considered necessary for catalyst addition and withdrawal. The 27-foot diameter by 80-foot tall quench tower is unique to the entrained bed reactor system, and is included in the design because it is required for separation of catalyst fines carried over from the catalyst receiver, from the reaction products. The quench also is an integral part of the heat recovery system and so cannot be excluded. The quench tower contributes about one-third of the total system cost. Moreover, the investment cost difference between the entrained bed reactor system and the two liquid-phase systems is due primarily to the quench section.

The final portion of the entrained bed reactor investment cost is for heat exchangers. The heat exchange section is different for this reactor system than for the others, due to the quench oil circuit. Quench oil is exchanged against combined feed and the cost of this exchanger is on a par with the feed/effluent exchangers for the other reactor systems. Heat exchange of a portion of the quench oil against boiler feed water allows further heat recovery and also provides a means of temperature control for the quench tower. Finally, heat exchange of the quench vapor against boiler feed water allows recovery of useful heat of the reactor effluent down to 250°F.

The annual cost for catalyst replacement in the entrained bed reactor system is double that in the slurry reactor system. This difference results entirely from the difference in catalyst inventory. The bulk of the 900 ton catalyst inventory in the entrained bed reactor is contained in the catalyst hopper and standpipe. The quantity of catalyst actually in the reactor is similar to that contained in the slurry reactors.

The entrained bed reactor catalyst inventory must be replaced quite frequently; every two months is typical (4, 9). In addition approximately 1% of the inventory must be added daily to make up for catalyst loss due to attrition. This high rate of catalyst replacement is necessitated by the high operating temperatures and consequent free carbon formation. Deposition of product wax on the catalyst also creates more of a problem in the gas phase system.

The entrained bed reactor is the only Fischer-Tropsch reactor operating on a commercial scale. While the cost of the reactor section is more than that of some of the potential systems, the reactor section is a relatively small part of the overall cost of a complete coal liquefaction plant. Until an alternative system has been demonstrated on a commercial scale, investors in indirect liquefaction may choose to go with the proven system.

### 5.2.3.2 Tube-Wall Reactor

The tube-wall reactor is a heat exchanger with catalyst flame-sprayed on the tube surface. The Parsons conceptual design called for applying the catalyst on external fins. It appears that recoating the tubes in a reactor of that design would require completely dismantling the reactor, an operation which seems unrealistic on a commercial scale. For the present design, it was decided to apply the catalyst to the inside of the tubes; with this design, it is possible to reapply catalyst without dismantling the reactor. The design also makes it possible to design a flame-spraying unit which can coat multiple tubes simultaneously. One drawback to the design is the 2-inch minimum diameter which can be flame-sprayed with currently available techniques (developed at PETC). Because present Fischer-Tropsch catalysts have little useful internal surface area, catalyst activity is mainly dependent on external surface area, and this increases the size of the reactors over what would be required if smaller diameter tubes were used.

More than with the other reactor types, the kinetic model was used in the design of the tube-wall reactor. This was necessary in order to predict the effects of changes in geometry and operating conditions, as most of the experimental work was done at different operating conditions than the design. All of the modeling work was based on properties of taconite catalyst. The reactor design is also based on taconite catalyst. As discussed in Section 4 of this report, the Parsons study used an activity based on tests with a flame-sprayed magnetite and a yield structure based on tests with a taconite catalyst. It is possible that the magnetite is more active catalytically than taconite, although the available data are inconclusive on this point. If this more active catalyst were used, the tube-wall reactor would be smaller. As the reactors alone are nearly twice as expensive as the entire entrained bed reactor system, a more active catalyst could result in significant savings. However, it has not been demonstrated that a magnetite catalyst can give the same yield structure as the potassium-promoted taconite, and this is still the primary consideration.

The tube-wall reactor design used in this comparison calls for 4 parallel trains of 13 reactors each. The reactors are 16-foot diameter by 64-foot long heat exchangers, containing bundles of 2-inch diameter tubes with taconite catalyst flame-sprayed on the inside of the tubes. The heat of reaction is removed by boiling oil. The temperature of the oil can be controlled by adjusting the pressure on the hot oil receiver. Oil is preferred over steam because the steam temperature is relatively insensitive to pressure in the temperature range required for this application. Given the high heat transfer coefficients in the tube-wall reactor, the catalyst temperature is very close to the oil temperature and, therefore, close control of coolant temperature is essential. The hot oil goes to a steam generator where it is condensed, and 600 psig steam can be produced.

The numerous large reactors, with the associated hot oil receivers, comprise over 90% of the cost of the tube-wall reactor system illustrated in Figure 5.2-2. Four parallel feed/effluent heat exchangers add modestly to the cost of the system, and allow recovery of sensible heat from the reaction products. Cost of the steam generators is also included in the "exchangers" cost figures. As shown in Table 5.2-7, the tube-wall reactor system as presently conceived represents an investment cost more than twice that of the entrained bed reactor system. This figure could be improved considerably by the development of a more active catalyst but it is unlikely that it would ever be significantly better than the entrained bed reactor.

Catalyst replacement costs for the tube-wall reactor are the highest of the four systems studied. The estimated annual cost for catalyst replacement shown in Table 5.2-8 is based on an assumed catalyst life of 6 months. This assumption is based on an experiment in which PETC operated a bench-scale unit with flame-sprayed taconite catalyst for 6 months before it began to rapidly deactivate. Regeneration allowed an additional 2 months operation (64). Even with a 6-month catalyst life, catalyst replacement costs for the tube-wall reactor are twice those for the entrained bed reactor. This high cost is due entirely to the expensive and labor-intensive flame-spraying method of catalyst application. In addition, six month catalyst life may be overly optimistic at the high temperature and relatively low $H_2/CO$ ratio called for in this design. The ability to achieve this operation would have to be proven before building a tube-wall reactor. This additional work may not be justified, however, for a reactor system which shows the potential for only marginal, if any, improvement over the entrained bed reactor.

### 5.2.3.4 Slurry Reactor

The slurry reactor conceptual design is based on information published by Koelbel and others (2, 20), on the Koppers-Rheinpreussen demonstration unit. In addition comments received in direct correspondence with Professor Koelbel were helpful in setting design parameters.

The reactor system as illustrated in Figure 5.2-3 consists of a reactor with steam generation coils located internally, a feed/effluent heat exchanger, and a small trim cooling system. The trim cooler was not a part of the demonstration unit, where temperature control was achieved by adjusting the pressure (and thus the temperature) of steam generation in the coils. As most operators would probably prefer to produce steam at constant pressure, the small oil circulation system is included for fine temperature control. For the design basis of 28 MM SCFH CO + $H_2$ conversion, at 400 psig, 18 of these reactor units in parallel are required. The reactors are 14 feet in diameter by 27-feet tall, the diameter being set by limits of shop fabrication and transport. Koelbel (2) mentioned a possible requirement for baffles in a large-size reactor to ensure good contacting between gas and liquid. Baffles are not included in the present design, and some additional study would be required to determine if they are truly needed. One catalyst hopper supplies fresh catalyst to all 18 reactors. A filtering system, the size of which is dependent on the type of product and operating conditions, is required to separate catalyst from the net product. The filter was not included in the cost estimate, but would not contribute significantly to the total system cost.

As shown in Table 5.2-7, the reactor accounts for three-quarters of the total cost of the slurry reactor system and is approximately equal to the entrained bed reactor cost. With the major heat-removal taking place in the reactor, very little additional heat exchange is required. The simplicity of the system then contributes to keeping the investment cost of the complete system low, equal to about half that for the entrained bed reactor system.

The catalyst consumption of the slurry reactor is very low (Table 5.2-8) representing a catalyst consumption of about 11% of the entrained bed system. However, as Koelbel used a precipitated catalyst for the slurry reactor while fused iron is used in the entrained bed and assumed for the ebullating bed reactor, a higher catalyst price ($1.80 per lb) has been used for estimating the annual catalyst cost of the slurry reactor. This results in an annual catalyst cost that is about 51% of that of the entrained bed system. This estimated annual cost shown in Table 5.2-8 is also based on a catalyst life of 38 days, based on Poutsma (10). This is the shortest of any of the systems, and under the mild operating conditions (low temperature, low CO concentration) in the slurry reactor, it would not be unreasonable to expect longer catalyst life.

The reason for the low catalyst costs in the slurry reactor is the small inventory required. The kinetic modeling work has shown the catalyst activity to be closely related to surface area and, therefore, the very small catalyst particle size results in a high activity per pound. In the slurry reactor system there is no lower limit on catalyst particle size other than that imposed by the ability to separate the solids by filtration. For this study, an average particle size of 30 microns was assumed. This results in the slurry reactor requiring roughly half as much catalyst as is contained in the entrained bed reactor. (The total entrained bed system inventory is several times that, due to the catalyst receiver inventory, as discussed in Section 5.2.3.2.)

Thus the slurry reactor is very attractive in terms of both investment and catalyst cost.

### 5.2.3.5 Ebullating Bed Reactor

An ebullating bed reactor conceptual design was prepared by Chem Systems, Inc. based on their experience in the design and operation of ebullating bed reactors for the production of methane and methanol. The design as received from Chem Systems is included in Appendix E. Based on this information, a design scaled-up to the common basis was prepared.

The system shown in Figure 5.2-4 includes a reactor, a product separator, a circulating oil cooling system, and a feed/effluent heat exchanger.

For the design rate of 28 MM SCFH CO + $H_2$ conversion at 400 psig, 20 parallel reactor trains are required. The reactors are empty shells, 14-feet diameter by 30-feet tall. The product separators are 14-feet diameter by 15-feet long, horizontal vessels. They serve the dual purpose of allowing vapor/liquid disengaging and providing overflow capacity for the liquid inventory. As shown in Table 5.2-7, the cost for 20 ebullating bed reactors plus product receivers is about the same as for two entrained bed reactors plus catalyst receivers.

A very high rate of oil circulation is required to hold the temperature rise in the reactor within reasonable limits. For this conceptual design, the maximum $\Delta T$ was set at 20°F. To achieve this, an oil circulation rate of about 20,000 gpm is required for each reactor. With this large oil circulation system, pumping costs become considerable. The pumps account for 25% of the cost of the reactor system. The circulating oil is cooled by heat exchange in a steam generator. This heat exchange adds 15% to the total system cost. It is the cost of the oil circulation system, including the pumps and the oil-versus-steam heat exchanger, that sets the cost of the ebullating bed reactor system above that of the slurry reactor system. Otherwise investment costs for the two systems are about equal.

It is in catalyst replacement costs that the slurry and ebullating bed reactors are notably different. As discussed in Section 5.2.3.4 of this report, catalyst costs for the slurry reactor are low due to the low inventory. The ebullating bed reactor, on the other hand, has a much higher catalyst replacement cost. For the ebullating bed reactor, a catalyst life of 2 months is assumed. This assumption is based on work at the U.S. Bureau of Mines (26), where over two months operation was possible with fused iron catalysts. The two month catalyst life is on the same order as that achieved in the slurry and entrained bed reactors. However, there could be mechanical difficulties due to the effect of fines in the oil circulation system. This potential problem has not been addressed in this study.

Because catalyst activity is largely dependent on surface area, the ebullating bed reactor requires much more catalyst than is contained in the slurry reactor. On a per pound basis, the 30 micron slurry catalyst has about 50 times as much surface area as the 1/16 inch ebullating bed catalyst. Catalyst replacement cost is 4 times that for the slurry reactor, and similar to that for the tube-wall reactor.

While the ebullating bed reactor is more attractive in terms of investment costs than the entrained bed reactor, there is as yet no catalyst with the structural strength to withstand the constant agitation in the ebullating bed. The slurry reactor, so similar in many ways, is less costly to build and operate and, therefore, there is little incentive to develop an ebullating bed catalyst.

### 5.2.4 Thermal Efficiency Comparison

For the purpose of this discussion the term "thermal efficiency" is defined as that portion of the heat of reaction which is recovered in some useful form. The heat of reaction in a Fischer-Tropsch system is equal to 20 to 25% of the heat of combustion of the CO and $H_2$ converted.

The conceptual designs used for the cost estimates, and shown in Figures 5.2-1 through 5.2-4, also form the basis for determination of thermal efficiencies of the units. In order to compare the units on a consistent basis, the envelope is drawn to include introduction of feed to the system at 120°F. As far as possible the enthalpy of the reactor effluent is recovered by heat exchange against the cold feed, or in the case of the entrained bed system, against quench oil and boiler feed water. The actual amount of heat that can be recovered differs according to the requirements of the individual systems. Heat recovery for each system is shown in Table 5.2-9. The ebullating bed reactor is considered to have the same thermal efficiency as the slurry reactor.

In the entrained bed reactor, 36% of the heat of reaction is recovered by steam generation in the reactor cooling coils. The reactor effluent is taken to the quench tower, where circulating oil removes catalyst fines and also cools the vapor product from 635 to 280°F. The quench vapors are exchanged against boiler feed water, where another 164 MM Btu/hr, or 8.6% of the $\Delta H_R$, is recovered. The temperature of the quench oil is maintained by the heat exchange of the oil against combined feed to the reactor and by boiler feed water heating. Thus 30% of the heat of reaction is recovered by heating boiler feed water. This low temperature heat is generally considered to be less valuable than high temperature steam; however, the quench system leaves no option for additional steam generation. The total heat recovery, or thermal efficiency, of the entrained bed reactor system then is 66%. The difference between the enthalpy of the quench vapor at 250°F and the combined feed at 120°F represents an enthalpy loss of 640 MM Btu/hr. This constitutes the remaining 34% of the heat of reaction.

In the tube-wall reactor, 85% of the heat of reaction is removed by boiling oil in the reactor. This heat is recovered from the oil by external steam generation. The reactor effluent is cooled by heat exchange against feed, to 220°F. The difference in enthalpy between the products at 220°F and the feed at 120°F is 300 MM Btu/hr, or 15% of the heat of reaction. The large amount of steam in the tube-wall reactor effluent causes a pinch point in the exchanger and thus sets the limit of heat exchange for this system.

Direct steam generation in the slurry reactor removes 91% of the heat of reaction, for a thermal efficiency of 91%. The reactor effluent is heat exchanged against fresh feed, and thereby cooled to 180°F. Because the slurry reactor produces primarily $CO_2$ and very little water, the difference in enthalpy between feed and products is considerably less than in the tube-wall system.

The ebullating bed conceptual reactor recovers the heat of reaction by allowing a 20°F temperature increase in the circulating oil. This heat is then recovered by generation of high pressure steam in the external steam generator. If feed and product similar to those of the slurry reactor are assumed, the overall thermal efficiency for the system is also similar to that of the slurry reactor.

The conceptual designs for the three-phase reactors are based on operation near the product dew point, and the thermal efficiencies shown are valid only for this case. If operating conditions are such that a significant quantity of the liquid phase is vaporized with the effluent vapor, the net thermal efficiency will be lower.

### 5.2.5 Upstream and Downstream Processing

While the scope of this study is restricted to a comparison of Fischer-Tropsch reactors, the synthesis section accounts for only 20 to 25% of the cost of all processing units in an indirect liquefaction plant. It is important, therefore, to consider what possible impact the choice of reactor will have on upstream and downstream processing requirements. These requirements are discussed in a qualitative fashion in this section.

The most important difference in upstream processing is caused by varying requirements for syngas $H_2/CO$ ratio. The three-phase systems operate preferably with a $H_2/CO$ ratio of 0.6 to 0.7. This ratio is supplied by modern gasifiers directly, without the need for a shift reactor. The gas-phase reactors on the other hand require a considerably higher $H_2/CO$ ratio. The tube-wall reactor conceptual design is for a $H_2/CO$ ratio of 2.0, and the entrained bed reactor requires a $H_2/CO$ ratio of 2.4 in the fresh syngas. Use of either of these reactors thus mandates the inclusion of a shift reactor upstream of the synthesis section. Depending upon the particular reactors chosen, the cost of the shift reactor may be one-tenth or more of the cost of the Fischer-Tropsch section.

An additional cost when using an external shift reactor is for an extra Acid Gas Removal (AGR) system upstream of the Fischer-Tropsch reactors. One AGR unit is required before the shift reactor and a second one after it. This reduces the $CO_2$ content of the shifted syngas. For operation without a shift reactor, only one AGR system is required before the Fischer-Tropsch reactor. If we assume, as a base case, that tail gas from the Fischer-Tropsch section is to be used as pipeline gas, then $CO_2$ must also be removed from this stream. The $CO_2$ content in the effluent from the three-phase reactors is much higher than that from the entrained bed and tube-wall reactors, as shown in Table 5.2-6. Total $CO_2$ production, if that from the shift reactor is included, is the same for all four Fischer-Tropsch systems. The difference between whether the $CO_2$-producing shift reaction takes place in the reactor or externally, determines the number of acid gas removal units, and the liquid phase systems will always have one less.

The entrained bed reactor requires a large amount of gas recycle. As discussed in Section 5.1.2, the recycle gas serves three main functions:

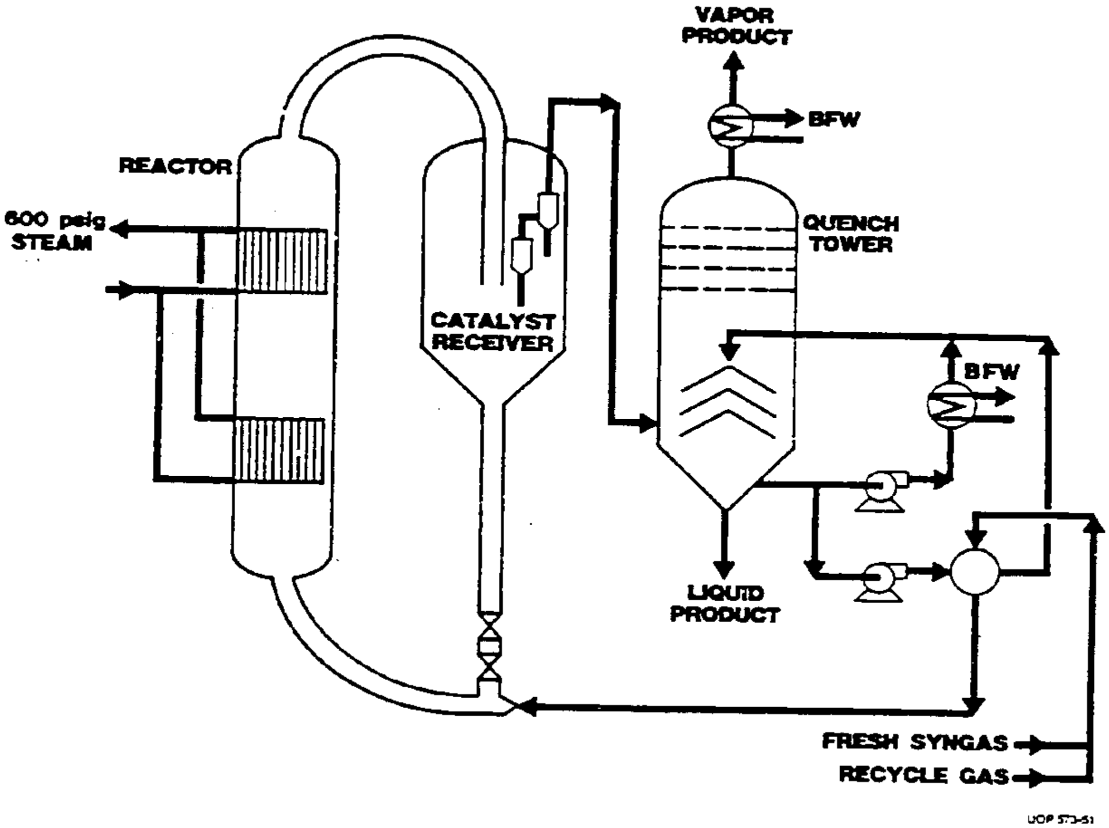
- Reduces CO content in combined feed
- Aids in temperature control
- Improves fluidization

The other three reactor systems are capable of operation without gas recycle. As shown in Table 5.2-2, little or no gas recycle is required to achieve 90% CO + $H_2$ conversion in the three alternative reactor systems. The impact of the recycle system is to increase the size of separations facilities to handle the increased quantity of reactor effluent (the volume of recycle gas in the entrained bed reactor system is 2.3 times the volume of the syngas feed). The recycle gas must be separated from the reactor effluent and scrubbed to reduce $CO_2$ content. A compressor is required to increase the pressure of the recycle gas stream to that at the reactor inlet.

It is apparent from this analysis that a liquid phase system shows a significant advantage over a gas phase system in not requiring an external shift reactor. The entrained bed reactor is at a further disadvantage in requiring a large amount of gas recycle.

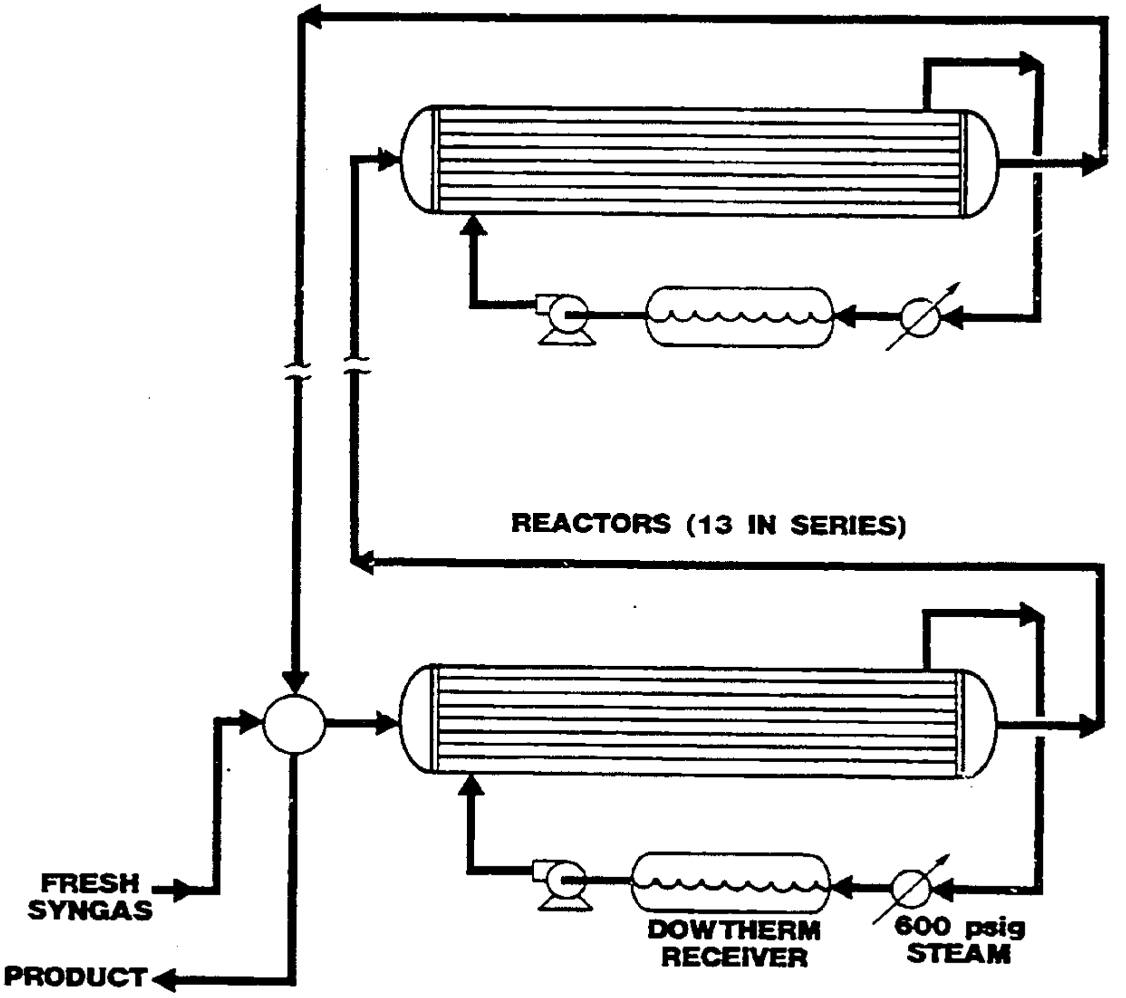
## FIGURE 5.2-1

## ENTRAINED BED REACTOR SYSTEM



## FIGURE 5.2-2

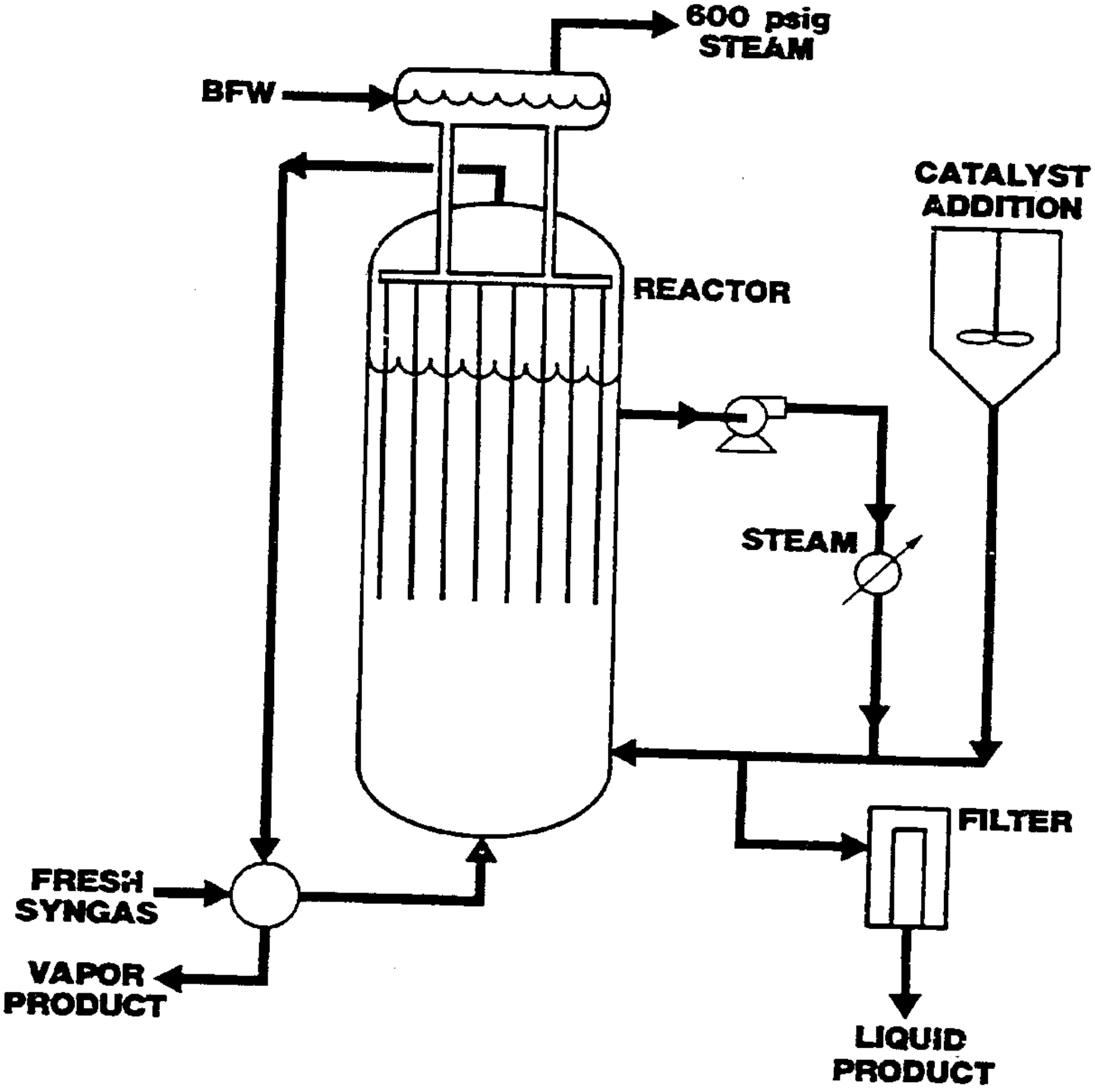
# TUBEWALL REACTOR SYSTEM



UOP 573-48

## FIGURE 5.2-3

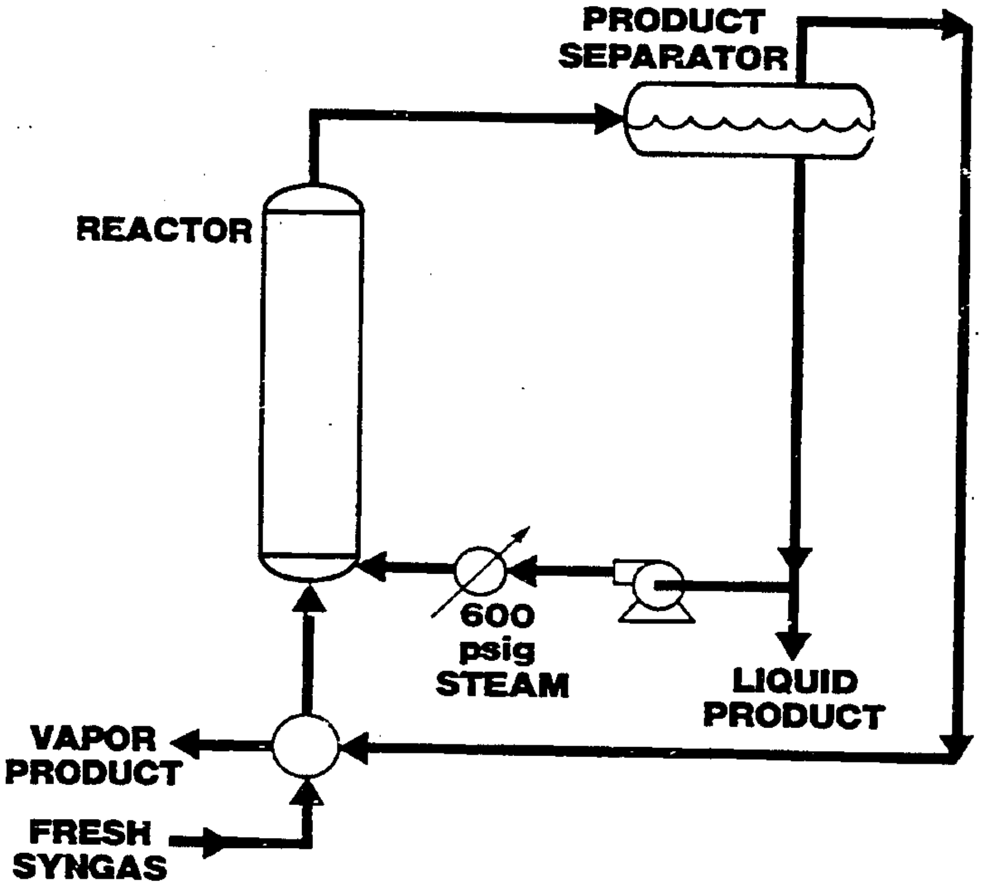
# SLURRY REACTOR SYSTEM



UOP 573-50

## FIGURE 5.2-4

# EBULLATING BED REACTOR SYSTEM



UOP 573-49

TABLE 5.2-1

Syngas Feeds for Fischer-Tropsch Reactor Systems

| Component | Entrained Bed Reactor | Tube-wall Reactor | Slurry Reactor |
|---|---|---|---|
| $H_2$, MM SCFH | 21.8 | 25.6 | 13.6 |
| CO, MM SCFH | 9.1 | 12.8 | 19.3 |
| $CO_2$, MM SCFH | 1.3 | 1.2 | 1.8 |
| $H_2O$, MM SCFH | - | 0.1 | - |
| $N_2$, MM SCFH | 0.3 | - | 1.1 |
| $H_2$:CO ratio | 2.4 | 2.0 | 0.7 |

Quantities required for conversion of 28.0 MM SCFH of CO + $H_2$:

once-through basis for tube-wall and slurry reactors,

recycle basis for entrained bed reactor.

## TABLE 5.2-2

## Fischer-Tropsch Reactor Feeds Recycle Operation

| Component | Entrained Bed Reactor |  | Tube-Wall Reactor |  | Slurry Reactor |  |
|---|---|---|---|---|---|---|
|  | Syngas | Combined Feed | Syngas | Combined Feed | Syngas | Combined Feed |
| $H_2$, MM SCFH | 21.8 | 52.1 | 18.7 | 25.6 | 12.4 | 13.6 |
| CO, MM SCFH | 9.1 | 11.1 | 12.2 | 12.8 | 18.5 | 19.3 |
| $CO_2$, MM SCFH | 1.3 | 15.9 | 1.0 | 1.3 | 1.6 | 1.8 |
| $H_2O$, MM SCFH | - | 0.2 | 0.1 | 0.1 | - | - |
| $N_2$, MM SCFH | 0.3 | 4.1 | - | - | 1.0 | 1.7 |
| $C_1$ + HC's, MM SCFH | - | 24.1 | - | 4.5 | - | 0.9 |
| Total, MM SCFH | 32.5 | 107.5 | 32.0 | 44.3 | 33.5 | 37.3 |
| $H_2$:CO ratio | 2.4 | 4.7 | 1.5 | 2.0 | 0.7 | 0.7 |

## TABLE 5.2-3

### Entrained Bed Reactor Product Yields

| Kellogg Basis, lb/hr | |
|---|---|
| Component | Kellogg Yield |
| $H_2O$ | 408,500 |
| $H_2$ | 14,500 |
| $N_2$ | 24,900 |
| CO | 13,400 |
| $CO_2$ | 156,900 |
| $C_1$ | 44,000 |
| $C_2^=$ | 18,600 |
| $C_2$ | 21,300 |
| $C_3^=$ | 35,900 |
| $C_3$ | 10,000 |
| $C_4^=$ | 33,200 |
| $C_4$ | 6,800 |
| $C_5$ | 26,200 |
| $C_6$ | 16,700 |
| $C_7$ | 14,000 |
| $C_{8-9}$ | 22,300 |
| $C_{10-12}$ | 28,200 |
| $C_{13-18}$ | 18,600 |
| $C_{19}+$ | 18,700 |
| NAC | 27,900 |
| Acids | 4,300 |
| Total | 964,900 |
| Total HC's | 346,700 |

| Comparison Basis, lb/hr | | | |
|---|---|---|---|
| Component | Kellogg Yield | Modified Yield | Sasol Yield |
| $H_2O$ | 408,500 | 403,800 | |
| $H_2$ | 14,500 | 14,400 | |
| $N_2$ | 24,900 | 24,900 | |
| CO | 13,400 | 15,300 | |
| $CO_2$ | 156,900 | 159,400 | |
| $C_1$ | 44,000 | 44,000 | 37,700 |
| $C_2^=$ | 18,600 | 18,600 | 25,700 |
| $C_2$ | 21,300 | 21,300 | |
| $C_3^=$ | 35,900 | 35,900 | 44,600 |
| $C_3$ | 10,000 | 10,000 | |
| $C_4^=$ | 33,200 | 33,200 | 37,700 |
| $C_4$ | 6,800 | 6,800 | |
| Gasoline ($C_{5-11}$) | 99,800 | 122,100 | 126,800 |
| Diesel ($C_{12-25}$) | 32,800 | 22,300 | 37,700 |
| Heavy ($C_{25}+$) | 12,100 | 300 | 12,000 |
| Alcohols | 27,900 | 27,900 | 20,600 |
| Acids | 4,300 | 4,300 | |
| Total | 964,900 | 964,500 | |
| Total HC's | 346,700 | 346,700 | 342,800 |

## TABLE 5.2-4

### Tube-Wall Reactor Product Yields

| Component | Parsons Yield, lb/hr | Modified Yield, lb/hr |
|---|---|---|
| $H_2O$ | 207,400 | 257,900 |
| $H_2$ | 30,100 | 50,100 |
| $N_2$ | 24,800 | - |
| CO | 123,800 | 63,600 |
| $CO_2$ | 560,200 | 513,900 |
| | | |
| $C_1$ | 40,400 | 42,600 |
| $C_2^=$ | 5,000 | 5,200 |
| $C_2$ | 20,200 | 20,100 |
| $C_3^=$ | 3,400 | 3,600 |
| $C_3$ | 11,800 | 12,000 |
| $C_4^=$ | 10,100 | 10,400 |
| $C_4$ | 30,200 | 30,200 |
| Gasoline | 139,500 | 135,700 |
| Diesel | 54,000 | 52,100 |
| Heavy | 8,200 | 10,400 |
| Alcohols | 16,100 | 13,300 |
| Acids | 1,800 | 5,200 |
| | | |
| Total | 1,287,000 | 1,226,300 |
| Total HC's | 340,700 | 340,800 |

## TABLE 5.2-5

## Slurry Reactor Product Yields

Literature Basis, lb/hr

| Component | Koelbel Yield |
|---|---|
| $C_1 + C_2$ | 10,800 |
| $C_2^=$ | 12,000 |
| $C_3^=$ | 61,200 |
| $C_3$ | 15,300 |
| $C_4^=$ | 13,000 |
| $C_4$ | 4,300 |
| 104-356°F | 181,300 |
| 356-428°F | 13,500 |
| 428-608°F | 20,300 |
| > 608°F | 6,300 |
| Total HC's | 338,000 |

Comparison Basis, lb/hr

| Component | Koelbel Yield | Modified Yield |
|---|---|---|
| $H_2O$ | 59,800 | 57,200 |
| $H_2$ | 13,500 | 12,900 |
| $N_2$ | 79,200 | 79,200 |
| CO | 171,000 | 171,600 |
| $CO_2$ | 1,117,600 | 1,120,200 |
| $C_1$ | 7,800 | 8,300 |
| $C_2^=$ | 12,000 | 21,800 |
| $C_2$ | 3,000 | 11,700 |
| $C_3^=$ | 61,200 | 24,500 |
| $C_3$ | 15,300 | 12,900 |
| $C_4^=$ | 13,000 | 24,500 |
| $C_4$ | 4,300 | 12,700 |
| Gasoline ($C_{5-11}$) | 193,900 | 166,600 |
| Diesel ($C_{12-25}$) | 25,100 | 53,500 |
| Heavy ($C_{26}+$) | 2,300 | 1,400 |
| Alcohol | 5,700 | 5,700 |
| Total | 1,784,700 | 1,784,700 |
| Total HC's | 343,600 | 343,600 |

TABLE 5.2-6

Comparison of Product Yields for Fischer-Tropsch Reactors

| Component | Entrained Bed, lb/hr | Tube-Wall, lb/hr | Slurry, lb/hr |
|---|---|---|---|
| $H_2O$ | 408,500 | 257,900 | 59,800 |
| $H_2$ | 14,500 | 50,100 | 13,500 |
| $N_2$ | 24,900 | - | 79,200 |
| CO | 13,400 | 63,600 | 171,000 |
| $CO_2$ | 156,900 | 513,900 | 1,117,600 |
| | | | |
| $C_1$ | 44,000 | 42,600 | 7,800 |
| $C_2^=$ | 18,600 | 5,200 | 12,000 |
| $C_2$ | 21,300 | 20,100 | 3,000 |
| $C_3^=$ | 35,900 | 3,600 | 61,200 |
| $C_3$ | 10,000 | 12,000 | 15,300 |
| $C_4^=$ | 33,200 | 10,400 | 13,000 |
| $C_4$ | 6,800 | 30,200 | 4,300 |
| Gasoline ($C_{5-11}$) | 99,800 | 135,700 | 193,900 |
| Diesel ($C_{12-25}$) | 32,800 | 52,100 | 25,100 |
| Heavy ($C_{26}$+) | 12,100 | 10,400 | 2,300 |
| Alcohols | 27,900 | 13,300 | 5,700 |
| Acids | 4,300 | 5,200 | - |
| | | | |
| Total | 964,900 | 1,226,300 | 1,784,700 |
| Total HC's | 346,700 | 340,800 | 343,600 |

## TABLE 5.2-7

## Investment Cost Comparison for Fischer-Tropsch Reactor Systems

| Reactor Type<br>No. of Reactors | Entrained Bed<br>2 | Tube-Wall<br>52 | Slurry<br>18 | Ebullating Bed<br>20 |
|---|---|---|---|---|
| Relative Investment Costs: | | | | |
| Reactor and Receiver | 34 | 189 | 33 | 28 |
| Other Vessels | 30 | - | <1 | - |
| Heat Exchangers | 32 | 15 | 10 | 21 |
| Pumps | 4 | 4 | 2 | 16 |
| Total | 100 | 208 | 45 | 65 |

## TABLE 5.2-8

## Catalyst Replacement Costs for Fischer-Tropsch Reactors

| Reactor | Entrained Bed | Tube-Wall | Slurry | Ebullating Bed |
|---|---|---|---|---|
| Catalyst Inventory, tons ($ft^2$) | 900 | ($4.4 \times 10^6$) | 100 | 3000 |
| Catalyst Usage, tons/yr ($ft^2$/hr) | 8,400 | ($8.8 \times 10^6$) | 950 | 18,000 |
| Catalyst Cost, $10^3$ \$/yr | 6,720 | 14,200 | 3,420 | 14,400 |

TABLE 5.2-9

## HEAT RECOVERY IN F-T REACTORS

- Entrained Bed Reactor ($\Delta H_R$ = 1900 MM Btu/Hr)

| | MM Btu/Hr | % of $\Delta H_R$ |
|---|---|---|
| Steam Generation | 690 | 36% |
| BFW Heating | 570 | 30% |
| $H_{Products} - H_{Feed}$ | 640 | 34% |

- Tube-Wall Reactor ($\Delta H_R$ = 1960 MM Btu/Hr)

| | MM Btu/Hr | % of $\Delta H_R$ |
|---|---|---|
| Steam Generation | 1660 | 85% |
| $H_{Products} - H_{Feed}$ | 300 | 15% |

- Slurry Reactor ($\Delta H_R$ = 1960 Btu/Hr)

| | MM Btu/Hr | % of $\Delta H_R$ |
|---|---|---|
| Steam Generation | 1790 | 91% |
| $H_{Products} - H_{Feed}$ | 170 | 9% |

## 5.3 CONCLUSIONS OF THE PHYSICAL COMPARISON

### 5.3.1 General

Phase I of this study has undertaken a comparison of four reactor systems for the production of gasoline via the classic Fischer-Tropsch synthesis. Certain generalizations can be made as to the most desirable mode of operation.

1. The Fischer-Tropsch section is a small part of an indirect liquefaction plant and, therefore, the most important economic consideration is that of product yield. With the objective being transportation fuel, especially gasoline, this means the ideal process should maximize gasoline production and minimize the amount of methane produced. A Schulz-Flory degree of polymerization near 4 corresponds to maximum gasoline production.

2. Because the Fischer-Tropsch reaction is highly exothermic, the reactor must be designed to control the temperature by removing the heat generated. To improve thermal efficiency, the heat of reaction should be recovered in a form that is useful elsewhere in the plant.

3. Use of a low $H_2/CO$ ratio synthesis gas as feed to the Fischer-Tropsch reactor eliminates the need for a separate shift reactor. This decreases investment cost and increases thermal efficiency for the total indirect liquefaction plant.

### 5.3.2 Entrained Bed Reactor

1. This is the only one of the four reactor systems studied which is operating commercially. In light of the inevitable problems encountered when commercializing a new process, this is a significant advantage.

2. In order to minimize condensation of heavy products in the reactor, the entrained bed reactor is operated at a degree of

polymerization around 3.3. Thus the gasoline production is considerably less than the theoretical maximum. In addition, the high temperature operation results in a large methane yield.

3. The entrained bed reactor consists of three adiabatic reaction sections in series, with cooling sections between. This method of heat removal does hold the temperature increase across the reactor to a reasonable limit. The amount of temperature increase is very sensitive to changes in catalyst circulation rate, reactant concentration and quantity of recycle gas. The interrelationships between all these variables limit the flexibility of the process.

4. The entrained bed reactor must use a high $H_2/CO$ ratio feed. In addition, the $CO_2$ in the recycle gas prevents the shift reaction from occurring in the reactor. Therefore, all the hydrogen (above that produced in the gasifier) must be produced in an external shift reactor.

5. Fluidization characteristics as well as other operating requirements unique to the entrained bed reactor, mandate the use of a large volume of recycle gas. This decreases thermal efficiency of the process and increases operating costs.

6. The entrained bed reactor typically operates at temperatures above 600°F where free carbon formation becomes a significant problem. This is presumably a key factor in limiting useful catalyst life to two months. As a result, catalyst replacement is a significant operating expense in this system.

### 5.3.3 Tube-Wall Reactor

1. Operational requirements should not prevent operating the tube-wall reactor at a degree of polymerization of 4. However, all flame-sprayed catalysts tested to date have produced a large amount of light gases and very low gasoline yields. The high temperature proposed in the conceptual design will also result in additional methane production.

2. The tube-wall reactor achieves excellent temperature control and isothermal operation. In addition, 85% of the heat of reaction is recovered as high pressure steam, resulting in a good thermal efficiency.

3. A high $H_2/CO$ ratio is required to limit free carbon formation. This necessitates the use of an external shift reactor.

4. The flame-sprayed catalyst should be applied on the inside of the catalyst support tubes in order to facilitate replacing the catalyst. This results in a much larger reactor section than envisioned in the Parsons design.

5. The investment cost for major equipment items is more than twice that of the entrained bed reactor system. The annual catalyst replacement cost is also expected to be more than twice that for the entrained bed reactor.

### 5.3.4 Slurry Reactor

1. The slurry reactor is able to operate at conditions which produce a gasoline yield equal to, or possibly even greater than, the maximum predicted by a Schulz-Flory product distribution. Methane yield is minimized by the low temperature operation.

2. The slurry reactor design allows very good temperature control and high thermal efficiency. In addition, the presence of the liquid phase provides a margin of safety in case of operational difficulties.

3. A syngas feed with a $H_2/CO$ ratio typical of that produced in a modern gasifier presents no problem in slurry reactor operation. The water-gas shift reaction produces the necessary $H_2$ within the reactor.

4. Once-through conversion of over 95% should be possible with the proper choice of operating conditions. This potentially can lead to a much-simplified process.

5. Maintenance of oil quality is essential to the successful operation of a slurry reactor. Further study is required to determine the best liquid for this use, and the conditions which will allow continuous operation.

6. It should be possible to select a catalyst that will make operation at 400 psia feasible, however, further study is required to prove that this is the case. Operation at 174 psia, as in the German demonstration unit, would adversely affect the investment cost.

7. Major equipment items for a slurry reactor system cost only half as much as those for an entrained bed reactor system of equal capacity. Catalyst replacement cost is expected to be only 51% of that for an entrained bed reactor, and other operating costs are also much lower.

### 5.3.5 Ebullating Bed Reactor

1. It was not possible to determine whether the ebullating bed reactor has a yield advantage over the slurry reactor. It is believed that the two liquid-phase reactors will give very similar product yield structures.

2. The liquid circulation system provides very good temperature control, though at considerable cost. Thermal efficiency is also high.

3. An external shift reactor is not required, as low $H_2/CO$ ratio syngas can be used as feed to the reactor.

4. Once-through conversion of over 95% should be possible.

5. Maintenance of oil quality is critical to the success of this operation.

6. As with the slurry reactor, the choice of operating pressure will affect the overall economics of the system. Further study is required to determine whether continuous operation is possible at 400 psia.

7. It appears that major equipment items will cost more than for the slurry reactor, but still only a fraction of that for the entrained bed reactor. Catalyst costs are extremely high because a large quantity is required.

8. Developing a catalyst with the physical strength to withstand the constant agitation in an ebullating bed reactor appears to be difficult, if not impossible. The only catalysts that held together for a reasonable length of time had very low catalytic activity.