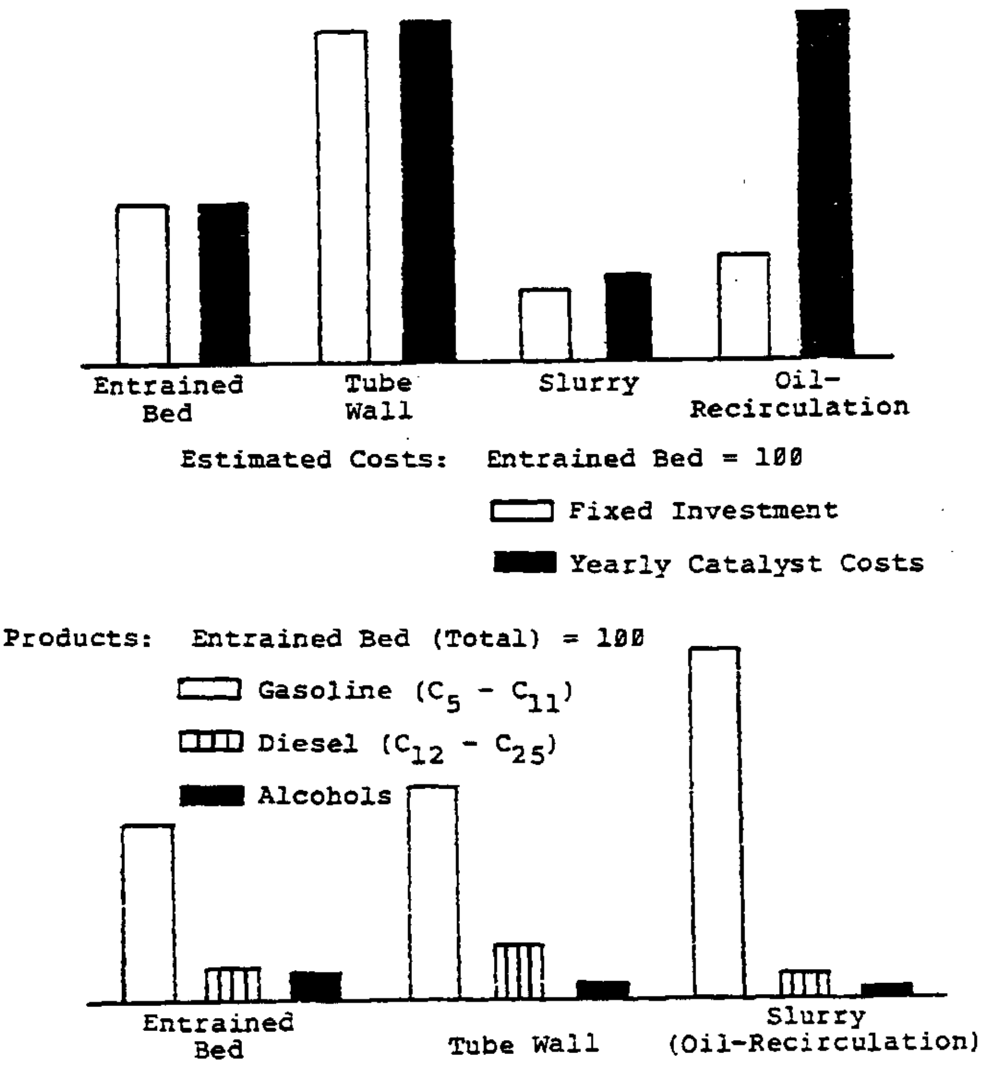

Figure 7. Comparison of costs and performance of Fischer-Tropsch reactor system (43).

In addition to the advantage of cost, slurry reactors are able to achieve high single pass conversions at near isothermal conditions, eliminating the need for recycle compressors. With good temperature control, methane yields are typically low (57). It has also been observed that slurry reactors can handle a wide range of feed compositions, particularly carbon monoxide rich feeds, without excessive carbon formation (50).

Much of the early work with slurry reactors was done by Kolbel, et. al., in Germany from 1938-44, 1951-53 (28). The research culminated with the construction and operation of a 10-ton/day demonstration plant, which was designed to produce gasoline from coal-derived synthesis gas. A potassium and copper promoted, precipitated iron catalyst was used, and a high molecular weight paraffin wax was used as the slurry liquid. Cooling was obtained using an internal bayonet-type heat exchanger. Kolbel was able to achieve a 90% single pass synthesis gas conversion, with roughly 85% of the C_3+ products in the gasoline boiling range, and about 12% diesel fuel.

From 1951 through 1964 there were at least five other well documented slurry studies which enjoyed at least partial success. All of these early studies used iron based catalysts in reactors similar to Kolbel's (21,37,49). More recently, workers at Air Products and Chemicals, Inc. (7) have developed proprietary slurry catalysts highly selective towards diesel fuel. Deckwer, et. al. (13), and in a separate study Satterfield (51), have looked at producing gaseous olefins in slurry reactors using manganese/iron catalysts. At ASU, Campbell (9) investigated biomass-derived pyrolysis gas conversion to diesel fuel in a slurry reactor using a cobalt based catalyst. A summary of slurry reactor studies appears in Table 4.

Table 4. Summary of previous slurry reactor research.

RESEARCHER	CATALYST	TEMPERATURE (°C)	PRESSURE (atm)
Kolbel (28) (1947-53)	ppt Fe	200 - 320	8 - 30
Schlesinger(52) (1951-54)	ppt Fe	220 - 280	8 - 21
Hall(49) (1952)	ppt Fe	260 - 300	21 - 31
Calderbank(49) (1963)	ppt Fe	265	11 - 22
Farley & Ray(21) (1964)	ppt Fe	265 - 285	1.5 - 11
Deckwer(13) (1978)	ppt Mn/Fe	282 - 303	12
Air Products(7) (1983)	proprietary	240 - 280	20 - 33
Campbell(9) (1983)	Co/Al_2O_3	210 - 310	7 - 21
Satterfield(51) (1984)	ppt Mn/Fe	283	12.4

III. Equipment and Procedures

1. Experimental Equipment.

All experiments were conducted in a 304-stainless steel reactor of 5.25-cm (2-in) i.d. and a height of 2.1-m (7-ft). A cross section of the reactor used appears in Figure 8. The non-expanded slurry heights ranged from 59-cm to 132-cm. The reactor heads were made from 2" 304-stainless steel caps. Teflon seals were used between the reactor heads and body. The top head was fitted with a 1/2" Swagelock to tube socket weld union, which served as the reactor outlet, and a similar 1/4" Swagelock weld union, used as a port for a thermocouple well. The thermocouple well ran the length of the reactor, and was large enough to hold four 1/16" thermocouples. The bottom head was fitted with a single 1/2" Swagelock tee, used for the reactor inlet. A 100-micron stainless steel sintered plate was used as the gas distributor. The plate was held in place by a Pyrex wool packing between the bottom head and distributor plate.

The reactor was heated by two 1" by 8' heating tapes. 2" of Kaowool in sheet metal casing was used as insulation around the reactor. The lower heating tape,

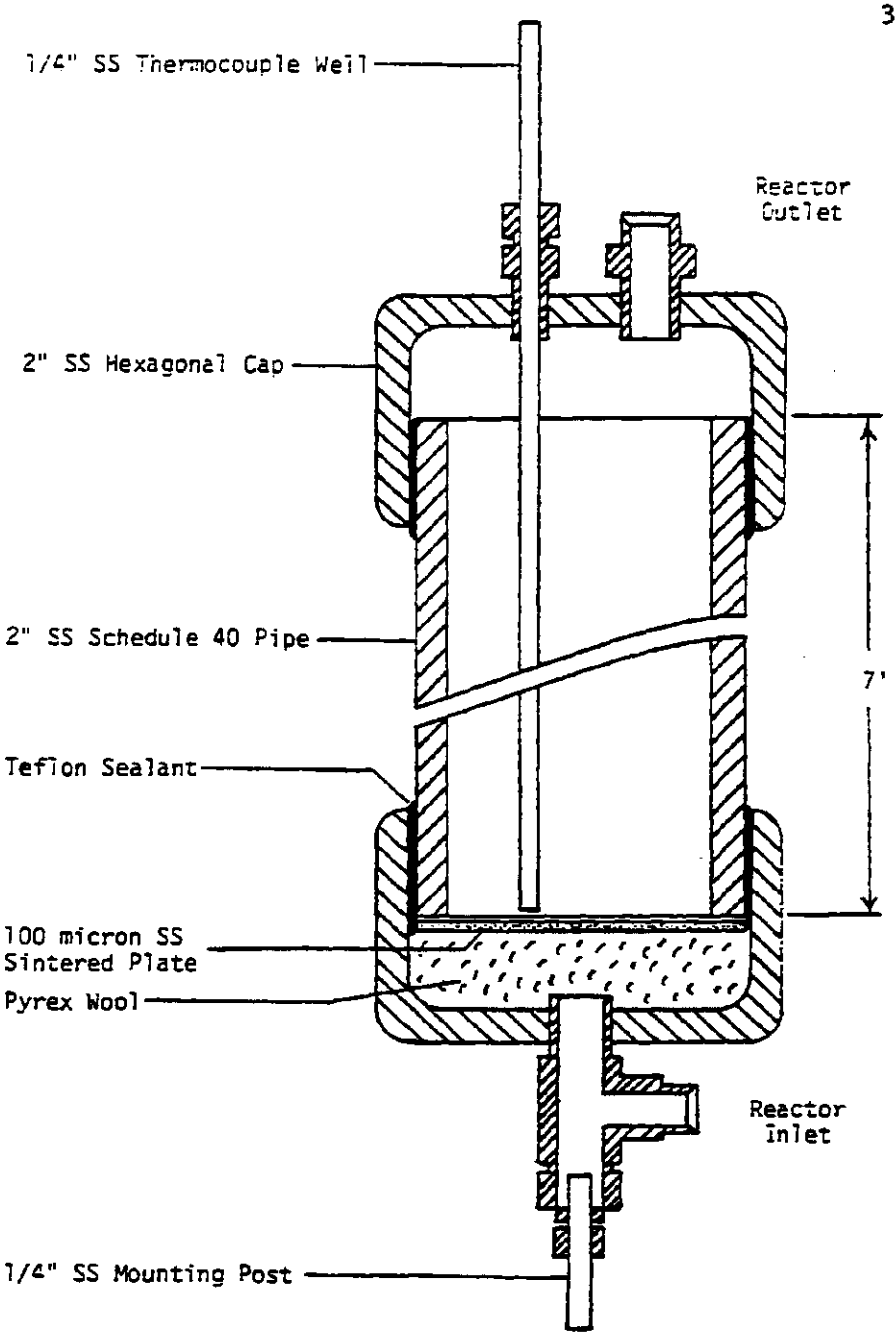

Figure 8. Cross section of slurry reactor used in study.

used to heat the slurry, was controlled by an Omega Engineering Model 22 temperature controller. The controlling thermocouple was located in the middle of the slurry bed. Type-K thermocouples were used throughout the system, and the temperatures were monitored on a Leeds and Northrup Speedomax temperature recorder. The output of the upper heating tape was controlled manually.

A system schematic appears in Figure 9. Synthetic pyrolysis gas was obtained by mixing pure hydrogen, carbon monoxide, carbon dioxide, methane, and ethylene available from gas cylinders via a high pressure manifold. The flowrates of the individual gases were regulated by Brooks 5850 mass flow controllers. The feed gas passed through a total inlet rotameter and a preheater before entering the reactor.

Upon leaving the reactor, the product and residual gases passed through a heated outlet line into a wax trap. The outlet line was heated such that the wax trap operated at about 80°C. The remaining product and gases were cooled to about 10°C in a condenser, and collected in a second trap. A second set of ice cooled traps, located downstream, acted as surge tanks and guard traps

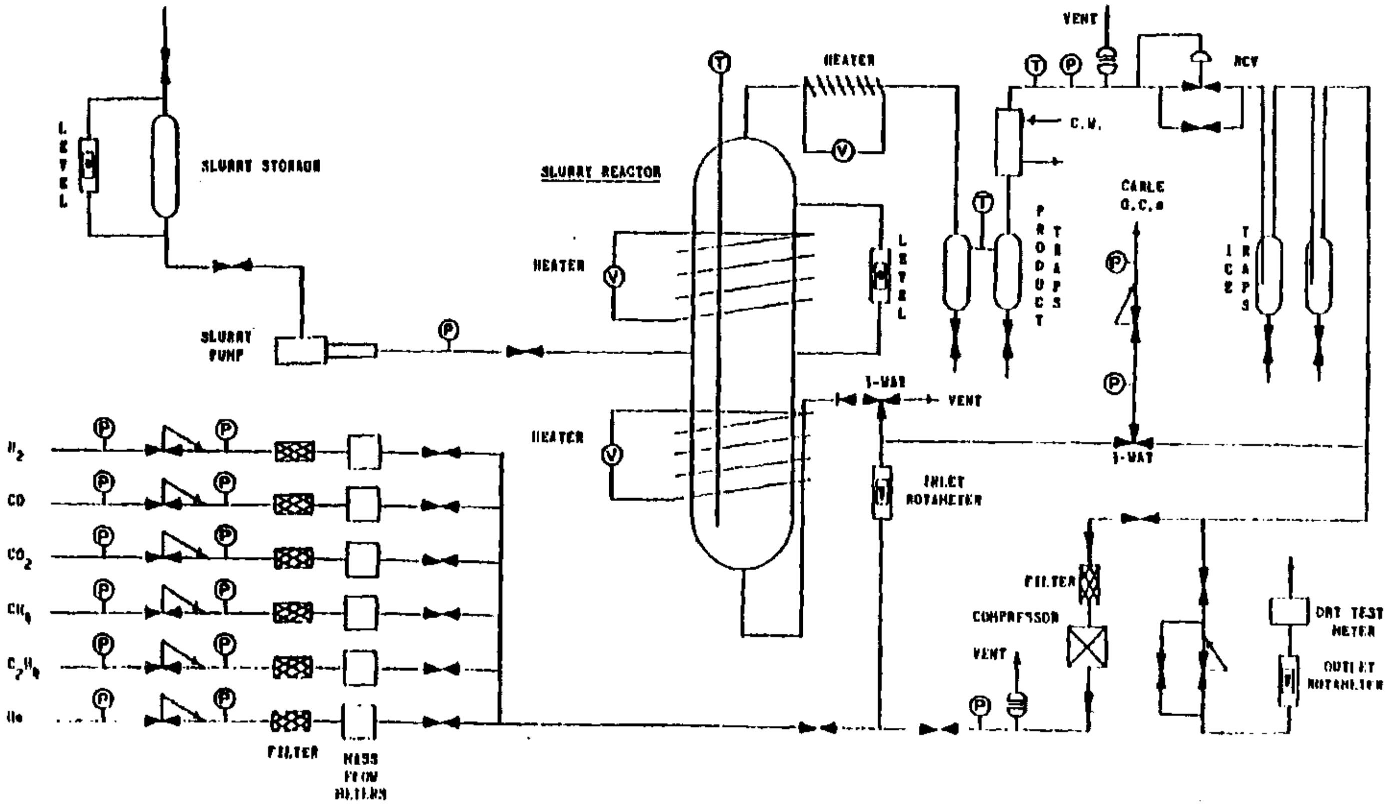

Figure 9. System schematic for slurry phase Fischer-Tropsch reactor system.

to prevent liquid product or slurry from accidentally entering the gas chromatograph sample lines.

The reactor pressures was always taken to be the pressure of the system above the slurry bed. This pressure was controlled by regulating the gas flowrate out of the system with an air-to-close Badger Meter Research Control Valve. The control loop consisted of a Fischer 1151 absolute pressure transmitter, a Westinghouse 55CC Veritrak PID controller, and a Foxburo 69TA current to air transducer. The volumetric flowrate of offgas was measured by a Singer dry test meter before venting to atmosphere.

The system was set up with the option of adding slurry liquid to the reactor during operation. A Ramoy Series 600 progressing cavity pump could be used to transfer slurry or slurry liquid from a storage tank into the reactor, in order to maintain a constant reactor bed level. This is usually not necessary, except in the case of low-boiling slurry liquids, such as Fischer-Tropsch product.

2. Analytical Equipment.

On line composition analysis of the reactor feed and offgas was accomplished using three Carle Model 111

Analytical Gas Chromatographs (Carle GC's). The Carle GC's can separate mixtures of hydrogen, carbon monoxide, carbon dioxide, nitrogen, oxygen, and the C_1 through C_5 paraffins and olefins. Spectra-Physics recorder/integrators were used to plot and integrate the gas chromatograms. The Spectra-Physics units are also able to identify each previously identified peak, and calculate the gas compositions based on predetermined thermal conductivity detector response factors. The response factors were determined by calibration with hydrogen, carbon monoxide, carbon dioxide, and methane mixtures of known composition, as shown in Appendix A. Response factors for the remaining components were taken from the literature (15).

Aqueous phase liquid product analysis was performed on a Hewlett-Packard 5730A Gas Chromatograph equipped with a thermal conductivity detector. A 1/8" by 6' Poropak Q column was used to separate the water and alcohols; a 5A molecular sieve column was used in parallel as a reference column. Response factors for the detector were also taken from the literature. An example of an aqueous liquid product analysis appears in Appendix B.

A Hewlett-Packard 5710A Gas Chromatograph equipped with a flame ionization detector was used for the analysis of the liquid organic product. The C_6+ hydrocarbons were separated with a 1/8" by 6' 3% Dexsil 300 on 100/120 Supelcoport high temperature column. All samples were diluted to 10mg/cc carbon disulfide before injection into the column. FID response factors for the C_6+ hydrocarbons are all essentially the same, with the exception of some aromatics; hence, the normalized peak areas will be the weight composition of the sample. An example of the organic liquid product analysis appears in Appendix C.

3. Catalyst Preparation.

All of the iron catalysts used in this study were prepared by precipitation. Details of the catalyst preparation procedure are located in Appendix D. Hot, dilute (less than 10 weight %) solutions of ferric and cupric nitrates were used. Dilute ammonium hydroxide was used as the precipitant because it is easily and quickly washed from the precipitate. Potassium or sodium carbonate precipitants require extensive washing to remove them from the precipitate. The catalyst reduction was usually carried out in the slurry phase, at relatively low temperatures (ca. 260°C). In order to facilitate the reduction under these mild conditions, the catalysts were promoted with copper to a nominal value of 10 weight % of the reduced iron present in the catalyst. The catalysts were ground to 200 to 270 mesh (53 - 74 microns) before their use.

4. Operating Procedures (8).

Before performing an experiment, the system is pressure tested with hydrogen at 200 psig in order to locate all gas leaks. After the pressure test standards have been met, the system is depressurized, and the reactor outlet line is removed. A small helium purge is initiated, and the reactor is preheated to 100°C. Weighed amounts of catalyst and slurry liquid are loaded into the reactor through the open reactor outlet line with the aid of a funnel.

Prior to reduction, the reactor outlet line is installed and the helium purge is replaced with a hydrogen flow of 20 scfh. The system is brought up to operating pressure and reactor heating is started. Typical reduction conditions used were 160 psig and 260°C, with a flowrate of 20 scfh of hydrogen. After reaching full temperature, the aqueous product flowrates are monitored until reduction water is no longer produced. This ranges from 6 to 24 hours, depending on the type of catalyst used.

Following reduction, the reactor temperature is lowered to about 30°C below the desired synthesis temperature. The hydrogen feed is switched to the desired simulated pyrolysis gas feed at a set total flowrate. Cooling is initiated, if required, and after the reactor temperature stabilizes, the temperature is slowly raised to its desired value. Samples of the feed gas are taken immediately after start up to calibrate the Carle GC's for the run as per Appendix A. Gas and liquid flowrates, feed and off gas compositions, temperatures and pressures are monitored hourly. At least 8 hours of full flows/temperatures were normally required to reach steady state; the total length of the run varied accordingly with the run objectives.

In order to complete a material balance for the run, the slurry drained from the reactor was weighed to determine the net loss (gain). Solids such as blown over catalyst or wax were removed from the traps. Gas chromatograms were obtained for the aqueous and liquid products, and the used slurry liquid.

5. Laboratory Safety.

A general guideline for safety requirements is the ASU Biomass Conversion Group Laboratory Safety and Operation Manual (8).

Cobalt and iron slurry catalysts are very fine powders which are easily suspended in air and inhaled. The use of a particulate respirator is recommended when handling iron catalysts, and is required when handling cobalt catalysts because of their toxicity. Whenever possible, work with dry catalysts under a fume hood.

Waxes are often used in the slurry reactor, and is kept hot to facilitate handling. Eye protection and gloves must be worn for protection in case of a spill. A respirator should also be worn to minimize the amount of hydrocarbons inhaled.

Synthetic pyrolysis gas and reactor offgas are flammable and usually contain carbon monoxide, so care should be taken not to vent the gas into the laboratory. The lab area should be adequately ventilated, and a carbon monoxide monitor should be used when the system is operating. The system should be depressurized and purged with an inert gas, (e.g., helium) before opening any lines into the laboratory.

An air to close control valve is used to control system pressure, and rupture disks have been strategically placed to allow for a controlled venting of gases to atmosphere in the event of a power failure or pressure surge. Care should be taken not to interfere with the proper operation of these safety devices.

6. Experimental Plan.

The major objective of this study was to continue the development of the slurry reactor for pyrolysis gas liquefaction. To achieve this goal, three separate, but related, investigations were performed:

A. Iron Catalyst Testing.

Although the use of iron based Fischer-Tropsch catalysts has become very popular since WWII, there has been only one previous study of iron based catalysts at ASU, performed by Min-Jan Lu (35). He tested three commercially available iron catalysts in a packed bed reactor. These catalysts were originally designed to perform as dehydrogenation or ammonia synthesis catalysts. The purpose of the iron catalyst testing performed in the current study was to evaluate catalysts prepared specifically for use in the Fischer-Tropsch synthesis. The vast body of literature available in Fischer-Tropsch catalysts was used to select the catalysts and arrive at a preparation procedure.

B. Slurry Liquid Testing.

The ideal slurry liquid would be inert, exert low vapor pressures at elevated temperatures, and be inexpensive. Campbell (9) tested several liquids for use in slurry reactors, and that testing was continued as part of this study. It has been recognized that the presence of slurry liquid in the synthesis product can lead to erroneous yields if not properly accounted for. Also, slurry liquid in the product may not be compatible with the ultimate goal of producing high quality paraffinic fuels. Consequently, the motive behind the liquid testing was to evaluate liquids which exhibited low vapor pressures and/or were compatible with, and similar in structure to, Fischer-Tropsch product.

C. Factor Study and Optimization.

The purpose of the factor study and optimization was to determine the operating conditions which gave the best overall system performance (i.e., the highest organic product yields). Yate's analysis of two level factor study experiments were used as an efficient method of ranking the factors and their combinations in order of importance. Polynomial equations were fit to the results of the factor study, and were optimized, subject to constraints, to obtain the most suitable operating conditions.

A flow diagram of the experimentation performed appears in Figure 10.

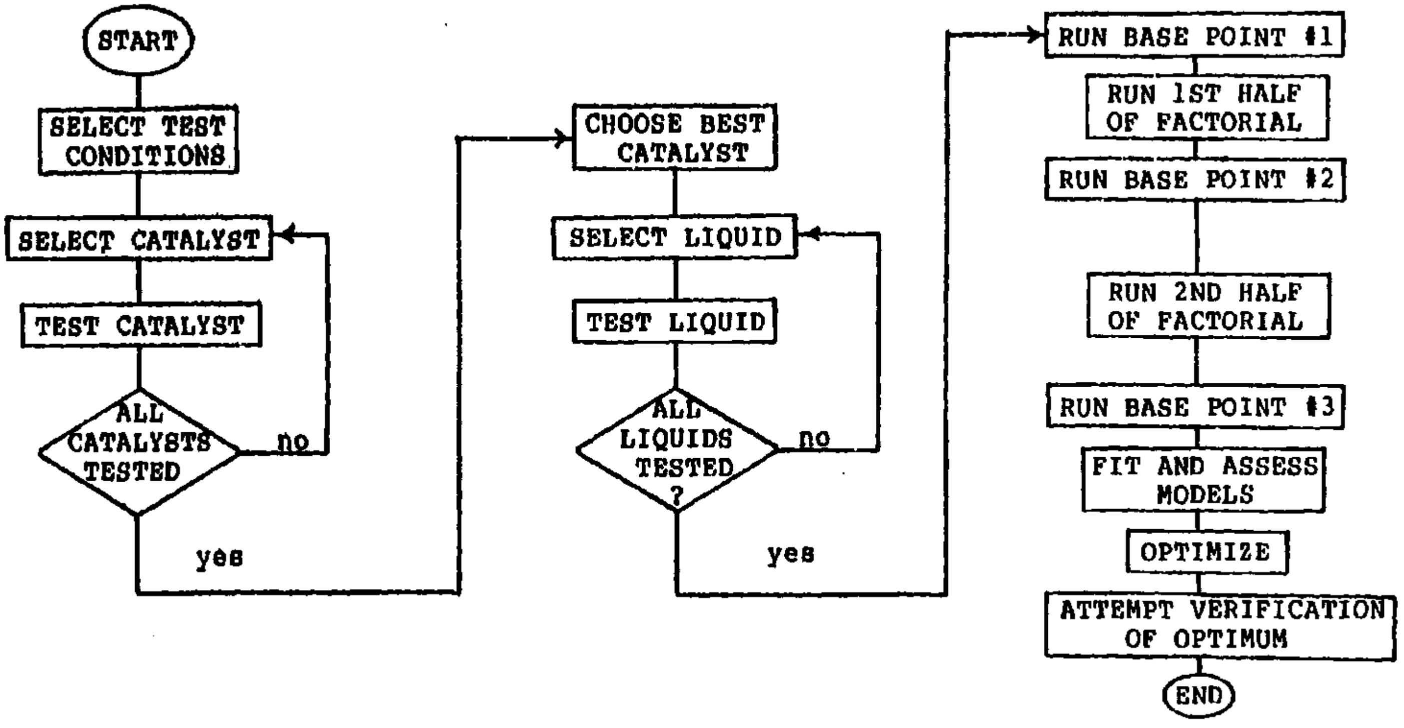

Figure 10. Flowsheet of experimental plan

IV. Results and Discussion.

1. Catalyst Testing.

Five iron based catalysts were tested in this study: unsupported, unsupported with potassium promoter, alumina supported, alumina supported with potassium promoter, and kieselguhr supported. All of the catalysts were prepared by precipitating ferric nitrate solutions, and all contained a copper promoter.

The unsupported catalysts were selected for screening because they are the most popular slurry catalysts reported in the literature (21,28,37). These catalysts have been generally considered to be wax-producing catalysts, although Kolbel used them to selectively produce gasoline and diesel boiling range products (7,20,28). The precipitated, unsupported catalysts are preferred over other bulk iron catalysts, such as fused iron, for use in slurry reactors because they are more active. A fused iron ammonia synthesis catalyst tested by Lu (35) produced very low yields of liquid organics; fused iron catalysts are more suitable for fluidized or entrained bed reactors, where catalyst strength is important, and higher reaction temperatures can be tolerated.

Alumina was chosen as a support because of its popularity as a carrier for many types of metal catalysts. Initially, an attempt was made to prepare these alumina supported iron catalysts via impregnation, because the impregnation procedure is much simpler and easier than precipitation. Unfortunately, during the impregnation the concentrated ferric nitrate was observed to partially dissolve the alumina. When tested, these catalysts displayed very low activity. Consequently, the precipitation method, using dilute solutions of ferric nitrate, was adopted for all catalysts. Impregnation may have been suitable for the kieselguhr support, but for consistency, a common preparation procedure was used for all catalysts.

Kieselguhr is a widely used support for Fischer-Tropsch catalysts, particularly for the cobalt based catalysts. With iron catalysts, kieselguhr is known to shift the selectivity towards lighter hydrocarbons, (1,2,54). Although this may be detrimental in some situations, kieselguhr was chosen as a support because of its common usage in Fischer-Tropsch catalysts. It has been observed that the alkali react with kieselguhr, neutralizing the effect of the alkali unless excessive promotion levels are used, (54). For this reason, a