

SECTION 1 -- SUMMARY

Franz Fischer and Hans Tropsch are credited with the discovery, in the 1920's, that carbon monoxide and hydrogen can be converted in the presence of a metal catalyst to a variety of hydrocarbon products. Just prior to and during World War II the "Fischer-Tropsch" reaction was commercialized in Germany and used to produce military fuels in fixed bed reactors. It was recognized from the start that this reactor system had severe operating and yield limitations and alternative reactor systems were sought. In 1955 the Sasol I complex, using an entrained bed (Synthol) reactor system, was started up in South Africa. Although this reactor was a definite improvement and is still operating, the literature is filled with proponents of other reactor systems, each claiming its own advantages. This report provides a summary of the results of a study to compare the development potential of three of these reactor systems with the commercially operating Synthol-entrained bed reactor system.

1.1 DESCRIPTION OF REACTOR SYSTEMS

The three reactor systems to be evaluated are:

- 1) The tube-wall reactor, developed by the U.S. Bureau of Mines (1), resembling a shell and tube heat exchanger having catalyst flame-sprayed onto the cooling tubes.
- 2) The slurry reactor as proposed by Koelbel (2), with catalyst suspended in an inert liquid, cooled by immersed coils, with syngas bubbled through the catalyst slurry.
- 3) An ebullating bed reactor, which is also a liquid phase reactor, but with larger size catalyst and heat removal from a circulating liquid stream that is also used to keep the bed expanded (3).

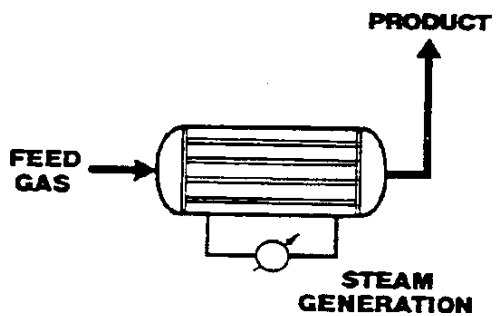
These three reactors and the entrained bed reactor are shown in Figure 1.1-1.

The commercial Synthol reactor is used as a benchmark against which the development potential of the other three reactors can be compared. This reactor system is operated by Sasol in South Africa. However, most of the information on which this study is based was supplied by the M. W. Kellogg Co. (4). No information beyond that in the literature on the operation of the Synthol reactor system was available for consideration in preparing this study, nor were any details of the changes made to the original Synthol system to overcome the operating problems reported in the literature (5).

Because of conflicting claims and results found in the literature, it was decided to concentrate a large part of this study on a kinetic analysis of the reactor systems, in order to provide a theoretical analysis of intrinsic strengths and weaknesses of the reactors unclouded by different catalysts, operating conditions and feed compositions. The remainder of the study considers the physical attributes of the four reactor systems, and compares their respective investment costs, yields, catalyst requirements and thermal efficiencies from simplified conceptual designs.

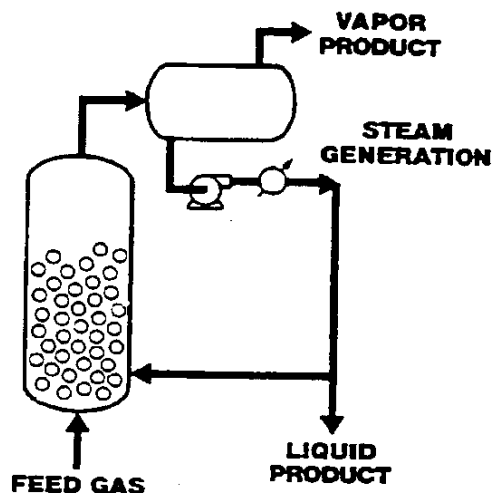
FIGURE 1.1-1

TUBE WALL



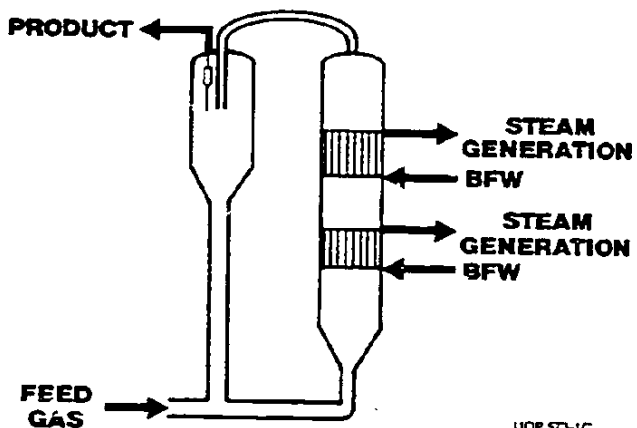
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EBULLATING BED



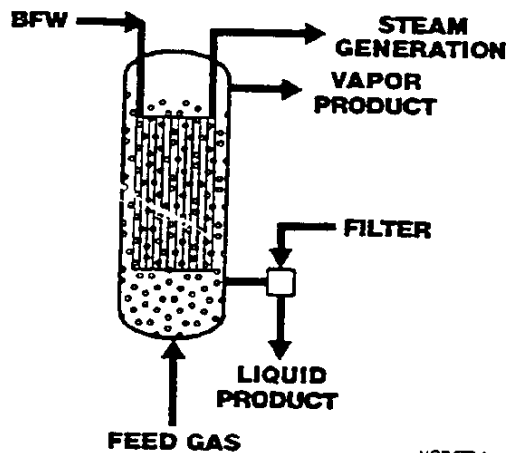
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ENTRAINED BED



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SLURRY



UOP 573-1

1.2 KINETIC ANALYSIS

Before computer models for any of the reactors could be written, it was necessary to develop a mathematical description of the basic Fischer-Tropsch reactions. As none of the kinetic analyses in the literature were judged to be appropriate for this purpose, a new kinetic analysis was made which provided the basis for all of the work that followed. The mechanism selected for the basic Fischer-Tropsch reactions, shown in Figure 1.2-1, is discussed in detail in Section 4. The term "mechanism" as used here and elsewhere in this report refers to the reaction scheme used as the basis for the kinetic analysis. The principal features of this mechanism are the equilibrium between the olefin product and the catalyst sites, and the inclusion of the concentration of free catalyst sites $[MH]$ in our assumption of steady state concentrations for all intermediates attached to the catalyst sites.

Once the steady state assumption is made, the mechanism can be analyzed by a simple mathematical definition of the reaction system that will predict the product composition from the concentrations of the reactants, and from the values of the various rate constants indicated on Figure 1.2-1. While further work is required to check the validity of this kinetic model of the Fischer-Tropsch reaction, the fact that good agreement was obtained on predicted values of rate constants when it was applied to data from different reactor systems operating under different conditions, does provide some encouragement that this rather simple analysis may be correct. Reactor models using this kinetic scheme, combined with the parallel shift reaction, were then prepared for the entrained bed, slurry and tube-wall reactors, and a considerable number of variable studies are presented in Section 4.

From consideration of the general mathematical definition of the Fischer-Tropsch reactions, combined with other reactions that may occur in parallel, the following general conclusions can be drawn regarding the best results that can be expected from this route for the liquefaction of syngas:

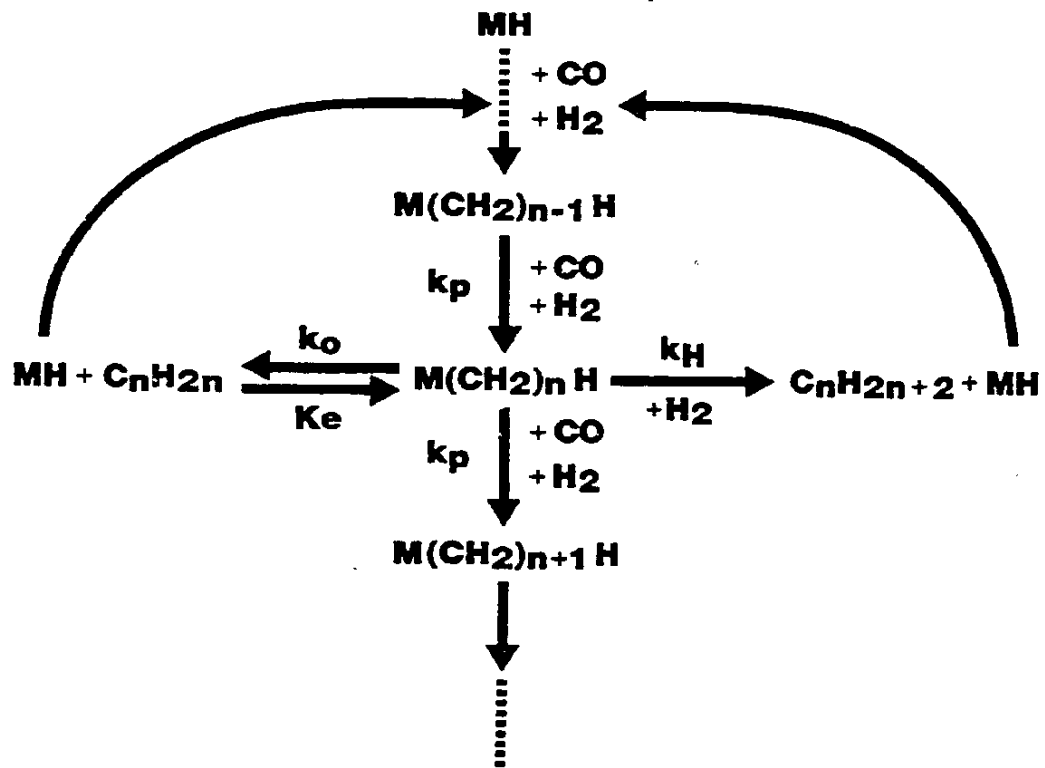
- 1) While further studies to determine if rate constants vary with carbon number are required before absolute conclusions can be drawn, it does appear that the reaction mechanism will not permit significant departure from the Schulz-Flory distribution of products, except with respect to methane and to a lesser extent light olefins (see Section 4.1).
- 2) Methane appears to result from at least two parallel reactions. The methane produced from the basic Fischer-Tropsch reactions will fall on a Schulz-Flory distribution with other paraffins, but considerably below a Schulz-Flory distribution for paraffins plus olefins, particularly for conditions that give high olefin-to-paraffin ratios. At high temperatures a significant increase in methane yield will result from a second route to methane, probably that suggested by Dry (6), and the methane yield will be significantly above that of a Schulz-Flory distribution.
- 3) The equilibrium between olefins and the catalyst site assumed in the kinetic analysis provides a basis for explaining why the light olefin yield can be below that predicted by a Schulz-Flory distribution, particularly when the light olefin concentration is increased by recycling light olefins to the reactor.
- 4) The shift reaction can be combined with the Fischer-Tropsch reaction in a single reactor, provided that reactor is operated at a low enough temperature to effectively eliminate free carbon formation.
- 5) A significant departure from the Schulz-Flory distribution could result if an additional termination step, such as aromatization of the olefins, is added to the reaction mechanism. This is not included in the scope of this paper.
- 6) The degree of polymerization of the product is highly dependent on CO concentration and, to a lesser extent, H₂ concentration, in addition to catalyst composition and temperature. The use of a kinetic model is, therefore, almost essential for understanding the significance of experimental data at various conversion levels and feed compositions, or when comparing results from plug flow reactors with those from a back-mixed system.

It is immediately apparent that these general kinetic conclusions support almost all of the claims made by Koelbel and co-workers (2, 7) for the superiority of the slurry reactor system. Koelbel operated his reactor at high conversion and low temperature. As this is a back-mixed reactor, these conditions resulted in a low CO concentration throughout the reactor. This in turn gave a degree of polymerization of about 4, which is close to the gasoline optimum, even at the low operating temperature. Had Koelbel operated at lower conversion at this low operating temperature, he would have had a much higher degree of polymerization and perhaps duplicated the serious problems related to the high liquid viscosity that were characteristic of Farley and Ray's work (8). The low temperature could also explain the low methane yield and lack of free carbon formation, while exploiting a simultaneous shift reaction by operating on feed gas with a low (0.7) H_2/CO ratio. The slurry reactor model also confirms Koelbel's claim that mass transfer has little influence under the operating conditions used. The only item in Koelbel's data not consistent with the kinetic model is the gasoline yield. With a Schulz-Flory product distribution, the gasoline yield peaks at about 48 wt-% of the product with a degree of polymerization of 4. The gasoline yield shown in Table 1.3-2 corresponds to 56 wt-% of the product. However, the gasoline yield for the operating conditions chosen for the slurry reactor, that does correspond to a Schulz-Flory distribution, is still substantially above that of the vapor phase reactors.

Similar application of these general conclusions to the entrained bed reactor serves to explain some of the weaknesses of this system. In this vapor phase reactor, the degree of polymerization must be held below that which would result in the condensation of liquid on the surface of the heat removal coils. It is, however, a plug flow system and the CO concentration at the entrance to the reactor will inherently be higher than in a back-mixed reactor running at high conversion. The degree of polymerization, therefore, is reduced by a combination of dilution of the feed CO with large amounts of recycle gas and by operation at high temperature. The high temperature puts the process into an operating region where free carbon formation is a substantial problem and causes deactivation and disintegration of the catalyst. To minimize free carbon formation, the

process is operated at a high hydrogen concentration. This combined with high temperature results in high methane yield. Also, the high hydrogen concentration combined with high levels of CO₂ in the recycle gas effectively eliminates the shift reaction, requiring external shift and an extra step for removal of acid gas on the syngas feed. The reactor model of this system also show it to be the least flexible of those studied due to the intermittent heat removal and the interrelation between operating variables.

**FIGURE 1.2 -1
MECHANISM**



UOP 573-2

1.3 PHYSICAL COMPARISON

The basis used for physical comparison is shown in Table 1.3-1. The details of this physical comparison are presented in Section 5. The reactors were compared at the same operating pressure, but otherwise the operating parameters are those suggested in the literature for the entrained bed, slurry and ebullating bed reactors. The operating conditions for the tube-wall reactor were purposely selected to arrive at as reasonable a design as possible for this system. The tube-wall reactor model allowed a set of yields to be estimated consistent with these operating conditions. The model also showed that because of low catalyst concentration, this reactor must be operated at high temperature if the size of the reactor is to be reasonable. This will result in a high methane yield, and it is doubtful that the reactor could be operated at the conditions selected without appreciable problems with free carbon formation.

Table 1.3-2 provides a comparison of the yields claimed for Kellogg and Koelbel for the entrained bed and slurry reactors, respectively, with those estimated for the tube-wall reactor. Yields for the ebullating bed reactor would be similar to that shown for the slurry reactor. Only costs for major items of equipment are included in the cost comparison given in Table 1.1-3, where estimated costs of the three potential systems are presented as percentages of the commercially operating entrained bed system. A comparison of estimated catalyst requirements is presented in Table 1.3-4. This assumes that the cost per pound of the granular fused iron catalysts used in the entrained and ebullating bed reactors is the same. The costs per pound for the precipitated iron and flame-sprayed catalyst used in the slurry and tube-wall reactors, respectively, are estimated. Differences in energy utilization, expressed as percentages of the heat of reaction recovered, are shown in Table 1.3-5.

The results of the physical comparison indicate that two of the reactor types can be eliminated from further consideration. The tube-wall reactor can be dismissed because the investment cost and the catalyst replacement cost are more than double those of the Synthol reactor. Also, catalyst replacement is extremely laborious. The ebullating bed reactor

can be expected to show many of the advantages of the slurry system, but no catalyst is known to exist that combines physical stability with the activity assumed for this study. The catalyst replacement cost shown in Table 1.3-4 is, therefore, extremely high. The high cost of the liquid circulating system, combined with the low probability that this reactor will ever show a significant advantage over the slurry system, makes it unlikely that anyone will spend the effort required to develop a physically stable, high activity catalyst with large enough size for employing an ebullating bed reactor.

The physical comparison study shows a clear advantage for the slurry reactor over the others considered, and there is little doubt that the slurry reactor should be commercialized to provide a significant advance over the commercially operating Synthol-entrained bed reactor. The slurry reactor appears to be superior in having the lowest investment cost and catalyst requirements, combined with the highest gasoline yield and thermal efficiency and also providing the best hope for a continuously operating process. The final paragraphs of this summary briefly explain the reasons for the advantages of the slurry reactor over the entrained bed reactor.

TABLE 1.3-1 Basis for Physical Comparison

Design Rate: 28×10^6 SCFH CO + H₂ Converted
 Operating Pressure: 400 psig

<u>Reactor Type</u>	<u>Design Source</u>	<u>T_{out}, °F</u>	<u>GHSV, hr⁻¹</u>	<u>Recycle Ratio</u>
Entrained	Kellogg	635	1100	2.3
Tube-Wall	U.S. Bureau of Mines	640	230	0.4
Slurry	Koelbel	527	480	0.1
Ebullating	Chem Systems	547	390	0.1

TABLE 1.3-2 Product Yields for Fischer-Tropsch Reactors

	<u>Entrained Bed,</u> <u>lb/hr</u>	<u>Tube-Wall,</u> <u>lb/hr</u>	<u>Slurry,</u> <u>lb/hr</u>
C ₁	44,000	42,600	7,800
C ₂ -C ₄	125,800	81,500	108,800
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	346,700	340,800	343,600

TABLE 1.3-3 Relative Investment Costs for Fischer-Tropsch Reactor Systems

	<u>Entrained Bed</u>	<u>Tube-Wall</u>	<u>Slurry</u>	<u>Ebullating Bed</u>
No. of Reactors	2	52	18	20
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 1.3-4 Catalyst Requirements for Fischer-Tropsch Reactors

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

TABLE 1.3-5 Heat Recovery in Fischer-Tropsch Reactors

	<u>Entrained Bed</u>		<u>Tube-Wall</u>		<u>Slurry</u>	
	<u>MM Btu/hr</u>	<u>% of Δ Hr</u>	<u>MM Btu/hr</u>	<u>% of Δ Hr</u>	<u>MM Btu/hr</u>	<u>% of Δ Hr</u>
Steam Generation	690	36	1660	85	1790	91
BFW Heating	570	30	-	-	-	-
H _{products} - H _{feed}	640	34	300	15	170	9
Total Heat of Reaction Δ Hr	1900	100	1960	100	1960	100

1.4 COMPARISON OF SLURRY AND ENTRAINED BED REACTORS

The entrained bed reactor does have an advantage of scale over the other systems. For 28 MM SCFH of CO + H₂ converted, the basis used for this study, two entrained bed reactors were required in parallel compared to 18 in parallel for the slurry system. As would be expected, the cost of the reactors alone is lower for the entrained bed reactors. However, when the catalyst separation and catalyst recycle system are added, the cost advantage is completely offset. The cost of two entrained bed reactor systems, complete with catalyst separation and recycle equipment, is about equal to the cost of the 18 slurry reactors.

The vapor exiting the entrained bed system contains all of the catalyst lost due to the high rate of fracture and attrition (4.1 tons/day per reactor) (9). A quench tower is employed for the combined function of heat recovery and catalyst fines removal. This is a very expensive item that is not required for the slurry system. The heat exchange equipment is also much larger for the entrained bed system, reflecting lower temperature levels in the quench tower and higher flow rates due to the high recycle gas ratio. When the cost of all of the items included in the reactor/heat exchange envelope are added up, the entrained bed investment appears to be more than double that required for the slurry system. While it must be recognized that this was not a definitive cost analysis, this difference is large enough to show clearly that the slurry system should offer significant investment savings over the entrained bed system.

Two other points should be made in connection with this cost comparison. First, the cost comparison does not allow for any spare reactors. With 18 reactors in parallel and an apparent ability to operate continuously, it is unlikely that spare reactors would be required for the slurry system. However, the Synthol entrained bed system is apparently shut down every 50-60 days for catalyst replacement, and Sasol has reported adding an additional reactor system to Sasol I in order to maintain production rates (5). If spare reactors are required for the entrained bed system, this further increases the investment advantage of the slurry system. Second, the reactors were all compared at the same

operating pressure of 415 psig. While the entrained bed reactor is operated at 300 psig, the bulk of the work on the slurry system is at 160 psig. Although it is believed that operation of the slurry system at higher pressure could be accomplished with some modification to the catalyst composition, this requires pilot plant demonstration. If the slurry system were operated at 160 psig, more than twice the number of reactors would be required and a large portion of the investment advantage would be lost.

The higher thermal efficiency of the slurry system is readily explained by the much lower recycle gas requirements. The much lower content of water vapor in the slurry gas effluent is also a contributing factor.

The lower investment cost and higher thermal efficiency of the slurry reactor itself can be combined with further investment savings and increases in overall thermal efficiency when upstream shift and acid gas removal steps along with the downstream recycle gas system are eliminated.

While catalyst makeup requirements are not well established for the slurry system, the available data (10) indicate that the catalyst makeup requirement would be 11% of that required by the entrained bed system, if a precipitated catalyst is required.

Finally, it should be reemphasized that the above is a discussion of the potential advantage of a slurry reactor system over the commercially operating entrained bed system. The slurry system still has to be commercialized. However, a 5 foot diameter reactor was operated in the early 1950's, and scaleup to the 14 foot diameter reactor selected for this study should not be difficult. The potential advantages determined from this study for the slurry system, combined with similar conclusions arrived at in independent studies (10, 11), provide a clear incentive to justify work on its commercialization.