Abstract

An exploratory, experimental process study was conducted on the direct conversion of coal derived synthesis gas to gasoline. Novel, proprietary catalysts, supplied by Mobil Research and Development Corporation were used. These unique catalysts do not yield oxygenates and the hydrocarbons formed are limited in size to about C_{11}. Consequently, both gasoline selectivity and quality exceeds that of the gasoline produced in the Fischer-Tropsch process. This new technology was compared with conventional Fischer-Tropsch. The experiments were conducted in micro reactor (10 cc catalyst capacity) and in bench-scale units (150 cc catalyst capacity). The bench-scale unit was used in both a fixed and fluid bed mode. The studies included effects of temperature, pressure and space velocity on catalyst performance, and catalyst activation, aging and regeneration. Theoretical studies were made to support the process research.

I. Objective and Scope of Work

The overall objective of this contract is to develop a catalytic process for directly converting synthesis gas, of the type produced in a coal gasification, to a high octane gasoline based on a Mobil Research and Development Corporation proprietary catalyst. The immediate objective is to determine the optimum process conditions for the catalytic conversion and to obtain sufficient data to prepare a conceptual design for a 100 bbl/day pilot plant.

Task 1 - Exploratory Process Research

a. Process evaluation of syn gas catalysts.

Commercially feasible operating conditions for syn gas conversion processes will be determined as well as catalysts deactivation and aging rates.

b. Feed composition effects.

Effects of various feed compositions on operating conditions will be determined. These will include compositions that simulate gas streams obtained from air or oxygen coal gasification units.

c. Simulated fluid catalyst study.

The potential for developing a fluid bed version of the process will be determined from fixed bed studies using fluid bed versions of catalysts supplied by the Mobil financed catalyst development program.

d. Diffusion effects.

Where appropriate the effect of mass transport on process parameters will be investigated. Extrapolation of these effects to potential commercial operating conditions will be made.

e. Product tests.

Process potential will be evaluated primarily in terms of product composition and quality. Such factors as relative yields, chemical composition of gas and liquid products, octane number and distillation range will be calculated or measured.

Task 2 - Process Development Research

a. Pilot plant studies.

Those catalysts of particularly high performance, which are identified in Task 1, will be evaluated in greater detail in a 150 cc reactor equipped for both fixed bed or fluid bed operations.

b. Kinetic description and process model.

The effect of operating conditions on product distribution and yield versus catalyst age will be evaluated. Reactor design will be undertaken using information on heat release and catalyst stability to heat and steam obtained from Tasks 1 and 2. Quantification of process variables will be done to provide the basis for a kinetic scheme for use in a kinetic process model.

c. Life test.

A life study by either the fixed or fluid bed mode will be made on at least one preferred catalyst under optimum process conditions as defined in Tasks 1 and 2.

Task 3 - Product Evaluation

a. Lab tests.

Testing will include the use of additive packages, blending characteristics, storage stability, volatility, corrosion, odor, filterability and emulsion tests.

b. Vehicle test.

Where practical, automotive testing will be done using a fuel simulating the product from Task 2.

Task 4 - Economic Scoping and Scale-Up Design

a. Economic scoping to support process studies.

Scoping will include such possibilities as co-production of synthetic natural gas and gasoline.

b. Comparative scoping study.

At an appropriate time, a scoping comparison will be made with the SASOL type Fischer-Tropsch operation.

Task 5 - Report Writing

Periodic reports of progress will be submitted as required by the contract.

II. Summary

The most highly developed technology for the conversion of coal derived synthesis gas to liquid hydrocarbons, is the Fischer-Tropsch process. The Fischer-Tropsch technology, however, is not selective and the hydrocarbons produced range from methane to high molecular weight waxes. Of urgent need are catalytic systems with a high selectivity to specific, liquid hydrocarbon products, such as gasoline or diesel oil.

The work described here was, in part, a continuation of prior exploratory research at the Mobil Research and Development Corporation Laboratories. The early work had identified several catalytic systems for converting synthesis gas, in high selectivity, to high octane number gasoline. This contract, No. EX-76-C-01-2276, jointly funded by DOE and Mobil, was awarded to assess the process potential of these catalysts. The work was started in July, 1976.

The majority of the effort was concentrated on two developmental catalyst compositions, designated SGF-B-1 and SGF-A-3. Catalyst SGF-B-1 has little or no water-gas shift activity and requires, for high carbon monoxide conversion, a synthesis gas having a H_2/CO ratio of at least two. The preferred operating conditions for this catalyst are 500°F, 200 psig and 500 GHSV on fresh feed. The fresh catalyst gave a H_2+CO conversion of 94% and a selectivity to C_5^+ gasoline of 75% having a clear, research octane number of 83. In one series of experiments in the fluid, bench-scale unit, with intermittent regenerations, catalyst SGF-B-1 was used to process $2H_2/CO$ synthesis gas for 40 days. The H_2+CO conversion ranged from 83 to 94% with an average conversion of 89 mole %. The C_5^+ gasoline selectivity ranged from 50 to 75%, with an average selectivity of 63 wt %. The raw liquid product was low in oxygenates, boiled within the gasoline boiling range and had a clear research octane number of 83. Catalyst SGF-B-1 is amenable to a limited number of oxidative or hydrogenative regenerations. Conditions were not found where this composition is stable to multiple regenerations. Catalyst life is estimated to be about two months.

The second composition, catalyst SGF-A-3, has water-gas shift activity. Thus, catalyst SGF-A-3 can use low H_2/CO ratio synthesis gas, which is expected to cost less than higher H_2/CO gases. The expected lower cost is related to the smaller amounts of steam needed in the gasification system. In one continuous 23 day run in the fluid, bench-scale unit using synthesis gas with a H_2/CO ratio of one, the average H_2+CO conversion was 76%. The C_5^+ gasoline produced averaged 54% and had a 90.5 clear, research octane number. During the 23 day period the effects of temperature and pressure were studied at 1000 GHSV and a recycle ratio of two. The conversion ranged between 52 and 88%, the C_5^+ gasoline selectivity between 43 and 66% and the octane number between 87.6 and 94.9. Catalyst SGF-A-3 was shown to be stable to multiple regenerations in related micro reactor unit work. However, there was evidence of catalyst attrition in fluid unit operation.

In a study done in DOE Contract No. EF-76-C-01-2447, a gasoline of the type prepared with catalyst SGF-A-3 was compared to one obtained from the Fischer-Tropsch process. The comparison showed, that in preparing gasoline from coal, the Mobil route has the potential of being 20% less expensive than Fischer-Tropsch.

The contract work was exploratory in nature. The process studies were carried out using fixed bed, micro reactor units (10 cc catalyst capacity), and both fixed and fluid bed, bench-scale units (150 cc catalyst capacity). The Mobil Research and Development Corporation proprietary catalyst research effort provided the catalysts for the process development studies. A unique feature of these catalysts in synthesis gas conversion is that they do not yield oxygenates, and the largest hydrocarbon molecules formed boil within the gasoline boiling range. Thus, compared with Fischer-Tropsch catalysts, the Mobil catalysts are highly selective.

The scope of the work encompassed the definition of commercially feasible process conditions, the effects of a variety of feed compositions, the effects of various catalyst pretreatment procedures, catalyst aging rates, the effects of various catalyst regeneration procedures, the analyses of gas and liquid products, and the measurement of octane number and distillation range of the liquid product. The small amounts of product prepared at any one process condition, and the lack of a source for components to prepare a simulated product, precluded extensive bench and vehicle quality testing of the gasoline produced. In addition to the direct conversion work, a brief study was made on the preparation of methanol/dimethylether mixtures for subsequent conversion to gasoline. Completed theoretical studies in support of the process development included: thermodynamic equilibrium for carbon formation, relationship of single pass to total conversion, water-gas shift activity of specific catalysts, heat loss calculations for the bench-scale fluid unit, and a heat and mass transfer study.

Originally both an adiabatic fixed bed and a fluid bed process were considered for development. However, reactor plugging due to carbon deposition and/or heat removal problems, even at recycle ratios of light gas to fresh feed of 15/1, resulted in termination of the fixed bed work.

III. Introduction

As the world supply of petroleum diminishes, alternate sources of fuels are being sought. Power generation may be satisfied by coal or nuclear fuel, however, the need also exists for gaseous and liquid fuels. Low BTU gaseous fuel can be prepared by the gasification of coal, and methane (SNG) production from synthesis gas is a highly developed technology. The technology for the production of transportation fuels, such as gasoline and diesel oil, from coal at low cost is not highly developed.

In 1976, Mobil Research and Development Corp. announced a catalytic process for converting methanol to high octane gasoline in high yield(1,2). Commercial processes for the conversion of coal derived synthesis gas to methanol are known; thus, this new technology provides an indirect route for the preparation of gasoline from coal. The chemistry involved in going from methanol to gasoline has been outlined by Chang and Silvestri(3). Under an ERDA contract, No. E(49-18)-1773, the development of a fixed bed methanol conversion process was studied and a 100 BPD fixed bed pilot plant was designed(4). More recently, under DOE contract No. EX-76-C-01-2490, the conversion of methanol to high octane gasoline in a 4 BPD, fluid catalyst unit was demonstrated(5).

The direct conversion of synthesis gas to oily hydrocarbons was first reported in 1923 and the process, the Fischer-Tropsch reaction, is named for the discoverers(6). Excellent reviews on early Fischer-Tropsch chemistry have been written by Storch, et al(7) and by Anderson(8). One commercial plant, at SASOL in South Africa, is currently producing liquid fuels and alcohols using Fischer-Tropsch technology.

The Fischer-Tropsch process is nonselective, however, and the hydrocarbon products range from methane to high molecular weight waxes. The products are also of poor quality, the raw gasoline having a clear, research octane number of only 55. Product upgrading is complicated by the presence of appreciable amounts of oxygenates.

The Fischer-Tropsch reaction may be represented as a polymerization process with $[CO + 2H_2]$ as monomer and the

$$nCO + 2nH_2 \longrightarrow [CH_2]_n + nH_2O$$

molecular weight distribution of the primary products being described by the Schultz-Flory equation(9). Thus, the highest attainable selectivity for a given carbon numbered product can be calculated. Using iron catalysts similar to those used at SASOL, Dry reports(10) that in both theory and practice "...it seems impossible to produce more than ca. 17% C_2 or C_3, 40% gasoline, 18% diesel and 22% medium wax (C_{24}-C_{35})."

Mobil Research and Development Corporation has discovered a series of catalysts that will convert coal derived synthesis gas to high octane number gasoline in selectivities higher than predicted by the Schultz-Flory equation. The process potential of these catalysts was assessed under Contract No. EX-76-C-01-2276, jointly funded by DOE and Mobil Research and Development Corp.

IV. Detailed Description of Technical Progress

A. Experimental Equipment and Procedures

Process development studies on the direct conversion of synthesis gas to gasoline were done in both micro reactor (10 cc catalyst capacity) and in bench-scale (150 cc catalyst capacity) units. The bench-scale unit was operated either in the fixed- or fluid-bed mode. Preliminary catalyst fluidization studies were done using a plexiglass replica of the fluid-bed, bench-scale unit. One micro reactor unit was also used to study the conversion of synthesis gas to an equilibrium mixture of methanol/dimethylether.

Gas chromatography was used to identify charge stock and product composition. For bench-scale experiments, the analyses of products were automated and a sophisticated computer system was used for data reduction.

1. Task 1 - Exploratory Process Research

a. Units Used With SG-A and SG-B Catalysts

The micro reactor unit design permitted rapid catalyst loading and start-up and ready adjustment of process variables while on stream (Figure 1). The reactor was made from a single piece of 304 SS tubing (0.035" wall), 0.5"-O.D. and 14" long with a 0.063"-O.D. SS tubing thermowell extending the full length of the tube. Allowing for reasonable preheat and disengaging zones, this permitted catalyst loadings of up to 10 cc. Catalyst particle size was 12/25 mesh. A constant catalyst bed volume of 10 cc was maintained by dilution with 12/25 mesh quartz, which was also used to fill any reactor void spaces. The reactor was encased in a cylindrical aluminum block which in turn was inserted in a nominal 1"-I.D. pipe heat traced with nichrome ribbon and insulated. Temperature was controlled by an iron-constantan couple through a proportional band temperature controller. The couple was located beneath the nichrome ribbon furnace windings and insulated from them.

Gases of various compositions were fed from cylinders at operating pressures up to 600 psig and temperatures to 1000°F. When charging synthesis gas, activated charcoal scrubbers were used to remove iron carbonyl formed in the cylinders. Reactant flow was downward through the reactor and a Moore constant differential flow controller was used at operating pressures up to 400 psig. At higher pressures the controller was bypassed and flow rates were controlled by means of a fine metering valve. An ethylene glycol system was used to measure flow rates while processing was in progress. Reactor pressure was maintained with a back pressure regulator of the Grove type.

The micro reactor units were also equipped with safety features that resulted in automatic shutdown for high temperature, combustible gas, or low pressure. In addition, carbon monoxide was constantly monitored with an alarm sounding at the 50 ppm level.

For a typical experiment the catalyst loading and space velocity were selected to correspond to 1-3g of synthesis gas charge per hour. The catalyst was activated in situ and then cooled to about 180°F. The reactor pressure was adjusted to that of the experiment with the selected synthesis gas composition and the proper feed rate was established. The reactor was then heated, at about 18°F/min, to the desired experimental temperature. After a three hour equilibrating period at process conditions, the balance run was started. Material balances were 20-24 hours in order to provide sufficient liquid for analyses and to minimize errors resulting from losses due to hold up.

The total reactor effluent was cooled and passed into a high pressure separator. The high pressure off-gas was expanded continuously to atmospheric pressure through the back pressure regulator. After passing through a dry ice/acetone trap and gas sample bombs, the gas volume was measured with a wet test meter. At the completion of the balance, liquid in the high pressure separator was drained by gravity into the product receiver where it was isolated from the remainder of the system. The liquids that accumulated in the dry ice/acetone trap were weathered through gas sample bombs and the wet test meter at ambient temperature. The residual liquid was combined with the hydrocarbon collected in the product receiver.

Product separation and analytical tests used are shown in Figure 2. The liquid product was separated into a water and hydrocarbon phase. The water phase was intermittently analyzed for organic oxygen content and acid number. The two gas samples were analyzed by mass spectrometry. The liquid hydrocarbon product was subjected to various tests including simulated distillation by gas chromatography (GC), minimicro octane number, C_5 olefin distribution (GC), estimation of the 90% overhead boiling point, and a complete product breakdown (GC).

b. Units Used With SG-C and Ether Catalysts

The two micro reactor systems used in the fixed-bed studies with catalysts SG-C-1, -2, and -3, SG-A-3, and the dimethylether synthesis catalysts can be illustrated with the diagram in Figure 1. These units were similar in function to those already described but employed somewhat smaller reactor tubes. These tubular reactors were constructed from 3/8"-O.D. tubing with a 1/8"-O.D. annular thermowell. Typically 3 to 5 cc of catalyst were charged to the central portion of a vertical tube heated by a 12" tube furnace. The upper (preheater) and lower (supporter) sections were filled with an annular pyrex glass tube to reduce internal volume and provide heat transfer surface.

Figure 1

MICRO UNIT FOR SYNTHESIS GAS CONVERSION (SCHEMATIC)

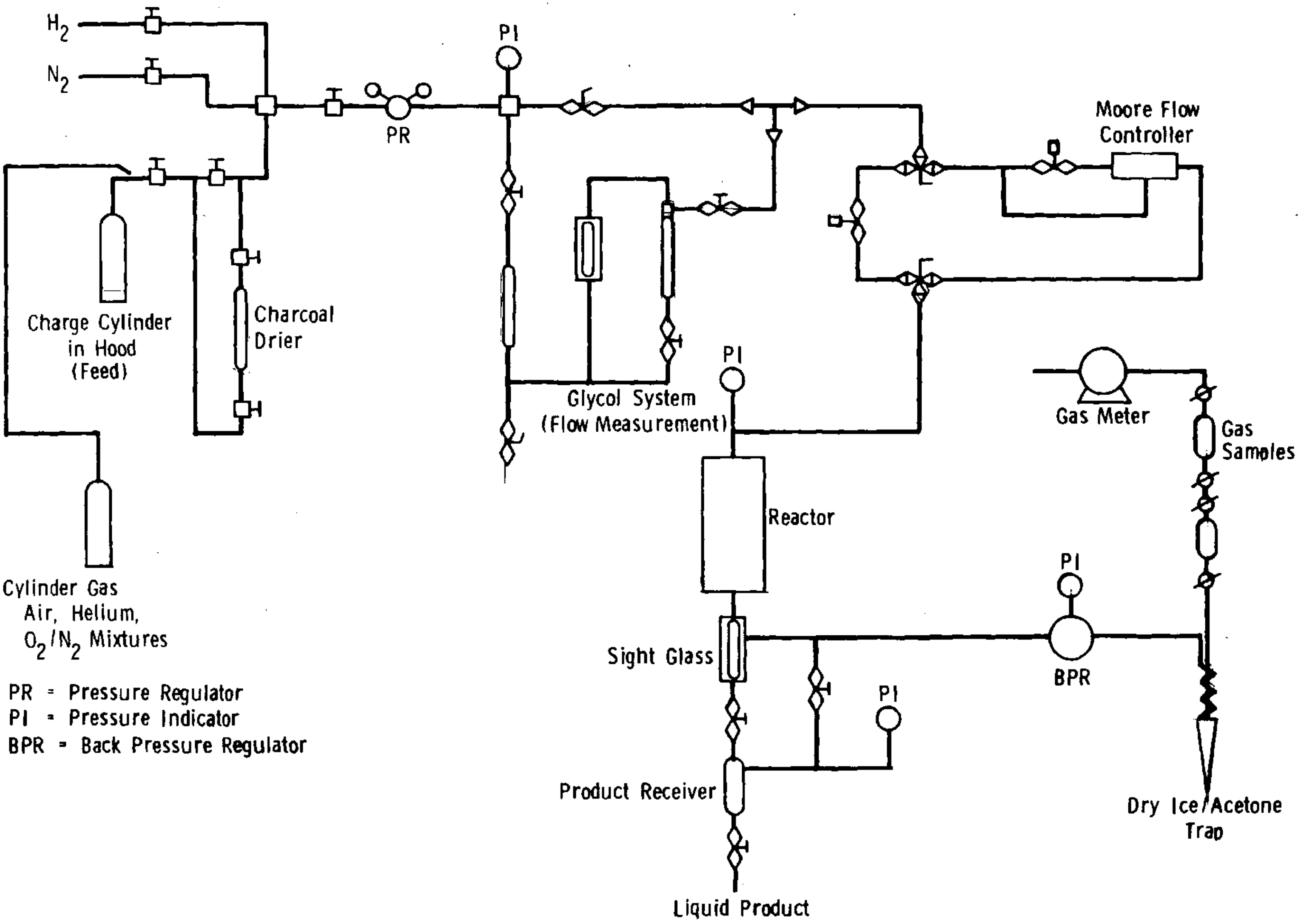
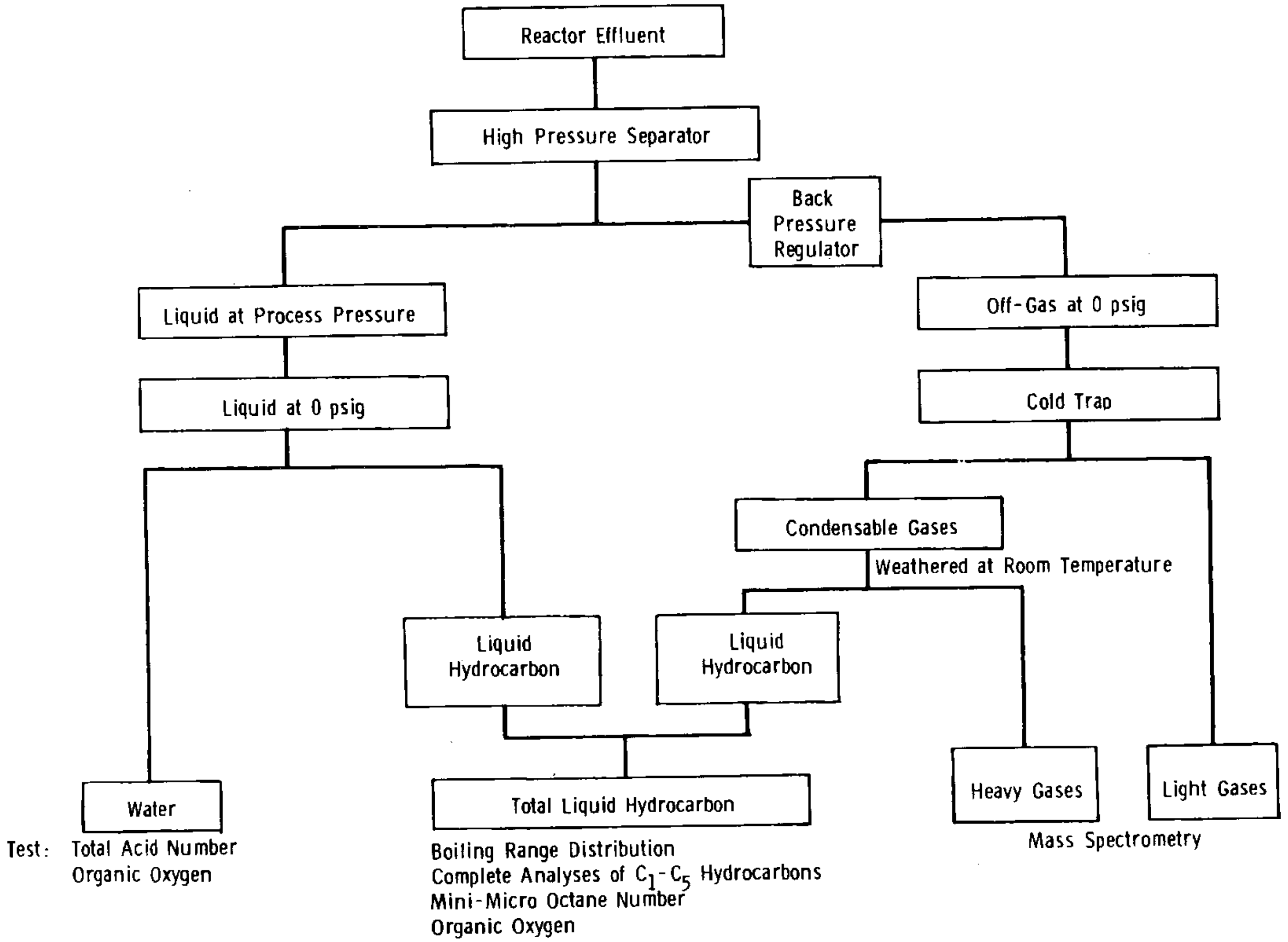


Figure 2

PRODUCT SEPARATION AND ANALYSES – MICRO REACTOR EXPERIMENTS



Following Pichler(11), and as in the case of those reactors described earlier, steel alloys containing more than 17% chrome were utilized throughout the reactive regions of these systems. Some "activation" for syngas conversion was observed in blank experiments (H_2/CO) at conditions more severe than our experiments [hydrocarbon production (∿70% CH_4) of <40 μgm/hr/hr-of-operation]. This small activity in the worst case amounted to less than 9% of the methane experimentally observed while processing with SG-C catalysts, and could be neglected.

Because of the higher pressures (up to 1500 psig) used in these experiments and the availability of other equipment, minor modifications of the reactor system illustrated in Figure 1 were made. For example, feed gas was pumped from 1500 to 500 psi gas cylinders to the reactor system by an air-driven compressor. Thermal mass flow controllers (Brooks Instrument Company Type 5810) provided constant mass input at pressures up to 1500 psi. Condensable liquids (room temperature) were collected in a trap at reactor pressure which could be isolated from the product stream, and allowed the condensed gases to be expanded into an evacuated bulb system (0.5 to 3.5 liter). This permitted removal of liquid products (H_2O, methanol, gasoline) in a 3 cc glass container.

Occasionally water or H_2S containing syngas was cofed to the inlet of the reactor using appropriate low flow piston pumps (Instrument Specialties Company Model 514) or separate (sulfur contaminated) high pressure tank-mass flow meter systems.

c. Plexiglass Flow Model

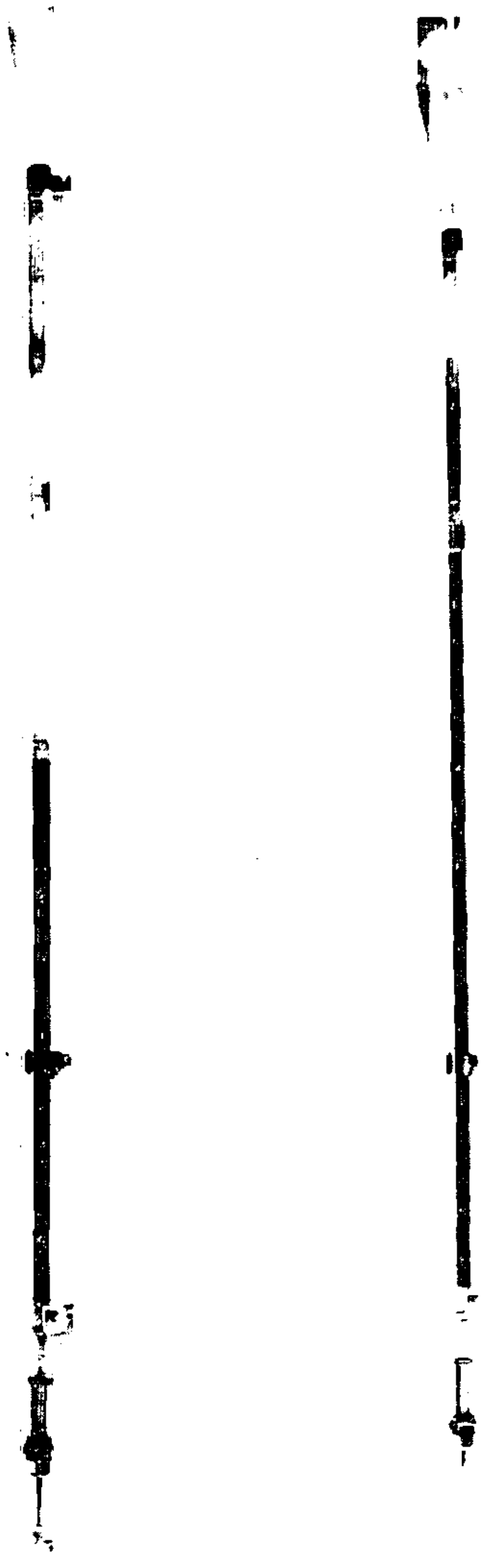
The plexiglass model of the bench-scale, fluid reactor consisted of a 3/4"-I.D. tube approximately 44" long with a 17" disengaging zone. Photographs of the model depicting settled and expanded catalyst beds are shown in Figure 3. Gas exiting this zone passed successively through a knock-out vessel, a 40-60 micron filter disk, and a water bubbler before being discharged into a hood. The distributor assembly slid into the plexiglass tube and was sealed at the distributor plate with asbestos packing, as well as at the gas inlet via a 3/4" Swagelok fitting.

The model was equipped to charge cylinder gases at pressures to 6 psig. The flow rates were measured with a dry gas meter. The flow studies consisted of visual observation and measurement of bed expansion at various linear velocities. No facilities were available to measure pressure drop or other parameters such as bubble size and frequency.

To observe the proper flow dynamics in the reactor model, it was necessary to choose gases having properties at ambient conditions similar to those of the total bench-scale unit charge at operating pressure and temperature (∿500°F and 200-300 psig). This could be done representatively with a gas having the same

Figure 3

FLUIDIZATION IN PLEXIGLASS MODEL



Reynolds number ($Re_p = d_p u_o \rho_g / \mu_g$) as the bench-scale charge. Since particle diameter (d_p) and superficial linear velocity (u_o) were constant, the gas density/viscosity ratio (ρ_g/μ_g) determined the gas to use at ambient conditions.

Assuming a total charge to the bench-scale unit of $0.9H_2/1.0CO/0.3CO_2/3.4CH_4$ at 500°F and 200 or 300 psig, the gases selected were Freon-22 and sulfur hexafluoride. They are both non-toxic and unreactive at ambient conditions and were readily available. The following data show why these gases were selected.

		Density, ρ gm/cc	Viscosity, μ gm/cm sec	Ratio of ρ gm/liter to μ centipoise
Bench-Scale Unit Charge				
500°F, 200 psig		5.78×10^{-3}	2.00×10^{-4}	289
500°F, 300 psig		8.46×10^{-3}	2.01×10^{-4}	421
Air	70°F, 1 atm	1.21×10^{-3}	1.8×10^{-4}	67
SF_6	70°F, 1 atm	6.41×10^{-3}	1.53×10^{-4}	419
Freon-22	70°F, 1 atm	3.64×10^{-3}	1.27×10^{-4}	287

Freon-22 and SF_6, thus, simulated 200 and 300 psig operation, respectively. Air is shown to illustrate the large difference in transport properties and would have resulted in quite misleading results had it been used.

2. Task 2 - Process Development

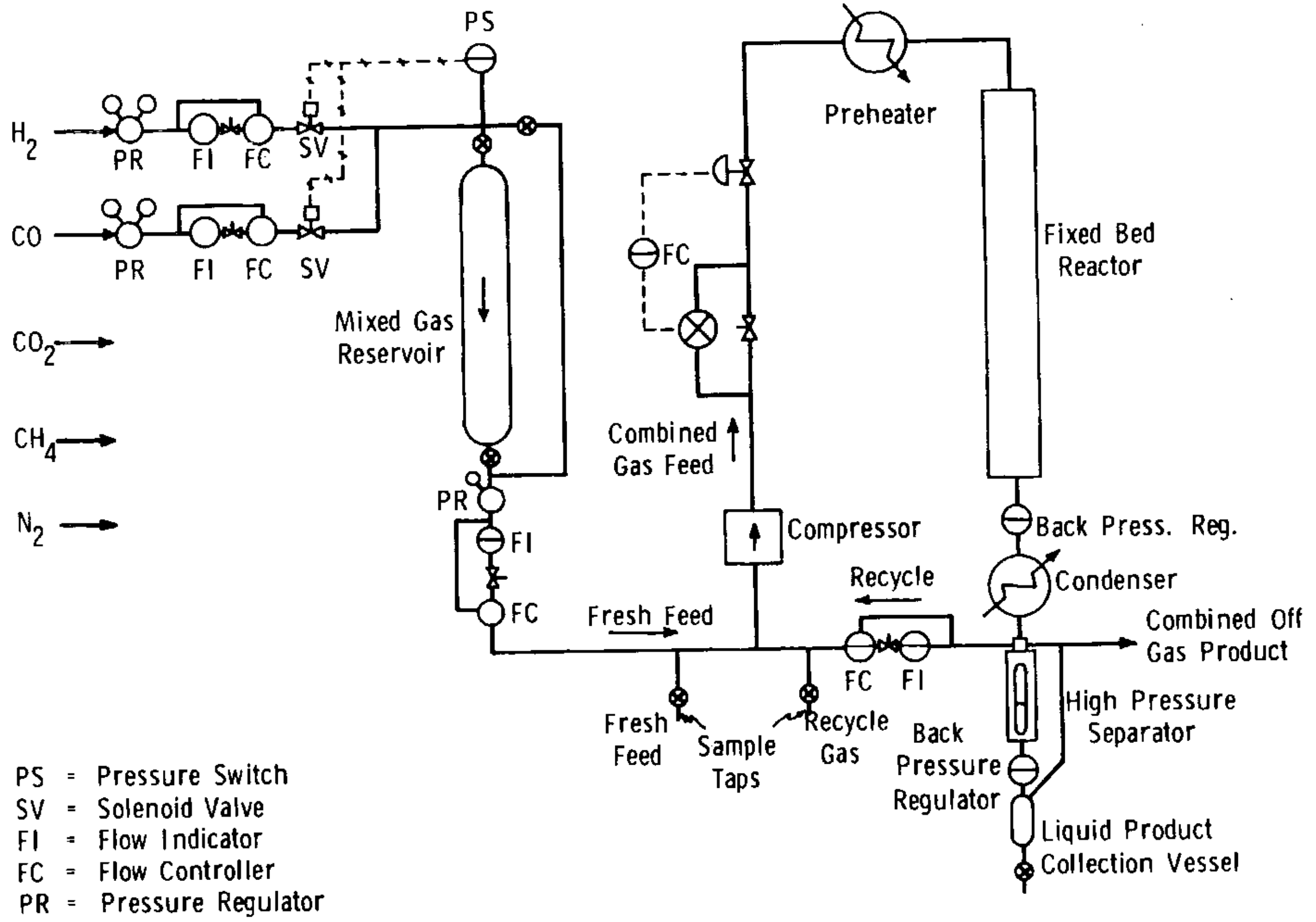
The bench-scale unit was designed to operate at pressures up to 1000 psig, temperatures up to 900°F, and at gas hourly space velocities (GHSV) between 500 and 2000 (Figure 4). By interchange of the reactor portion, the unit could function in either a fixed- or fluid-bed mode. The reactor capacity was 150 cc. Provisions were present for the mixing of up to five different gases, in any proportion, for use as fresh feed to the unit. The recycle system provided recycle ratios up to 25/1. The unit consisted of three primary parts: the fresh feed and recycle system, the preheater and reactor sections, and the product separation and collection system.

a. Fresh Feed and Recycle

Fresh feed mixtures of synthesis gas were prepared by blending up to five individual gas streams through a manifold and were stored in a reservoir which was regulated between 110 and 150 psig.

Figure 4

SCHEMATIC OF THE BENCH-SCALE UNIT FOR SYNTHESIS GAS CONVERSION (CT 225)



PS = Pressure Switch
SV = Solenoid Valve
FI = Flow Indicator
FC = Flow Controller
PR = Pressure Regulator

The fresh feed, controlled at 100 psig, was mixed with the recycle gas and supplied to the reactor by a compressor capable of delivering up to 70 SCFH at pressures in excess of 1000 psig. The recycled gas consisted of unreacted fresh feed gases and low molecular weight compounds formed in the reaction.

The flow rates of both the fresh feed and the recycle gases were monitored by a computerized glycol displacement measurement system. Adjustments of the flows were made manually.

b. Preheater and Reactor

The mixed feed gases were passed through an external preheater and a heat-traced transfer line to the reactor. The unit was designed so that either a fixed- or a fluid-bed could be used.

The fixed-bed, adiabatic reactor consisted of a 1-19/64" I.D. stainless steel tube with an internal preheater section (Figure 5) and contained a basket designed to hold about 25 to 100 cc of catalyst. The reactor was mounted vertically; the catalyst section was about 15" long and the feed flow was downward. The reactor was heated with an insulated furnace which had a set of heating coils adjacent to the reactor tube and additional heating coils removed from the reactor and used to neutralize heat losses.

Pelleted or extruded catalysts were used. Solid metal spacers, with longitudinal holes to allow passage of the thermocouple, were used to position the catalyst bed, stabilize flow patterns and minimized temperature gradients.

A computer controlled thermocouple traversed the reactor and automatically recorded temperatures above, below and within the catalyst bed.

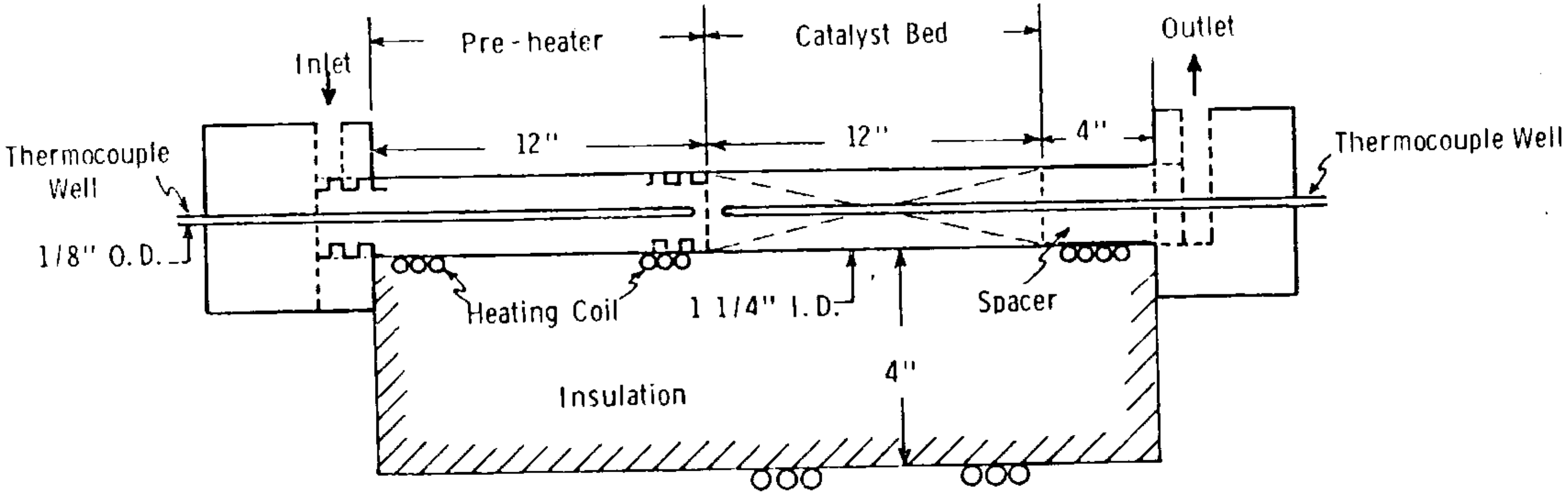
The fluid-bed reactor (Figure 6) was about 5-1/2' tall and consisted of a 3/4"-I.D. stainless steel tube 4' long surmounted by a 2-1/2"-I.D. catalyst disengaging section. The reactor section was surrounded by ten individually controlled heaters to maintain isothermal conditions along its length. Temperatures were recorded by thermocouples protruding into the reactor at set intervals.

Fluid catalyst was charged to the reactor through a side port at the disengager zone. A nitrogen flow of about one SCFH was maintained during loading to prevent packing of the catalyst. The normal catalyst loading was 100 to 150 cc. The length of the dense catalyst bed was dependent on packed volume, catalyst density and size distribution, linear gas velocity, and gas properties. In operation, the effective catalyst bed length was 2.5 to 3.5 feet.

A mixture of fresh feed and recycle gases entered the bottom of the reactor through a gas distributor composed of a stainless steel screen sandwiched between two metal plates perforated

Figure 5

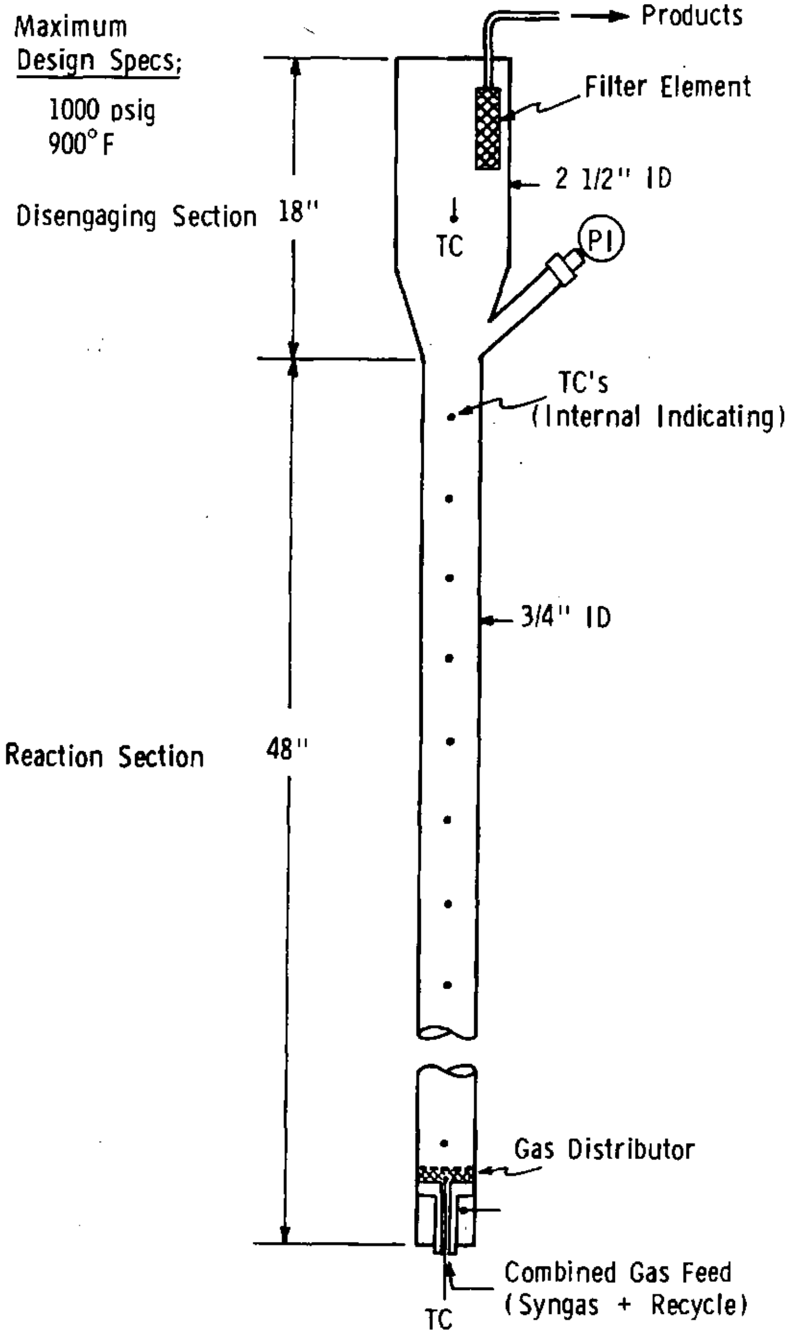
SCHEMATIC DRAWING OF FIXED BED BENCH-SCALE REACTOR



Dimensions Not To Scale

Figure 6

REACTOR FOR SYNGAS FLUID BED PROCESS (SCHEMATIC)



with 18 small orifices. The gas mixture reacted in the fluidized catalyst bed, passed up the reactor to the disengaging zone where it separated from the catalyst, and exited through two, parallel, stainless steel, porous filters where any entrained catalyst dust was removed.

In operation the catalysts were activated in situ using single-pass gas flow. The unit was then brought to process conditions. This entailed establishing the temperature followed by an increase from atmospheric to operating pressure. The pressure change was straight forward for the fixed-bed reactor. However, for the fluid-bed reactor it was necessary to maintain a gas linear velocity sufficient for fluidization of the catalyst yet not so high as to carry catalyst up against the filters in the disengager zone. Consequently, as the pressure was increased, the gas flow rate was also increased to compensate for pressure-volume contraction. Also for fluid operation, when changes in temperature were necessary, the gas flow was adjusted to compensate for the effect of temperature on volume.

c. Product Separation and Collection

The effluent from either reactor passed through a water cooled condenser to a high pressure separator. Some of the gaseous product was recycled the remainder was measured. The two phase (hydrocarbon and aqueous) liquid went to a product receiver. The "heavy" gas that weathered from the liquid product was combined with the light gas from the reactor and analyzed by GC (gas chromatography).

Approximately sixteen hours of operation were required to fill all vessels and lines between the reactor and the product receiver and to bring the recycle gases to equilibrium. Material balance runs varied from 15 to 24 hours, depending on space velocity, catalyst volume and conversion.

3. Analytical

Two types of analytical services were used in support of the process development studies. Gas chromatographs were used for on-site analyses and off-site services were furnished by the Paulsboro Analytical Section. Together these analyses allowed an evaluation of process potential by providing conversion, rate of catalyst aging, a detailed product composition and mass balance data. The material balance program listed the detailed weight and volume composition of about 90 single compounds or groups of compounds. Carbon, hydrogen and oxygen balances were also calculated from the compositional data.

Although the GC equipment used at the bench-scale unit differed from that used at the micro units, the primary difference was that bench-scale unit gas samples were obtained on-line via a sample manifold between the unit and the chromatograph. Batch samples from the micro units were collected in gas sample bombs. For both units the liquid phases were collected and submitted for detailed analyses.

a. Micro Reactor Units

Four samples were collected for analyses from the micro reactor units, two gaseous, one liquid hydrocarbon and one aqueous as shown in Figure 2.

The procedures used with the SG-C catalysts differed slightly from the above. Run times were shorter and a single batch gas sample was collected. This was analyzed using a Hewlett Packard Model 5830A Refinery Gas Analyzer. This was similar to the on-line gas analysis used with the bench-scale unit (below).

For the synthesis gas conversion to mixtures of methanol/ dimethylether the gas was analyzed as above, and a second portion was analyzed on a Porapak T column which separates components in the order: dimethylether, water, methanol. The aqueous phase was also analyzed on the Porapak T column.

b. Bench-Scale Unit

Samples of fresh feed, recycle and combined gases were obtained at the sample taps shown in Figure 4. The fresh feed and combined gas streams were delivered to the GC via a manifold maintained at ambient temperature. The recycle gas was delivered through a heated, rotary stream select valve and a heat traced sample line. Liquid hydrocarbon and aqueous samples were analyzed off-line(12).

Chromatograph peak detection and integration, timing functions, and post run data processing and reporting were performed on a Mobil-designed PDP 8/E based GC computer system(13). This system can monitor six detectors simultaneously and perform up to 58 events at the desired times.

The hydrocarbon liquid phase analyses were performed using a multicolumn GC system. A detailed composition of about 90 compounds or groups of compounds was reported(14).

4. Data Handling

Data generated at the bench-scale unit were transmitted through a Mobil-designed computer network(15). A DEC PDP 8/E based data logging computer was used to monitor operating conditions and also served as an alarm in the event of an upset. A PDP 8/E based GC-Computer was used for sample analyses. Operators added supplementary data from readings taken from the unit. These data were combined, entered into a computer file and made available to a material balance program.

The data from these computers are transmitted through a PDP 11/40 computer to a data base on a DEC 20/50 computer where the final results were readily accessed through time sharing terminals. Raw data and final material balance results are also available on back-up tapes. A portion of the final material balance is shown in Appendix A.

5. Task 4 - Studies in Support of Process Development

a. Single Pass Versus Total Conversion

All of the micro reactor units used in Task 1 were single pass reactors and gave "single pass conversions," C_s. The single pass conversion of a reactant, A, is defined as:

$$C_s \text{ of A(mole \%)} \equiv 100 \quad \left(1 - \frac{\text{moles A at reactor exit}}{\text{moles A at reactor inlet}} \right)$$

However, the fixed bed, bench-scale unit used in Task 2 removes exothermic reaction heat with a recycle stream of light gases from a separator located downstream from the reactor. Hence, conversions of either H_2, CO or (H_2+CO) observed in bench-scale unit experiments include the conversion of that component in the fresh charge plus conversion of that same component in the recycle stream. This type conversion, disguised by the recycle operation, is called "total conversion," C_t, and is defined as:

$$C_t \text{ of A(mole \%)} \equiv 100 \quad \left(1 - \frac{\text{moles A in product stream}}{\text{moles A in fresh charge}} \right)$$

Assuming that only negligible amounts of H_2 or CO are dissolved in the liquid products, the single pass conversion of H_2, CO or (H_2+CO) in bench-scale unit experiments can be estimated from the following equation,

$$C_s = C_t \left(1 + \frac{MR}{A_F} \right)^{-1}$$

where

M = reactant A in the recycle stream (mole %)
R = recycle ratio
A_F = reactant A in the fresh charge (mole %)

Thus, the single pass conversion could be readily estimated from the total conversion provided the recycle gas composition, recycle ratio and fresh charge composition were known. Knowledge of the single pass conversion in bench-scale unit experiments can be very useful, as it provides a direct measure of catalyst activity without the disguise of the gas recycle.

b. Survey of Coal Gasifiers

The synthesis gas that would be used in a Mobil direct conversion reactor would be obtained from coal gasification, water-gas shift reaction, and raw gas purification steps. Among these three steps, the choice of gasifier will have the biggest effect on the operation, thermal efficiency, and economics of the process. Hence, a survey on some promising coal gasification schemes was made(6-13). The information summarized in Tables 1 and 2 are for those gasifiers whose detailed process material and energy balances are presently available. Table 1 lists two moving bed and three fluidized bed gasifiers. Among them, the "Lurgi Dry Ash" and the "Winkler" have been commercially tested. Table 2 lists six entrained bed gasifiers and among them, only the "Kopper-Totzek" has been commercially tested.

The information in Tables 1 and 2 was used in the selection of feed gas compositions for the process variable studies.

6. Materials

All of the gases used were chemical grade and, with the exception of Freon-22 were purchased from Matheson Gas Products. Freon-22 was obtained fron Allied Chemical.

All catalysts were coded and supplied by the Mobil R&D Corp. proprietary catalyst research program. The catalysts provided are listed in Table 3. On occasion, spent catalysts were returned to the Mobil program for further study.

TABLE 1

MOVING AND FLUIDIZED BED COAL GASIFIERS

	Gasifier Type				
Gasifier	Lurgi Dry Ash	Lurgi Slagger	IGT U-Gas	IGT Hygass	Winkler
Coal	Illinois #6	Illinois #6	Illinois #6	Montana Subbituminous	German Dry Brown Coal
Temperature, °F	900-1078	900-2800	1550	600-1850	1700
Pressure, psia	355	300	340	1170	30
Raw Gas, % vol					
H_2	20.92	28.37	30.79	15.20	25.81
CO	7.49	54.15	36.27	12.92	23.46
CO_2	15.28	1.80	13.11	11.98	14.55
CH_4	4.28	7.24	5.88	8.26	1.23
H_2O	50.50	4.64	12.06	50.43	33.20
H_2S	0.59	1.28	1.11	0.12	0.90
COS	0.03	0.05	0.04	-	0.09
Balance	0.91	2.47	0.74	1.09	0.76
SCF(a)/lb Coal(b)	37.0	34.6	31.9	23.54	23.3
LHV Gas(c)/LHV Coal	0.737	0.889	0.839	0.825	0.614
H_2/CO	2.79	0.52	0.85	1.18	1.10
Steam/O_2	8.45	1.15	1.48	7.06	1.52
Steam/Coal(b), wt	2.58	0.35	0.58	1.05	0.64
O_2/Coal(b), wt	0.54	0.53	0.71	0.26	0.75
Char Recycle	No	No	Small	No	No
Reference	(6)	(7)	(6)	(8)	(9)

(a) Standard Cubic Feet (60°F) of clean dry gas.
(b) Dry ash-free coal
(c) Lower heating value of clean dry gas.

TABLE 2

ENTRAINED BED COAL GASIFIERS

Gasifier	Combustion Engineering	Foster-Wheeler	Bi-Gas	Babcock & Wilcox	Koppers-Totzek	Texaco
Coal	Illinois #6	Illinois #6	Montana Subbituminous	Pennsylvania	Illinois	Unnamed Bituminous 54 wt % Slurry
Temperature, °F	1700	1700	1500	1200	2700	2300
Pressure, psia	15	355	1215	30	15	815
Raw Gas, % vol						
H_2	30.00	30.10	20.51	24.84	30.79	25.54
CO	63.29	35.04	26.42	60.59	49.25	29.46
CO_2	2.44	12.31	16.06	6.48	6.26	13.58
CH_4	-	6.01	10.95	-	-	0.27
H_2O	1.75	14.39	25.52	5.35	11.06	29.56
H_2S	1.26	0.97	0.19	1.25	1.63	1.07
COS	0.09	0.10	-	0.10	0.11	0.06
Balance	1.17	1.08	0.35	1.39	0.90	0.46
SCF$^{(a)}$/lb Coal$^{(b)}$	35.7	34.2	25.8	39.3	34.3	30.8
LHV Gas$^{(a)}$/LHV Coal	0.795	0.859	0.823	0.789	0.724	0.615
H_2/CO	0.47	0.86	0.78	0.41	0.62	0.87
Steam/O_2	-	1.85	2.52	0.10	0.68	-
Steam/Coal$^{(b)}$, wt	-	0.70	0.70	0.07	0.34	-
O_2/Coal$^{(b)}$, wt	0.93	0.66	0.48	1.32	0.89	1.04
Char Recycle	Yes	Yes	Yes	Yes	No	No
Reference	(6)	(7)	(10)	(11)	(12)	(13)

(a) Clean dry gas

(b) Dry ash-free coal

TABLE 3

CATALYSTS PROVIDED FOR PROCESS DEVELOPMENT STUDIES

Identification

Synthesis Gas to Gasoline

Fixed Bed	Fluid Bed	Comments
SG-A-1	SGF-A-1	Fluid version was not used.
SG-A-2	-	Larger particle size SG-A-1.
SG-A-3	SGF-A-2	High attrition in the fluid unit.
SG-A-4	SGF-A-3	--
SG-A-5	SGF-A-4	Removed. More active but less selective than SG-A-4.
SG-B-1	-	Removed. Excessive methane formation.
SG-B-2	-	--
SG-B-3	SGF-B-1	--
SG-C-1	-	--
SG-C-2	-	Harder particles than SG-C-1.
SG-C-3	-	More active than SG-C-1 or -2.

Synthesis Gas to MeOH/MeOMe

Fixed Bed	
WHL 518	--
WHL 525	--
WHL 526	--
WHL 528	--
WB 120877	--