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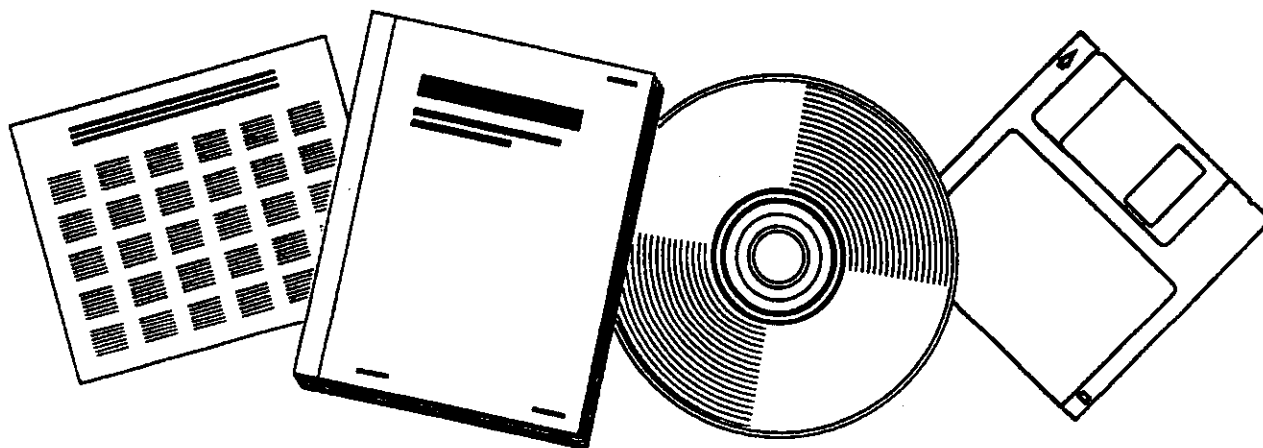Information is our business.

EXPERIMENTAL REACTOR SYSTEM FOR INVESTIGATION OF INDIRECT LIQUEFACTION CATALYSTS IN SLURRY PHASE OPERATION

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ABSTRACT

A detailed description of the slurry (three-phase) reactor scheme employed at the Pittsburgh Energy Technology Center for Fischer-Tropsch synthesis is reported. Emphasis is placed on materials of construction, equipment operation, and product collection and analysis. The unit's functional limits and safety features are also provided. Operational problems and the resolving remedial action are discussed. The reactor scheme now operates such that near isothermal conditions exist over the reactor internal length. Thus, with excellent temperature control assured, reliable information for evaluation of potential catalyst candidates for slurry phase Fischer-Tropsch synthesis is possible within a wide range of operating conditions. Test results with a fused-iron catalyst suspended in a paraffinic liquid medium are given as an example.

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ABSTRACT

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INTRODUCTION

The hydrogenation of carbon monoxide in the classic Fischer-Tropsch synthesis over an iron-based catalyst produces aliphatic hydrocarbons and oxygenates. The main technical problems associated with the Fischer-Tropsch (F-T) synthesis include the following: a large exothermic heat of reaction; local overheating of the catalyst, which favors methane formation; and, finally, a non-uniform distribution of the reactant gas over the catalyst. The slurry, three-phase reactor process was selected for evaluation over other reactor schemes, such as fixed-bed or fluidized-bed, because the slurry scheme for the F-T reaction offers several advantages over the alternative modes of operation (1,2). These advantages include the following:

o   Synthesis gas, rich in carbon monoxide, that will be efficiently produced from second generation gasifiers (3) can be used without plugging the reactor or fouling the catalyst particles, which is caused by the deposition of carbon by the Boudouard reaction.

o   Excellent temperature control and uniformity of temperature within the reactor eliminate local overheating that could lead to excessive methane formation and/or damage to the catalyst.

o   High flexibility with respect to gas composition and operating conditions maximizes yields of products of the desired molecular weight range.

o   High conversions of synthesis gas can be achieved in a single pass.

o   Reactor design and ease of scale-up are simplified.

o   No serious attrition or erosion problems arise.

One potential limitation on the application of synthesis in slurry reactors is the conversion capacity per unit volume of slurry. The ultimate capacity, especially with highly active catalyst and/or high loadings, will be set by gas-liquid mass transfer effects.

The pioneering work in this area culminated in operation of a demonstration plant in Meirbeck and has been summarized by Kolbel and co-workers (1,4). Additional critical input on slurry reactor technology has been provided by the British work at Warren Spring Laboratory (2,5,8), the U.S. Bureau of Mines' studies (6,7), and the investigations at the Kawasaki plant in Japan (9,10).

This report details the design, operation, and analytical techniques employed for a one-liter agitated reactor used at The Pittsburgh Energy Technology Center (PETC) for studying catalyst in a slurry mode.

DESCRIPTION OF SYSTEM

General Operation

A general flow schematic of the indirect liquefaction catalyst testing units at PETC is seen in Figure 1. Synthesis gas is stored in large outdoor (60,000 scf) gas holders at ambient conditions. The gas is then compressed to high pressures (500 psig) and sent through a silica gel trap for dehumidification and through an activated carbon trap at ambient temperature to remove sulfur impurities. The gas is then boosted to 2000 psig by a small Pressure Products Industries diaphragm compressor. The high-pressure gas is stored in a bank of aluminum cylinders, rather than carbon steel cylinders, to prevent formation of iron carbonyl. The gas is then reduced down to 500 psig and sent to another carbon trap that scrubs it of any residual sulfur compounds present. This clean gas is then sent to the slurry unit.

In this system, synthesis gas enters at a pressure of 500-550 psig. This pressure is reduced down, usually to 350 psig, by a pneumatic control valve. The gas flow is then metered and controlled by a Brooks mass flow-meter system. Gas enters the slurry reactor through a 1/8-inch-o.d. tube whose opening is located at the bottom of the reactor. The synthesis gas reacts with the suspended catalyst as it bubbles through the liquid medium. The slurry level within the reactor is maintained by removing excess liquid using pressure as the driving force. A dip-leg is placed at the desired level and connected to a collection trap; by opening the valve in this line leading to the trap, which is at atmospheric pressure, excess liquid is driven out of the reactor. A two-micron filter (porous type-316 stainless steel) is located in this flow scheme to prevent loss of catalyst. The temperature within the reactor is maintained isothermally. Reactor temperatures are periodically measured by a sliding thermocouple in the thermowell that is positioned in the slurry and in the gas headspace.

Products of the reaction and unreacted synthesis gas exit the reactor through a reflux condenser that is located above the slurry reactor and whose exit temperature is usually maintained at 200°C. The stream then enters the "hot" trap, which normally functions at 200°C. The uncondensed products and gases then enter several water-cooled traps. Finally, the remaining uncondensed material exiting the water-cooled traps passes through a trap filled with glass beads. The product gas is reduced in pressure by another pneumatic control valve. The gas is metered by a wet test meter and sent to the main plant flare line. The capability exists to divert a sample of the product stream directly after the pressure letdown valve to a gas chromatograph. This instrument permits determination of the composition of the exit stream for H_2, CO, CO_2, N_2, and C_1- to C_8-hydrocarbons. Gas bottle samples can also be taken of both the fresh feed and the product streams.

A detailed schematic of the experimental arrangement is shown in Figure 2. All components are made of type-304 or type-316 stainless steel. Major components are listed in Table 1. The unit can operate at pressures to 500 psig and temperatures to 340°C. Tubing is type-304 seamless stainless steel in sizes of 3.2, 6.4, and 9.5 mm outside diameter. Wall thickness for each size is 0.7 mm. Valves in the main system are forged-body design with Teflon packing. After the system was pressurized to 450 psig, a negligible decline in pressure was observed overnight before starting

TABLE 1. Major Equipment Items

Component	Manufacturer	Specification
Air-operated control valve	Badger Meter, Inc.	Air-to-open, Teflon-packed, research control valve with a 3-15 psig diaphragm, stainless steel 1/4" body and trims, and type BLRA positioner.
Pneumatic transmitter	Moore Products Co.	Model 173 Helix-Type measures process pressures and transmits a 3-15 psig pneumatic signal proportional to the input span (0-1200).
Flow control	Brooks Instrument Division	Thermal mass flowmeter with automatic control. Consists of (1) flow sensor Model 5810 range 0-5000 sccm, (2) blind controller with integral power supply, Model 5831, (3) final control valve, Model 5835A, (4) command potentiometer, Beckman Model 7246, and (5) digital flow-rate indicator, Model 5839A.
Reactor	Pressure Products Industries	Model 3M5 one-liter, stainless steel agitated reactor with permanent magnetic drive and two-zone mantle heater, with air motor.
Recording control station	Moore Products Co.	Model 5311 M/P (miniature panel) recording control station, single pen process recording with indicator showing control point or valve pressure. Attached manifold controller to plug in directly to station.
Pneumatic Controller	Moore Products Co.	Model 561MF Nullmatic Controller - input/output range is 3 to 15 psig. It controls the process variable in response to a signal from the process transmitter.

TABLE 1. Major Equipment Items (Continued)

Component	Manufacturer	Specification
Reactor Temperature Control - Lower Zone	Leeds & Northrup Company	Combination of Series 6430 Electromax III (current-adjusting type) controller, range of 0-1000°C, type 'K' input; and Model 11906, zero voltage power package (SCR), regulated voltage output.
Reactor Temperature Control - Upper Zone, Heated Lines and Trap	Athena Controls, Inc.	Model Series 2100, Type 'K' thermocouple input, solid-state triac output of 12.5 amps at 120 volts.

an experiment. Leaks were eliminated by checking all fittings with a liquid leak detector. System pressure is maintained by a pneumatic feedback control system. A pressure transmitter (12) measures the process pressure and transmits a 3- to 15-psig pneumatic signal proportional to the input span of the transmitter. The control station (13) and controller (14) accept this variable input and provide a pneumatic output to manipulate the final control element to control the process pressure at the prescribed operating point. The final control element is an air-to-open research control valve (15), which by varying the valve trim can accommodate a wide range of flows.

Reactor

Synthesis is carried out in a one-liter, stainless-steel Pressure Products Industries permanent magnetic-drive agitated reactor (16), illustrated in Figure 3. The reactor has a 7.6-cm (3-inch) inside diameter and an internal height of 24.1 cm (9.5 inch). The reactor also contains (a) baffle bars, (b) agitator, (c) thermowell, (d) cooling coil, (e) gas inlet, (f) slurry level dip-leg, and (g) outlet port. Three baffle bars are spaced 120 degrees apart. Each bar is 17.8-cm-long and 1.0-cm-wide. The agitators employed were of two types. The standard agitator is a six flat-blade turbine with a 5.1-cm diameter and is set 3.2 cm above the vessel bottom. Each blade is 1.3 x 1.0 cm, and a blade is positioned every 60 degrees. The agitator employed for the majority of experiments performed was the "Gaspersator" turbine. It consists of a hollow shaft and a shrouded, six flat-bladed turbine arranged so that the gas phase is drawn down through the hollow shaft and dispersed from the tips of the turbine blades. These two agitators are shown in Figure 4. This inner agitation assembly is driven by a magnetic coupling developed between two sets of ceramic magnets. The external set is rotated by an air motor and vee-belt drive. The air motor delivers up to 1.5 hp, and speeds may be varied from 300 to 2,500 rpm.

The gas-inlet sparger was originally a porous stainless steel sintered element. This, however, would become plugged with either catalyst or carbon over a period of time. It was replaced with an open-ended tube of 1.8-mm internal diameter. The inlet is located at the bottom of the reactor and directly in the center. As long as a slight positive pressure was maintained on the inlet line, plugging of the inlet stream was prevented.

The reactor outlet port is located on the cover flange. A porous type-316 stainless steel element was installed to prevent carryover of catalyst or carbon particles. The porous element was a 2-micron filter.

A level adjustment line containing a 2-micron filter is positioned to maintain an unexpanded slurry volume of 500 mL within the reactor at any operating temperature. The filter prevents the removal of free carbon or finely ground catalyst while adjusting the slurry level. In order to perform the adjustment, the agitator is turned off, the gas flow is reduced to ten percent of its value, and the contents are allowed to settle for 15 minutes. Backflushing with helium several times so that the liquid overflow approaches zero may be required. This procedure is performed on a daily basis to determine how much product has remained within the reactor. Depending on the particular experiment, the material collected can account

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for upwards of forty percent of the total liquid hydrocarbon material recovered.

The reactor is heated by a two-zone mantle furnace that fits snugly around the unit and a heating tape that fits around the body and cover flanges. The heat input to the lower zone of the mantle heater is regulated by the application of a solid-state (silicon) switching power package (17) in combination with a current-adjusting controller (18). The controller receives a dc signal from a chromel-alumel (Type K) thermocouple that is embedded in the furnace wall, compares the input signal with the set point, and then provides an output to the power package whose magnitude varies with the deviation of the input signal from the set point. The power package then provides load voltages up to 120 volts at a maximum rms current of 23 amperes to the heating element. The heat input to the upper zone is controlled by a three-mode controller with an analog set point (19). Input is provided by a chromel-alumel thermocouple embedded in the upper heating mantle, and the output is a triac, zero-voltage-switched. This operates in a similar manner to the previously explained lower zone.

A Briskheat flexible heating tape is wrapped around the flanges and covered with 2-inch-thick Fiberfrax insulation. This tape consists of finely stranded resistance wire with heavy braided fiberglass insulation. It is 2.5-cm-wide and 243.8-cm-long, delivers 768 watts at 120 volts, and can operate to 425°C continuously or to 540°C intermittently. This heater is controlled by the same type device described for the upper zone of the mantle heater. The reactor temperature over the entire length can be held within ±2°C, as measured by a Type K thermocouple located in the thermowell. This thermocouple is movable to a depth of 17.8 cm from the cover flange face, thus providing a detailed internal temperature profile of the reactor, both in the slurry and gas phases.

The reactor temperature is controlled on the skin between the vessel and heating mantle and between the flange surface and the heating tape to detect any temperature changes with little thermal lag. These dual-headed Type K thermocouples, one located in each of the areas described above, provide information necessary to maintain the internal reactor temperature at isothermal conditions. One lead from the dual-headed thermocouples supplies information to a multipoint recorder to maintain a permanent record. The second lead provides the input signal to the various controllers. A correlation between the outside temperature and that measured in the thermowell is required. In the system, for example, to maintain the reactor at an isothermal temperature of 275°C requires the following settings: 270°C in the lower zone, 277°C in the upper zone, and 270°C in the flanges. These settings will change with amount of synthesis gas converted.

The heat produced by the exothermic Fischer-Tropsch reaction is partially removed by air passing through the internal "cooling" coil. The wrapped coil is type-316 stainless steel with a 0.95-cm outer diameter and 0.64-cm inner diameter, and is 86.4-cm-long. The flow of air to this coil is controlled by a regulating (research control) valve, activated by the reactor sliding thermocouple. The millivolt signal from the Type K thermocouple is converted to a 4-20 mAdc signal in a thermocouple-to-current transmitter (20). This signal is then the input to a current-to-pneumatic transducer (21), which is converted to a 3- to 15-psig output. This signal

is compared to the set point, and a proportional pneumatic signal is sent to the regulating valve adjusting the flow of cooling air.

Flow Control

Two separate feed gas streams are employed. System one is used exclusively for a synthesis gas mixture, which is usually a one-to-one ratio of hydrogen-to-carbon monoxide. The second system is used as the inlet for bottled H_2, CO, or inert gas; in addition, this system functions as backup for system one. Normal operating pressures will be an inlet pressure to the reduced pressure control value of 500 psig and a discharge pressure of 350 psig.

The flow of gas to the reactor inlet is regulated by means of a thermal mass flowmeter system with automatic control [22]. The flowmeter with automatic control consists of four units: (1) flow sensor, (2) controller, (3) command (set-point) potentiometer, and (4) blind controller/power supply. Basically, this system continuously compares the output signal from the thermal mass flow sensor to the command signal, and any deviation creates an immediate correction in the associated flow control element.

The sensor unit has a stainless steel flow tube and a range of 0-5000 sccm. A heater coil is wound around the center section of its length. Sensor coils are wound on either side of the heater coil. A uniform amount of heat, generated by the heater coil, is conducted through the flow stream to the temperature sensitive sensor coils that form part of a bridge current. The sensor coils detect the resulting temperature difference during the flow of gas. This resulting differential is applied to a differential amplifier that generates a dc voltage output that is directly proportional to the mass flow rate. The controller is a flow control valve located adjacent to and downstream of the flow sensor. It responds to an error signal and increases or decreases the mass flow until the measured flow equals the required flow. The command (set-point) potentiometer permits accurate and repeatable adjustments of the flow. The blind controller/power supply provides all required voltages to operate the flow sensor. In addition, it contains (1) the precision current supply for the command potentiometer, (2) the controller, and (3) the drive circuits for the final control element. Two of the above setups are installed in parallel in the reactor scheme. This type installation permits blending of any synthesis gas compositions of hydrogen and carbon monoxide. Gas-out flow rates are measured on an hourly basis with a wet test meter during operation. For each test, the mass flowmeters are calibrated before the experiment and recalibrated after the test.

Product Collection

Material exiting the reactor travels through a heated coil (0.8-cm-i.d., stainless steel tube, 121.9-cm-long), with a final coil exit temperature of 200°C. The coil is located above the reactor. Liquid hydrocarbons and water are then condensed in a series of traps. The initial trap, referred to as the "hot" trap, is wrapped with a Briskheat heater and controlled by a temperature controller as described for the upper zone of the reactor mantle heater. This trap is normally maintained at 200°C. Material exiting the "hot" trap, consisting of water, oxygenated compounds,

hydrocarbons, carbon dioxide, and unreacted synthesis gas, then enters a series of water-cooled traps. The connecting line between the "hot" trap and the first water-cooled trap is wrapped by a Briskheat heater and controlled by a Powerstat variable transformer. During operation for a particular period of time, the products in the water-cooled traps are bled into a common collection beaker. The condensed products from these traps are then placed into a separatory funnel and physically separated into an oil phase and an aqueous phase. The oil phase contains the bulk of the liquid hydrocarbon product, and the aqueous phase consists of water plus oxygenated product. Noncondensable gases are passed through a system pressure letdown valve, metered, and vented. The gas is also periodically sent to an on-line gas chromatograph. The heavier hydrocarbons remain within the reactor and are collected as referred to in the "Reactor" section. The traps are constructed as shown in Figure 5.

A simplified diagram of the collection points and products recovered is presented in Figure 6. Figure 7 illustrates a typical product breakdown by carbon number from the various sampling points with a fused-iron catalyst. The deviation of the curve in the C_2 and C_3 fraction of the residual gas and the water-cooled traps is due to the fact that a substantial proportion of these carbon number products is oxygenated compounds, e.g., alcohols, and is recovered in the water-cooled traps. The illustration shows that the C_2 fraction consists of 75% of this carbon-numbered material being within the residual gas and 25% from the water-cooled traps. Likewise for the C_3 fraction, 90% is within the residual gas, and 10% from the water-cooled traps.

Product Analysis

The noncondensed gases are analyzed by an on-line chromatograph (23) (Hewlett-Packard 5730A gas chromatograph), using an in-line sampling valve before the wet test meter so that gases will not be condensed in the mineral oil of the meter. Combining a thermal conductivity detector (TCD) and a hydrogen flame ionization detector (FID), the following gases are determined: H_2, CO, N_2, CO_2, and hydrocarbons from carbon number one to eight, with isomers reported only up to a carbon number of four. The two columns used are both Porapak "R" (80/100 mesh, 1/8-in.-o.d.). One column is 24-feet-long and uses argon as the carrier gas with the TCD. The second column is 6-feet-long and uses helium as the carrier gas with the FID. The oven is temperature-programmed from 343°K (6-minutes hold) to 473°K (16-minutes hold) at a rate of 4°K/min.

The aqueous product is subjected to a mass spectral method (11) modified by PETC analytical personnel and to the ASTM standard test method E203, "Water Using Karl-Fischer Reagent." The modification to the mass spectral method was to include acetic acid, acetone, and water; however, only alcohols up to C_4 (including branched alcohols) are in the analysis. The liquid hydrocarbon product from the water-cooled traps undergoes GC-simulated distillation ASTM D-2887 to determine boiling-range distributions, fluorescent indicator adsorption analysis ASTM D-1319 to determine the functionality of the liquid oil, and bromine number ASTM D-1159 to check the olefin content. The heavier hydrocarbons from the reactor and "hot" trap undergo GC-simulated distillation. Combining information on quantities of materials recovered from the various collection points and on the analyses

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of these products is necessary to obtain an accurate material balance. Overall material recoveries ranged from 95 percent to 105 percent. Trap drainings, flows, and gas analyses are usually done on a 24-hour basis for material balance determinations. The tail-gas compositions were taken approximately one hour before the end of the particular time period. This information also yields detailed hydrocarbon distributions and Schulz-Flory plots. A computer program was written that calculates the composition within the reactor. All draining weights, the carbon number distribution as approximated by GC-simulated distillation, etc., must be entered for the program. Schulz-Flory plots are then calculated from this information.

Reduction Unit

A fused-iron catalyst investigated required a reduction temperature of 450oC with hydrogen for activation. This procedure could not be performed in the slurry unit because the liquid medium would volatilize at such temperatures. Therefore, a vapor phase unit was constructed and is depicted in Figure 8. The reduction tube is type-304 stainless steel and measures 2.4-cm-i.d. by 20.3-cm-long, with concentric reducing couplings on each end. A porous filter, 2-micron size, is welded to the smaller end of one of the couplings and supports the catalyst during reduction. This fixed-bed reactor is located in a tubular furnace controlled by a silicon switching power package in combination with a current-adjusting type controller. A thermal mass flowmeter controls flow from 0-5000 sccm of hydrogen. A KIMAX brand drying jar packed with moisture-indicating, 8-mesh Drierite is located downstream of the reduction unit. The extent of reduction is monitored by observing the rate that the Drierite changes color, as water is a product of the reduction. The reduction tube, upon complete catalyst reduction, is cooled to room temperature and left under 200 psig of hydrogen. The tube is then removed from the reduction unit and transferred under pressure to the slurry reactor, where the catalyst is injected via a side port in the body flange into the reactor. Several pressure purgings with hydrogen were done to assure complete transfer of catalyst to the main reactor. The reduction unit was always checked after the injection to verify that all the catalyst was indeed transported to the main reactor. Before the catalyst injection, the main reactor was charged with the wax medium (melted), leak-tested, pressure-purged, and then held under 50 psig of hydrogen. The transfer was conducted at ambient temperature.

Safety

Due to unattended operation of the unit during off-hours, various additional safety mechanisms were installed on the reactor system as described in the Safety Analysis Review System Report (24): The feed line from the synthesis gas storage cylinders is protected by an excess velocity check valve. The unit is equipped with two relief valves set to relieve pressure at 500 psig. One relief valve is positioned before and the other after the reactor. Electrical power to the unit and the air supply to the agitator motor are shut down if the following occurs: (1) the pressure on the reactor system drops below a preset value; (2) an over-temperature condition arises at any measured station; and (3) the electrical power is interrupted. The system must be manually restarted because a return to normal operating conditions does not automatically reactivate the system.

Audible alarms are located near the unit and are activated by the following events:

1. Carbon monoxide concentrations greater than 50 ppm.
2. Combustible alarms that respond at 40 percent of the lower explosive limit of hydrogen (4 percent H_2 in air).
3. Low pressure (15 percent of normal pressure) on the circulating cooling water, which cools the reactor bearings.
4. Low instrument air pressure (70 percent of the normal value).

RESULTS

Non-Catalytic Unit Operations

The initial experiments provided an opportunity to gain operating experience on the unit and yielded information about the various liquid media (two paraffin waxes and two paraffinic oils) to be used in the program. Gas-chromatographic simulated distillation and other information concerning the liquid media are presented in Table 2. The selected candidate was a paraffinic wax (designated P-22) from Fisher Scientific Company. It is a high-boiling, relatively inexpensive paraffin that is low in sulfur content (< 40 ppm) and resembles waxes produced by the Fischer-Tropsch synthesis.

These series of tests yielded information on potential problem areas caused by the vaporization of the lighter ends of the liquid media and by condensation and eventual solidification in the exit lines. As a result, additional heat tracing of lines and an additional water-cooled trap were added.

Blank runs with syngas at representative space velocities, temperature, and pressure with the reactor charged with 500 mL of the liquid medium, but without catalyst, showed that no reaction occurred. This confirmed the inertness of the reactor walls and hot exit tubing lines. It also indicated that carryover of the wax medium can occur, depending on reactor temperature and pressure and on whether the reflux condenser was in operation. Note that the reflux condenser was not in service during the following experiments.

Catalytic (Fused-Iron) Experimentation

Initial experimental tests were performed with a fused-iron catalyst, type C73-1-01 from United Catalysts, Inc., normally employed for ammonia synthesis. Chemical analysis of the catalyst is shown in Table 3. Additional information about the catalyst is available from the literature [25]. The catalyst was crushed and sieved to a particle size less than 74 microns (200 mesh) and greater than 44 microns (325 mesh), and 50 grams was charged to the reduction reactor (Figure 8). The catalyst was reduced with hydrogen at 450°C, at atmospheric pressure, and at a space velocity of 3100 hr^{-1} for 72 hours. The catalyst was then transferred to the three-phase reactor under hydrogen and pressure-injected into the reactor so that final mixture of catalyst and P-22 wax was a 13 weight percent suspension based on unreduced catalyst weight. The induction period

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TABLE 2. Liquid Medium Information

Designation	P-21	P-22	O-119	O-120
IBP (°F)	192	704	196	641
10%	673	755	567	762
20%	708	782	626	795
30%	733	805	666	819
40%	754	828	701	839
50%	776	851	735	857
60%	798	877	769	875
70%	823	905	806	893
80%	855	939	848	913
90%	910	983	900	940
FBP (°F)	1024	1065	1024	1033

P-21: Wax* m.p. 135°F
P-22: Wax* m.p. 145°F
O-119: Liquid* Saybolt Universal viscosity, 125-135 sec at 100°F
O-120: Liquid* Saybolt Universal viscosity, 335-350 sec at 100°F

*At room temperature.

TABLE 3. Chemical Composition of United Catalysts, Inc's., C73-1-01 (Weight Percent)

FeO	30–37
Fe_2O_3	65–58
Free Fe	0.5
Total Fe	67–69
Al_2O_3	2.0–3.0
K_2O	0.5–0.8
CaO	0.7–1.2
SiO_2	0.4
P	0.015
S	0.001
Cl	0.002
Fe^{++}/Fe^{+++}	0.45–0.65

was 24 hours with $1H_2/1CO$ synthesis gas at atmospheric pressure, 250°C, and space velocity of 225 volume gas/volume slurry-hour. The pressure at the end of induction was increased to 300 psig, and the temperature adjusted to 260°C before synthesis began. Induction was done in two tests SL-9 and SL-14 but was not done in SL-11. Results of the tests are presented in the Appendix.

Good reproducibility between the two baseline tests, SL-9 and SL-14, was demonstrated (see Figure 9). Negligible deterioriation of activity occurred during 260 hours of operation. Altering the pressure and returning to standard operating conditions had no adverse effects. The typical hydrocarbon distribution was 7.5 weight percent CH_4, 30.0 percent C_2-C_4, and 62.5 percent C_5^+ material. The C_2-C_4 fraction contained 70-75 percent olefins. Lowering the pressure to 100 psig in SL-14 resulted in decreased activity to 60 percent of that attained at 300 psig. Also, the hydrocarbons, C_1-C_4, increased to 52 weight percent of the hydrocarbon make, and the olefin make in the C_2-C_4 fraction dropped to 60 percent.

The functionality of the liquid oil, as determined by FIA, was on the average 75 volume percent olefin, 21 percent paraffin, and 4 percent aromatic. Mass spectroscopic analysis and Karl Fischer titration of the aqueous fraction indicate about 10 to 15 weight percent was oxygenated compounds.

The effect of impeller revolution on mass transfer was investigated in SL-14. Changing the impeller speed from 500 to 1000 rpm made no difference in conversion or product slate when the other process conditions were held constant and deactivation effects were considered. Deactivation was determined by repeating the initial base conditions during various times on stream. However, gross differences were found when the speed was dropped to 250 rpm. Speeds in typical tests were always maintained between 750-1000 rpm. The catalyst activity declined after about 260 hours on stream for each test.

The molecular weight distribution of the primary products of the Fischer-Tropsch reaction can be described by the Schulz-Flory equation (26). A typical plot of the natural logarithm of the weight fraction for each carbon number divided by the carbon number versus the carbon number is seen in Figure 10 for period E from SL-9. The chain growth probability calculated from the slope of the straight line defined above for this catalyst at these conditions is 0.72. Oxygenates in the aqueous fraction are not included for each carbon number, but if included, the points for the lighter hydrocarbons -- most notably C_2 -- would be moved upwards to the least squares solid line.

In another test, SL-11, with fused iron, variation in temperature was made to determine temperature effects on kinetic factors. A model for this type of stirred-autoclave, semicontinuous flow unit was developed by Satterfield (27) with the assumptions that the rate of hydrogen and carbon monoxide consumption is first order with respect to the partial pressure of hydrogen and that diffusional effects are minimal. The overall activity constant was calculated at the same process conditions except for the temperatures, which were 245°C, 260°C, and 275°C. An Arrhenius plot at the

three temperatures yields a straight line from whose slope an activation energy of 25.3 kcal/mole is calculated. If a correction factor of 1.2 kcal/mole is taken into consideration as explained by Satterfield (28), then the gas phase activation energy is 26.5 kcal/mole, and this value is within the range of those reported for fixed-bed, vapor-phase studies over an iron catalyst (17-27 kcal/mole).

SUMMARY

The slurry reactor offers several advantages over other reactor schemes to overcome the problems associated with the F-T synthesis. The three-phase stirred reactor system at PETC has a one-liter reactor capacity and can operate to temperatures of 340°C and pressures of 35 atm. The unit can operate unattended because of various safety features. These features include protection against overpressure, underpressure, excessive temperatures, hazardous gas leakage, and utility malfunctions.

Products of the F-T synthesis are varied and include hydrocarbons, (gaseous, liquid, and solid at room temperature), water, carbon dioxide, and oxygenated compounds. Collection and analysis of the various stream compositions are discussed. Analytical techniques employed included the following: a mass spectral method and Karl-Fischer reagent for the aqueous layer product; GC-simulated distillation, fluorescent indicator adsorption, and bromine number on the liquid hydrocarbons; GC-simulated distillation on the heavier hydrocarbons; and on-line GC on the gaseous products.

Initial experiments performed without a catalyst charge provided an opportunity to gain operating experience, define potential problem areas, select a liquid medium, and verify the inertness of the system.

Further experiments were conducted with a fused-iron catalyst. The high temperature necessary to activate this catalyst necessitated the construction of a vapor phase reactor for reduction of the catalyst. These experiments demonstrated reproducibility and showed negligible deterioration of activity during 260 hours of operation. Lowering the pressure resulted in decreased activity, a lighter-weight hydrocarbon product, and a decrease in olefin content within the C_2-C_4 fraction. The effect of impeller speed on mass transfer was not evidenced until below 500 rpm. The temperature effect on kinetic factors was investigated. A gas phase activation energy of 26.5 kcal/mole was determined using the overall activity constant determined at each temperature. This value is within the range (17-27 kcal/mole) reported for fixed-bed, vapor-phase studies over an iron catalyst. A typical Schulz-Flory plot for this catalyst at 260°C and 300 psig results in a chain growth probability of 0.72.

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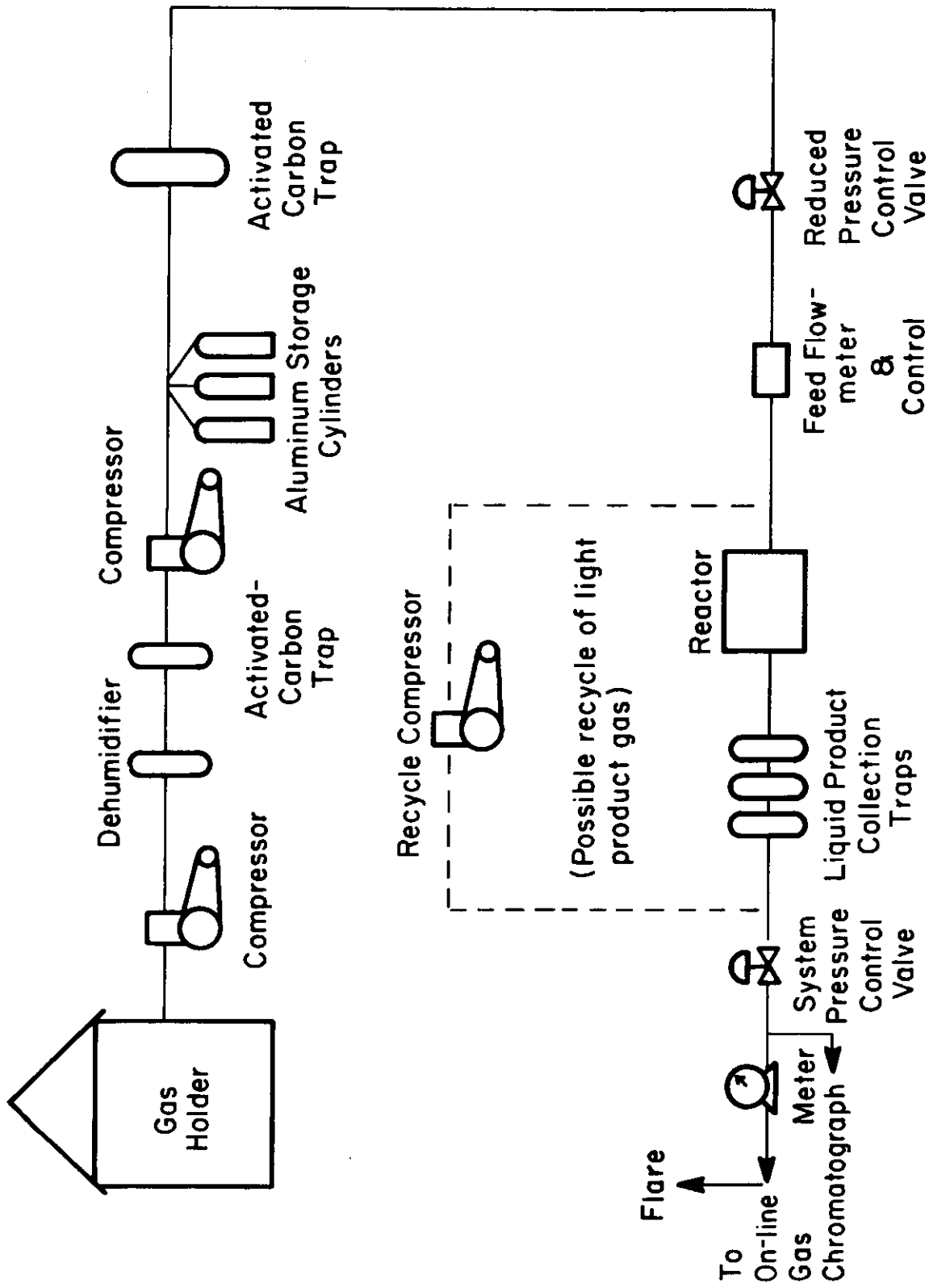
Figure I.- Schematic of typical bench unit for indirect liquefaction catalyst testing.

BSII/4499

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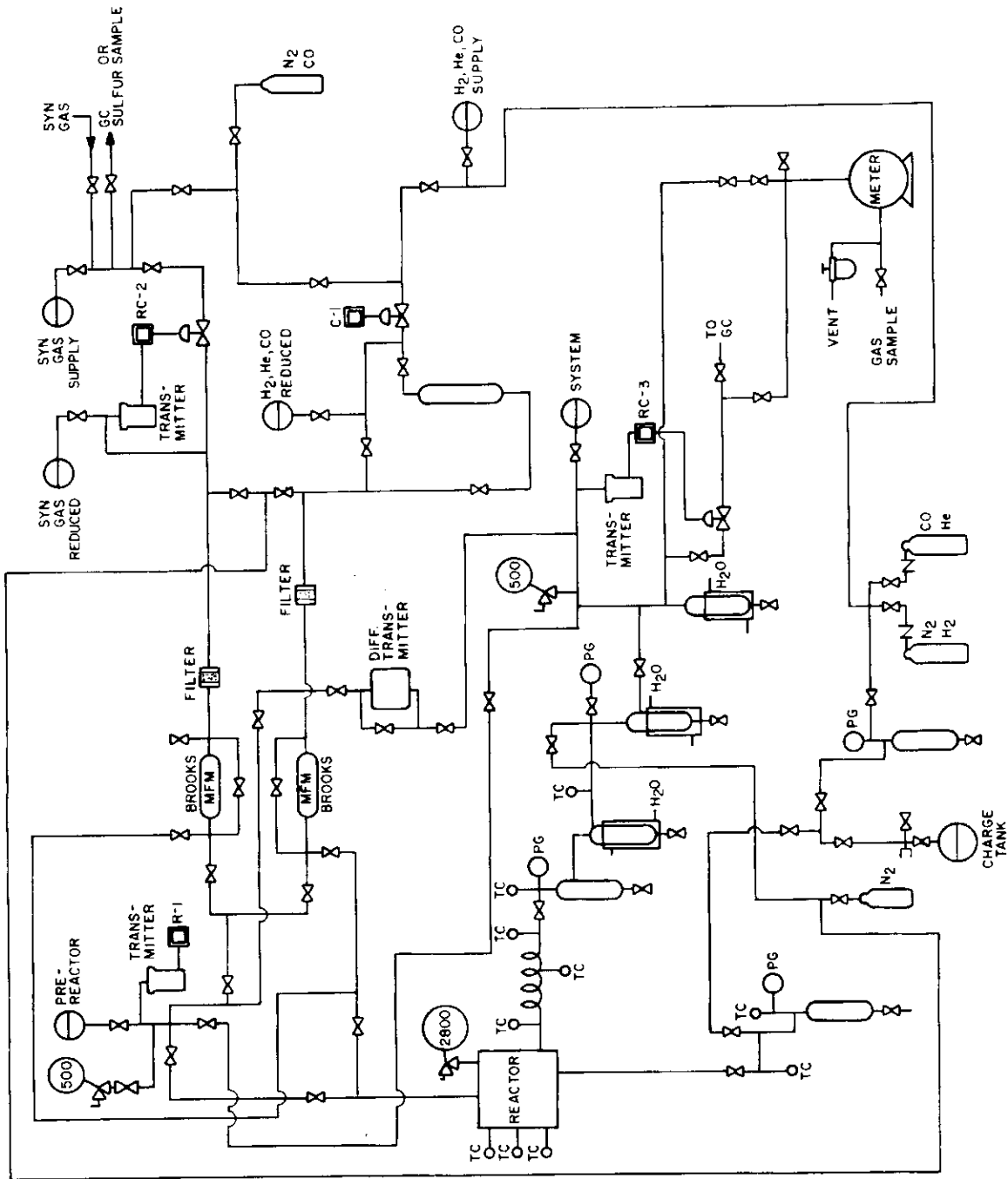
Figure 2.-Detailed schematic of slurry process unit.

BSI/4510

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COVER FLANGE

BODY FLANGE

Gas Outlet

Liquid Level Control Exit Line

Cooling Medium Inlet

Cooling Medium Outlet

Liquid/Vapor phase Thermowell

Rupture Disc

Plug

Catalyst Charge Port

Gas Inlet

Plug

Cover flange

Gas outlet with 2-micron frit

Catalyst charge port

Liquid level control exit with 2-micron frit

Baffle bars

Reactor body and body flange

Cooling coil

Thermowell with sliding thermocouple

Turbine impellor

Inlet gas feed line

Mantle heating furnace

Figure 3.- Three-phase slurry one-liter reactor.

BSI/4500

20
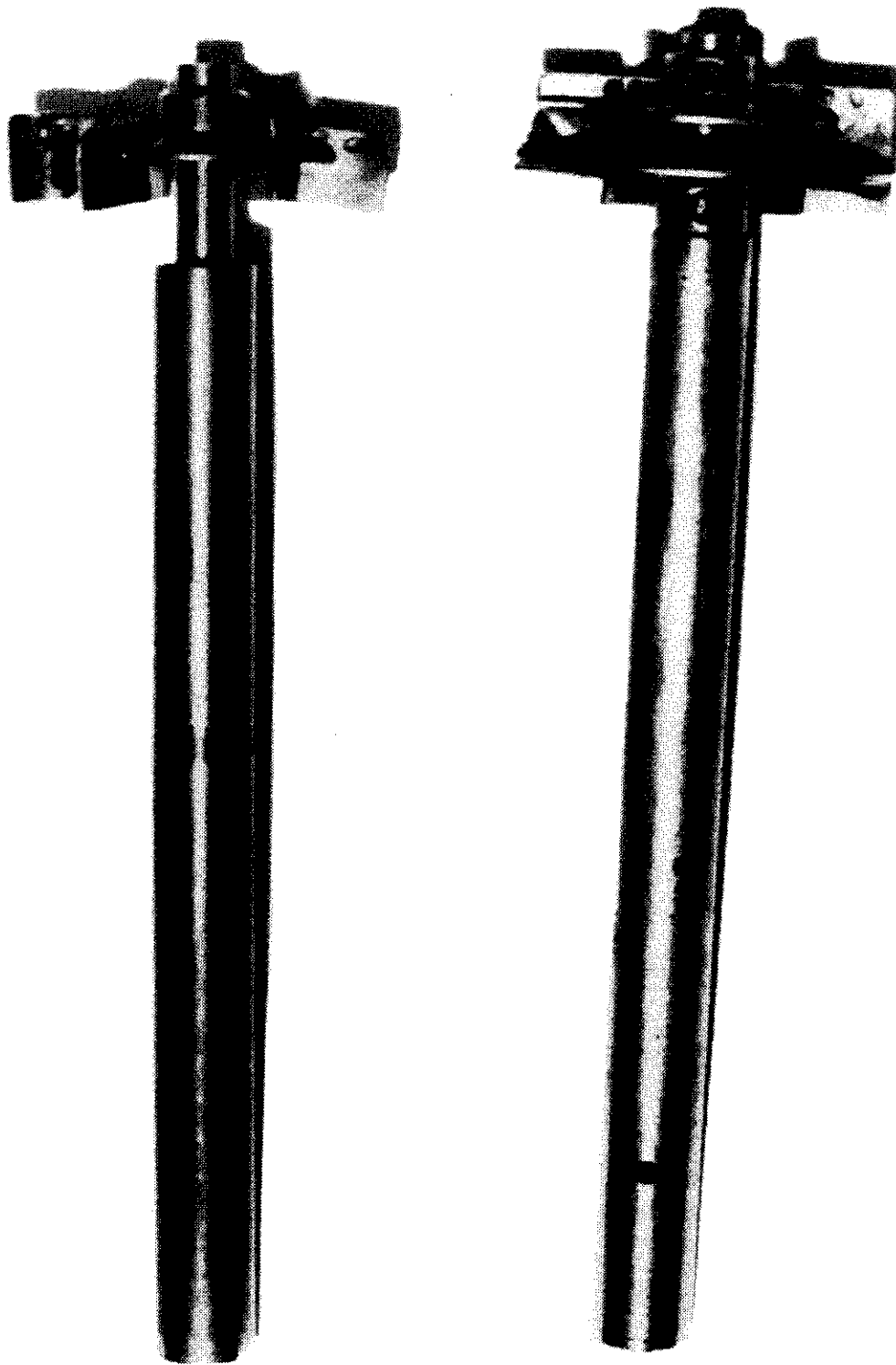
Figure 4.- Photograph of agitators.

BSI/4501

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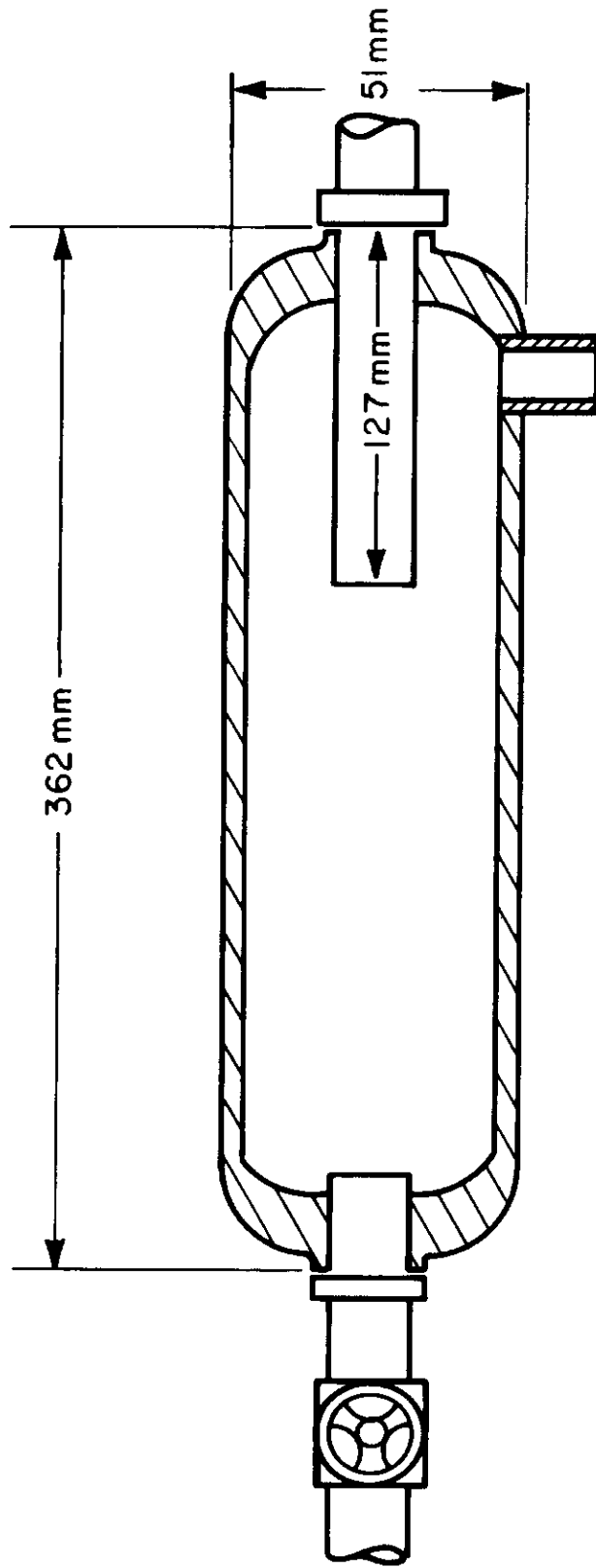
Figure 5.- Schematic of collection traps

51 mm

127 mm

362 mm

BSI/4506
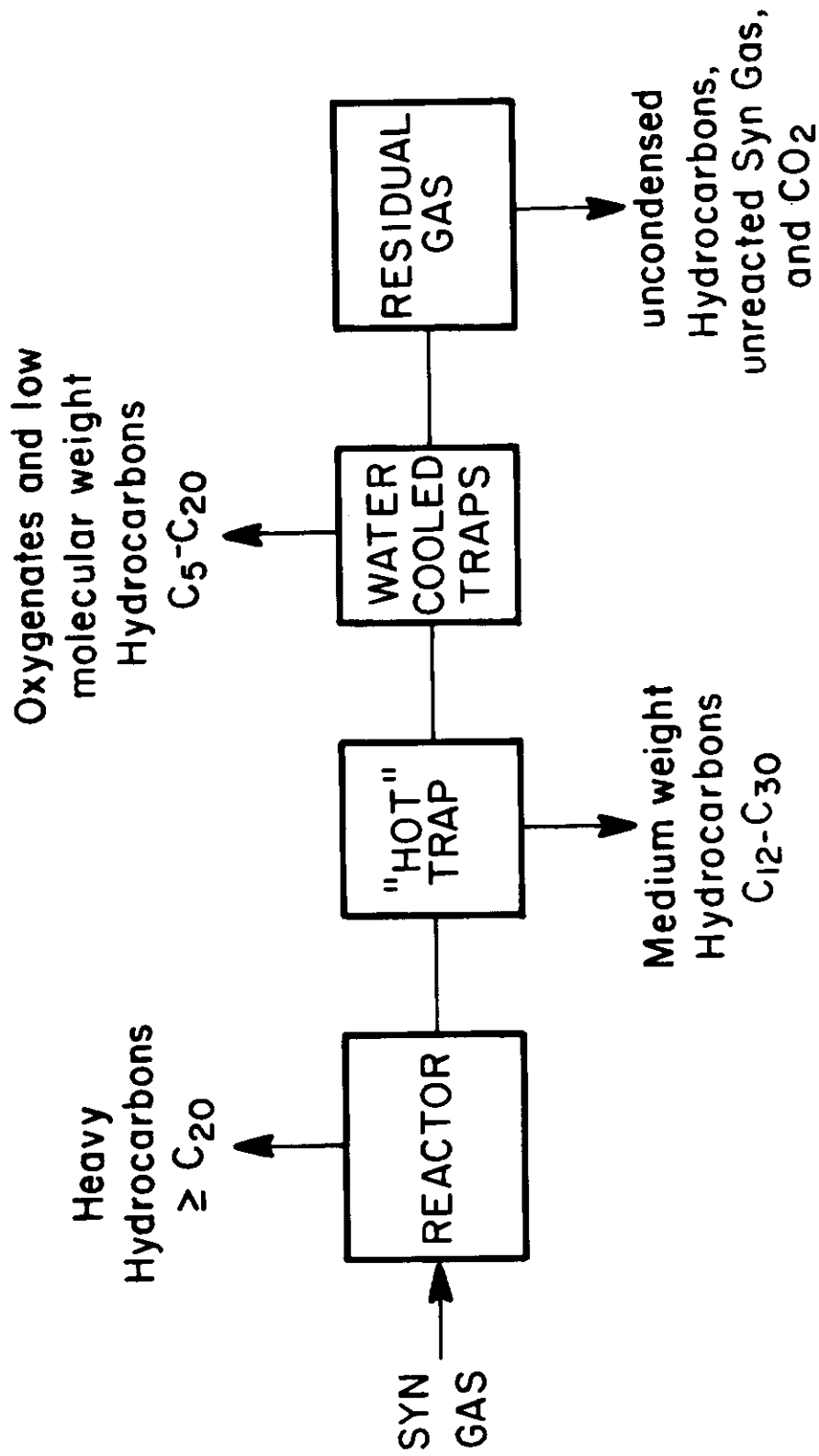
Figure 6.- Block diagram of sampling points

SYN GAS → REACTOR

Heavy Hydrocarbons ≥ C_{20}

"HOT" TRAP

Medium weight Hydrocarbons $C_{12}-C_{30}$

WATER COOLED TRAPS

Oxygenates and low molecular weight Hydrocarbons C_5-C_{20}

RESIDUAL GAS

uncondensed Hydrocarbons, unreacted Syn Gas, and CO_2

BSI/4502

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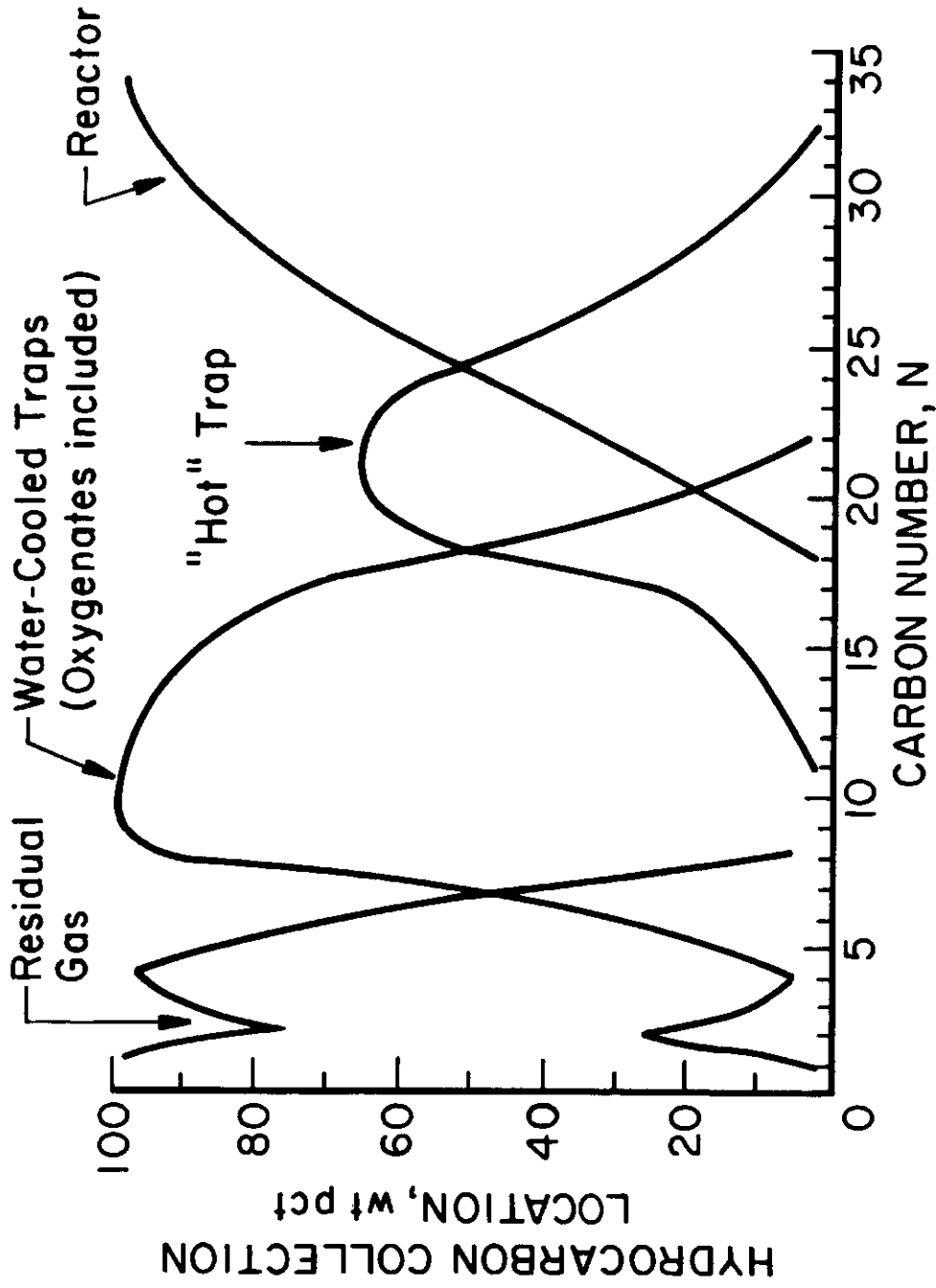
Figure 7.-Hydrocarbon breakdown by trap location with a fused-iron catalyst from test SL-9.

BSI/4544

A - Thermal mass flowmeter
B - Thermocouple (dual-head)
C - Reactor
D - Electric tube furnace
E - Drierite-filled drying jar
F - Wet test meter
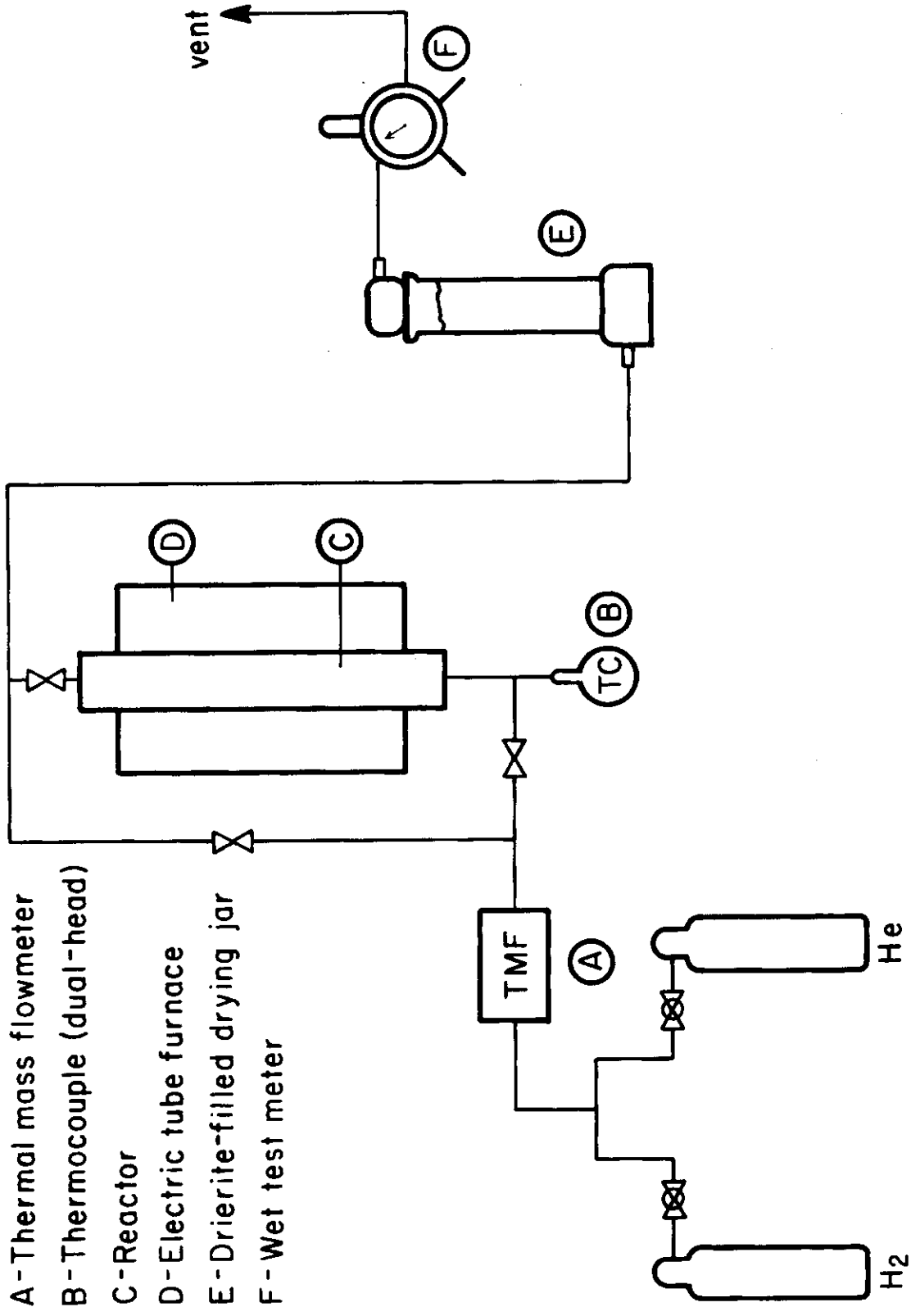
Figure 8.-Schematic of reduction unit.

BSI/4505

Figure 9.-Carbon monoxide conversion for a fused-iron catalyst.

OPERATING PARAMETERS:
TEMPERATURE: 260°C
PRESSURE: 300 psig
SPACE VELOCITY: 255 hr^{-1}

BSI/4503

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Figure 10.- Typical Schulz-Flory plot for fused-iron catalyst.

BSI/1512

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APPENDIX

The terms and symbols used in the Appendix are defined as follows:

* ≡   No 'on-line' chromatographic analysis available. The analysis of the product stream was performed on a reserve gas chromatograph (GC) because the primary chromatograph was inoperative. The reserve GC contained only a thermal conductivity detector and did not detect the C_5-C_8 material because of their low concentrations.

X_N ≡   Percent conversion of component $N = \dfrac{(\text{moles } N_{in} - \text{moles } N_{out})}{(\text{moles } N_{in})}$

Hydrocarbon ≡   Percentage of total hydrocarbons recovered within a defined
Distribution   carbon number or carbon number range but not including aqueous oxygenated products in the total.

C_{5+} ≡ C_5-C_8 material in the residual gas, and all 'oil' recovered in the water-cooled traps compose this fraction.

Wax ≡   Materials from the 'hot' trap and the level trap are summed without considering the carbon number breakdown of the material and are presented as wax.

EXPERIMENT: SL-9

Activation: H$_2$ - 72 hr
4500C - 0 psig - 2.0 ft3/hr

Catalyst/Weight: Fused Iron

50 grams - Unreduced
UCI C73-1-01

Induction: 1/1 - H$_2$/CO - 24 hr
'0' psig - 2500C - 4.5 scfh

Period	Time on Stream hr	Pressure psig	Temperature oC	GHSV hr^{-1}	rpm min^{-1}	X$_{CO + H_2}$	X$_{CO}$	X$_{H_2}$	Usage Ratio	Hydrocarbon Distribution				Material Recovery
										CH$_4$	C$_2$ - C$_4$	C$_5$+	Wax	
A	70	300	260	255	750	43.9	49.4	38.8	0.86	7.4	31.0	48.7	12.9	105.6
B	94	300	260	255	750	43.7	48.9	38.9	0.87	7.6	33.6	49.8	9.0	96.3
C	118	300	260	255	750	47.4	53.8	41.5	0.85	6.9	29.6	54.7	8.8	100.5
D*	138	300	260	255	750	51.5	59.8	43.5	0.76	8.1	40.9	42.3	8.7	96.2
E	162	300	260	255	750	51.6	56.8	46.8	0.90	5.8	22.3	41.6	30.3	106.6
F*	190	300	260	255	750	51.7	60.1	43.5	0.73	5.1	32.3	35.6	27.0	99.9
G*	214	300	260	255	750	50.3	56.2	44.4	0.79	3.1	17.7	22.1	57.1	101.9
H*	238	300	260	255	750	51.8	59.4	44.3	0.76	6.1	29.6	32.9	31.4	99.1
I*	262	300	260	255	750	49.7	56.3	42.8	0.74	5.4	27.8	36.2	30.6	98.9
J*	286	300	260	255	750	33.4	36.3	30.3	0.80	2.5	20.3	34.6	42.6	95.1
K	310	300	260	255	750	20.8	19.2	22.2	1.24	1.5	11.2	31.8	55.5	104.1
L*	330	300	260	255	750	15.1	15.5	14.7	0.97	6.4	48.0	31.6	14.0	98.6

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EXPERIMENT: SL-9

	FIA percent				Karl	Mass Spec – Mole Percent								GC-Sim. Dist. Weight Percent of Oil ≤204°C
Period	Saturate	Olefin	Aromatic	Bromine No.	Fischer No.	H_2O	C_1OH	C_2OH	$1C_3OH$	C_3OH	C_4OH	Acetone	HOAc	
A	17	66	17	65	89.0	95.9	0.7	1.8	---	0.6	0.1	0.1	0.8	63
B	23	61	16	63	92.5	96.0	0.8	1.9	---	0.7	0.1	0.1	0.4	57
C	20	66	14	66	89.0	95.2	1.0	2.2	---	0.8	0.2	0.1	0.5	63
D	24	62	14	66	86.6	93.9	1.1	3.2	---	1.1	0.2	0.1	0.4	59
E	15	80	5	N.P.	90.2	94.9	0.4	3.1	---	1.1	0.2	0.1	0.3	62
F	19	77	4	64	88.7	94.3	0.2	3.3	---	1.3	0.3	0.2	0.4	62
G		N.P.		N.P.	89.6	95.2	0.8	2.2	---	1.0	0.2	0.1	0.5	64
H		N.P.		N.P.	91.7	96.3	0.4	1.9	---	0.7	0.2	0.1	0.4	66
I	24	72	4	60	92.0	96.5	0.4	1.3	---	0.6	0.2	0.1	0.9	62
J	21	75	4	58	90.1	92.0	2.2	3.5	---	1.4	0.3	0.1	0.5	60
K		N.P.		N.P.	N.P.		N.P.							N.P.
L		N.P.		N.P.	N.P.		N.P.							N.P.

N.P. = Analytical Procedure Not Performed.

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EXPERIMENT: SL-11

Activation: H$_2$ - 72 hr
450°C - 0 psig - 2.0 ft3/hr

No Induction

Catalyst/Weight: Fused Iron

50 grams - Unreduced
UCI C73-1-01

Period	Time on Stream hr	Pressure psig	Temperature °C	GHSV hr^{-1}	rpm min^{-1}	X$_{CO + H_2}$	X$_{CO}$	X$_{H_2}$	Usage Ratio	Hydrocarbon Distribution CH$_4$	C$_2$ - C$_4$	C$_{5+}$	Wax	Material Recovery
A	48.5	300	260	255	750	56.9	66.5	47.7	0.75	10.2	22.0	39.2	28.6	106.9
B	72	300	260	255	750	57.7	65.3	50.5	0.82	5.3	22.7	43.2	28.8	102.0
C	95.5	300	260	255	750	64.9	75.2	55.0	0.77	7.6	27.8	41.2	23.4	105.0
D	119	300	260	255	750	63.3	72.8	54.4	0.80	6.2	25.4	45.0	23.4	100.5
E	142	300	276	255	750	76.8	89.2	65.1	0.78	10.9	35.6	46.4	7.1	95.4
F	163.5	300	274	255	750	74.6	88.9	61.3	0.74	11.9	32.0	50.3	5.8	110.7
G	189	300	260	255	750	59.9	69.9	50.6	0.78	9.7	30.9	45.4	14.0	106.7
H	212.5	300	260	255	750	56.6	65.0	48.4	0.77	5.9	25.5	49.0	19.6	100.5
I*	234.5	300	245	255	750	36.5	40.9	31.9	0.76	5.7	38.0	44.4	11.9	98.8
J*	259.0	300	245	255	750	27.5	28.4	26.5	0.90	2.8	17.6	51.2	28.4	99.3
K*	282.5	300	245	255	750	24.0	24.9	23.1	0.93	4.2	24.3	31.0	40.5	101.4
L	305	300	245	255	750	23.0	22.3	23.6	1.13	6.5	18.5	45.8	29.2	102.1
M	328.5	300	245	255	750	18.5	18.6	18.4	1.03	6.0	18.6	46.0	29.4	96.5
N	376	300	260	255	750	13.9	19.4	8.4	0.44	29.4	28.6	33.4	8.6	93.0

EXPERIMENT: SL-11

	FIA percent					Mass Spec – Mole Percent								GC-Sim. Dist.
Period	Saturate	Olefin	Aromatic	Bromine No.	Karl Fischer No.	H_2O	C_1OH	C_2OH	iC_3OH	C_3OH	C_4OH	Acetone	HOAc	Weight Percent of Oil $\leq 204°C$
A	14	82	4	67	87.4	96.0	1.4	1.7	---	0.5	0.2	0.1	0.1	65
B	12	84	4	71	89.0	92.9	---	4.1	---	1.9	0.7	0.3	0.1	68
C	26	71	3	73	89.7	93.4	---	4.3	---	1.3	0.6	0.3	0.1	65
D	23	72	5	73	87.9	91.0	1.0	4.9	0.2	1.6	0.8	0.4	0.1	68
E	32	64	4	79	86.7	88.7	---	6.3	0.9	2.7	0.7	0.7	---	78
F	35	62	3	69	86.4	93.7	0.8	3.2	0.4	1.5	0.3	0.1	---	71
G		N.P.		N.P.	N.P.			N.P.						N.P.
H	30	65	5	70	89.3	95.7	0.9	1.9	---	0.7	0.3	0.1	0.4	65
I	16	76	8	53	92.8	94.6	1.4	2.2	---	0.9	0.4	0.2	0.3	44
J		N.P.		51	92.1	96.8	0.7	1.4	---	0.5	0.2	0.1	0.3	49
K		N.P.		47	94.3									48
L		N.P.		N.P.	N.P.	N.P.		N.P.						N.P.
M		N.P.		N.P.	N.P.	N.P.		N.P.						N.P.

N.P. = Analytical Procedure Not Performed.

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EXPERIMENT: SL-14

Activation: H$_2$ - 72 hr
450°C - 0 psig - 2.0 ft3/hr

Induction: 1/1 - H$_2$/CO - 24 hr
'0' psig - 250°C - 4.5 Scfh

Catalyst/Weight: Fused Iron

50 grams - Unreduced
UCI C73-1-01

Period	Time on Stream hr	Pressure psig	Temperature °C	GHSV hr⁻¹	rpm min⁻¹	$X_{CO + H_2}$	X_{CO}	X_{H_2}	Usage Ratio	Hydrocarbon Distribution CH$_4$	$C_2 - C_4$	C_{5+}	Wax	Material Recovery
A	71.5	300	260	255	750	48.7	50.3	47.2	0.98	6.9	30.1	52.8	10.2	98.5
B	95	300	260	255	750	54.7	58.9	50.5	0.90	7.5	31.3	50.3	10.9	99.9
C	118.5	300	260	255	750	54.7	56.6	53.0	0.99	6.8	27.1	55.7	10.4	99.4
D	142	300	260	255	750	53.7	54.9	52.6	1.01	8.4	33.2	48.6	9.8	100.3
E	165.5	100	260	255	750	31.8	35.0	28.9	0.90	12.3	39.5	35.7	12.5	97.2
F	189	100	260	255	750	29.0	30.1	27.9	0.98	12.0	39.6	41.0	7.4	104.4
G	212.5	300	260	255	750	57.2	60.4	54.2	0.96	8.1	30.9	54.9	6.1	98.0
H	236	300	260	255	750	55.4	58.1	52.9	0.96	8.4	33.5	50.9	7.2	97.2
I	259.5	300	260	255	1000	51.0	53.4	48.8	0.96	8.1	31.7	52.2	8.0	99.3
J	283	300	260	255	500	46.8	48.1	45.6	1.01	8.6	31.5	51.4	8.5	91.5
K	306.5	300	260	255	250	13.3	12.3	14.2	1.23	6.9	24.2	51.5	23.4	94.8
L	330	300	260	255	750	33.8	33.0	34.5	1.11	9.5	34.3	48.5	7.7	99.3
M	353.5	300	260	255	750	35.8	35.4	36.2	1.09	9.3	32.8	49.3	8.6	98.2
N	377	300	260	255	750	36.4	35.9	36.8	1.07	8.7	31.8	51.0	8.5	96.2

Period	FIA percent Saturate	FIA percent Olefin	FIA percent Aromatic	Bromine No.	Karl Fischer No.	Mass Spec – Mole Percent H_2O	C_1OH	C_2OH	$1C_3OH$	C_3OH	C_4OH	Acetone	HOAc	GC-Sim. Dist. Weight Percent of Oil $\leq 204^{\circ}C$
A		N.P.		N.P.	N.P.	N.P.		N.P.						N.P.
B	25	71	4	77	90.0	95.7	0.9	1.9	---	0.9	0.2	0.1	0.3	62
C		N.P.	5	20	92.2	95.3	0.8	2.2	0.1	1.2	0.3	0.1	---	86
D	25	70	6	75	87.9	95.6	0.7	2.0	0.1	1.1	0.2	0.1	0.2	62
E	23	71		61	90.4	95.9	0.5	2.1	---	1.0	0.3	0.1	0.1	40
F		N.P.		58	93.9	95.7	0.8	2.0	0.1	1.0	0.3	0.1	---	39
G	21	75	4	74	91.7	92.3	2.1	3.1	0.2	1.7	0.3	0.2	0.1	58
H	21	75	4	72	90.0	91.5	2.2	3.5	0.3	1.9	0.4	0.2	---	60
I	14	82	4	75	89.0	92.3	1.8	3.4	0.2	1.7	0.4	0.1	0.2	75
J	17	79	4	72	92.6	94.0	0.5	2.7	0.1	1.8	0.5	0.3	0.1	58
K	23	69	8	60	94.8	95.8	0.8	1.7	0.1	1.1	0.3	0.1	0.1	45
L	20	74	6	67	93.7	90.0	2.8	4.2	---	2.3	0.5	0.2	---	54
M		N.P.		N.P.	N.P.	N.P.		N.P.						N.P.
N		N.P.		N.P.	N.P.	N.P.		N.P.						N.P.

N.P. = Analytical Procedure Not Performed.