ABSTRACT

An evaluation study was conducted on a novel two-stage slurry Fischer-Tropsch/ZSM-5 process for converting low H_2/CO ratio synthesis gas, which can generally be obtained from highly efficient, advanced coal-gasification systems, into high quality gasoline. The feasibility of this two-stage technology was successfully demonstrated in a newly designed and constructed bench-scale unit (BSU), consisting of a slurry bubble column reactor followed by a fixed-bed ZSM-5 reactor.

Three Fischer-Tropsch catalysts of $Fe/Cu/K_2CO_3$ type were evaluated. Total hydrocarbon production as high as 815 g/gFe was achieved, which is substantially better than other results reported in the literature. Methane + ethane yields ranged from 2 to 18 wt % of total hydrocarbons produced, with reactor-wax (those heavy hydrocarbons retained in the slurry reactor under reaction conditions) yields ranging from 3 to 85 wt %. Other investigations of the first-stage operation included process variable and hydrodynamic studies.

The second-stage ZSM-5 reactor performed smoothly and demonstrated the conversion of Fischer-Tropsch products into high quality gasoline. The gasoline yields, including the alkylate and excluding the reactor-wax and light paraffins in the feed to the second-stage reactor, were as high as 87 wt %. The raw gasoline samples had satisfactory stability properties.

A conceptual process design and scoping cost estimate for a battery-limit commercial plant to produce 27,000 BPSD gasoline from clean synthesis gas was conducted. The estimated cost is $700 million in terms of 1983 dollars at a Wyoming location.

I. Objective and Scope of the Project

The overall objective of the contract is to develop a two-stage slurry Fischer-Tropsch/ZSM-5 process for direct conversion of synthesis gas, of the type produced in a coal gasification system, to high octane gasoline. The specific objective is to design, construct, and operate a bench-scale pilot plant so that the economic potential of this process concept can be evaluated. To accomplish these objectives, the following specific tasks were undertaken:

Task 1 - Design of Bench-Scale Pilot Plant

A two-stage slurry F-T/ZSM-5 bench-scale pilot plant will be designed for conversion of synthesis gas to high octane gasoline. The slurry F-T reactor will be 5.1 cm diameter and 762 cm high. The fixed-bed ZSM-5 reactor will be 5.1 cm diameter and 10-46 cm high.

Task 2 - Construction and Shakedown of Pilot Plant

The pilot plant will be constructed in MRDC Paulsboro Laboratory. The unit will be shaken down after completion.

Task 3 - Operation of Pilot Plant

At least three slurry F-T catalysts will be tested in the bench-scale pilot plant. One of these catalysts may be provided by DOE's alternate catalyst development projects. The best first-stage catalyst together with a ZSM-5 class zeolite catalyst will be used for process variable studies and catalyst aging tests in the bench-scale unit. Products obtained from the unit will be evaluated to define their qualities.

Task 4 - Conceptual Design Study

A preliminary conceptual design of the process will be developed for a commercial size plant for the conversion of synthesis gas to high octane gasoline. Scoping costs of the plant will be estimated.

II. Summary

The Mobil Two-Stage Slurry Fischer-Tropsch/ZSM-5 Process provides a new and novel route for the conversion of coal to high quality motor fuels. The Mobil design combines the classic slurry-phase Fischer-Tropsch synthesis technology with a state-of-the-art fixed-bed ZSM-5 reactor which converts the vaporous Fischer-Tropsch products from the first-stage slurry reactor directly into high quality gasoline.

Due to the unique features of a slurry Fischer-Tropsch reactor, synthesis gas with H_2/CO molar ratios as low as 0.6 to 0.7 can be directly used, provided the Fischer-Tropsch catalyst has water-gas shift reaction activity. These low H_2/CO ratio gases can generally be obtained from the advanced coal gasification systems, such as BGC(British Gas Corporation)/Lurgi Slagger, Texaco, Shell-Koppers, and Westinghouse gasifiers. These gasifiers have high thermal efficiency and are potentially lower-cost than current one (Shinnar and Kuo, 1980). Consequently, a combination of these advanced coal gasification systems with this two-stage technology constitutes a novel and lower-cost route of converting coal to gasoline. In contrast, the methanol synthesis route stoichiometrically requires synthesis gas of at least 2/1 H_2/CO ratio. The use of a low H_2/CO ratio synthesis gas for hydrocarbon synthesis plus a simple step of upgrading the Fischer-Tropsch products into high quality gasoline in a single fixed-bed ZSM-5 reactor constitute two unique features of this two-stage technology.

The present work on the development of the two-stage process was initiated in October 1980, under DOE Contract No. DE-AC22-80PC30022. The specific objective was to develop the process in a bench-scale pilot plant consisting of a slurry Fischer-Tropsch reactor (5.1 cm ID x 762 cm high) and a fixed-bed ZSM-5 reactor in series. The scope of work encompassed design and construction of the pilot plant, evaluation of Fischer-Tropsch catalysts, process variable studies, characterization of the gasoline product, and a preliminary conceptual design and scoping economic study of a commercial plant.

The design and construction of the pilot plant was completed on schedule in December 1981. The slurry bubble-column reactor is connected at the top to a disengager which serves to prevent carryover of entrained slurry. The reactor temperature is controlled by circulating hydrocarbon oil (e.g., Mobiltherm-600) in a jacket surrounding the entire column. Individual streams of carbon monoxide and hydrogen are mixed and preheated before entering the reactor through a sintered metal distributor at the bottom. Reactor-wax which consists of heavy Fischer-Tropsch products accumulated in the slurry reactor was removed initially using filters suspended in the slurry medium

and later by on-line catalyst settling vessels. The second stage consists of two fixed-bed reactors arranged in parallel for swing operation. The reactors can be operated in both adiabatic and isothermal modes. Analysis of the combined gas product is accomplished by an on-line GC system.

The unit was put on stream in March 1982 after a brief shakedown operation. The first-stage catalyst was composed of $Fe/Cu/K_2CO_3$, while the second stage contained a ZSM-5 class catalyst. Operating conditions were selected based on prior experience and Fischer-Tropsch bubble-column mathematical model calculations. The feed H_2/CO ratio was 0.7. The startup and operation was very smooth, and conditions were varied during the run with no adverse effects. In all, five runs were achieved, ranging in length from thirteen to eight-six days. Three first-stage catalysts were evaluated and long-term stability of the slurry Fischer-Tropsch operation was demonstrated with a production of 815 gHC/gFe. Synthesis gas conversions as high as 85-91% were achieved and maintained for as long as sixty days, and methane + ethane yields as low as 1.7 wt % of hydrocarbons were observed. At low methane + ethane yields, reactor-wax yields up to 80 wt % were attained. First-stage temperatures ranged from 240 to 282°C, and the unit was operated at 1.13 to 2.52 MPa. High pressure operation reduced the methane + ethane yield substantially while greatly increasing the synthesis gas throughput. In process variable studies, the effects of 0.6 H_2/CO feed gas, as well as varying flow rates and different catalyst loadings were examined. Addition of a potassium-salt to the slurry reactor dramatically decreased the methane + ethane yield. The second stage performed well in converting the vaporous F-T products from the first-stage slurry reactor into gasoline. Temperatures in the fixed-bed reactors ranged from 288 to 466°C, and the catalyst was regenerated twice without any observable loss of initial activity.

Hydrodynamic studies were performed with hot and cold glass bubble-columns. Both Fischer-Tropsch wax and slurry, as well as n-hexadecane were used as mediums. The gas holdup varied strongly with static liquid heights, and moderately with the column diameter and solids concentration. Further work in this area is needed.

The raw gasoline collected in the cold and chilled condensers of the BSU had R+O octane numbers ranging from 82 to 98, depending on the second-stage severity. The gasoline also demonstrated satisfactory oxidation stability and corrosion protection qualities with standard additives. It also contained a small quantity of components heavier than gasoline, which could be easily removal using a conventional distillation technique.

A complex analytical scheme for defining the Fischer-Tropsch reaction products was developed. Total breakdown of the product stream was accomplished by using a variety of chromatographic techniques, along with distillation, scrubbing, and extraction. Various supporting tests, including acid number, bromine number, hydroxyl number, viscosity, and surface tension, were also employed.

Based on the process data developed, a conceptual design and scoping cost estimate of a commercial-scale plant to produce 27,000 BPSD of 10 RVP gasoline was completed. The cost estimate for the battery limit facilities at a Wyoming location is approximately $700 million, using mid-1983 instantaneous dollars.

III. Introduction

In view of the diminishing petroleum supply in the United States, new technologies for converting coal to transportation fuels are expected to become increasingly important in the future.

In 1976, Mobil Research and Development Corporation (MRDC) announced a catalytic process for converting methanol to high octane gasoline in high yield (Meisel, et al., 1976; Wise and Silvestri, 1976). Since commercial processes for the synthesis of methanol from coal-derived synthesis gas are known, this new technology provides a viable route for the conversion of coal to gasoline. The development of the fixed-bed MTG (Methanol-to-Gasoline) process was studied under an ERDA contract, No. E(49-18)-1733 (Voltz and Wise, 1976). In 1978, under DOE Contract No. EX-76-C-01-2490, the conversion of methanol to high octane gasoline in a 4 BPD fluidized-bed pilot unit was demonstrated (Kam and Lee, 1978). Currently, a 14,000 BPD gasoline plant using fixed-bed MTG technology is being constructed in New Zealand.

Another route of converting coal-derived synthesis gas to hydrocarbons uses the Fischer-Tropsch (F-T) reaction, which was first reported in 1923 and is named after its discoverers (Fischer and Tropsch, 1923). Excellent reviews on early F-T work have been given by Storch, et al. (1951) and by Anderson (1956). SASOL in South Africa is currently operating three commercial plants producing transportation fuels using F-T technology. Both fixed-bed tubular (Arge process) and fluidized entrained-bed (Synthol process) reactor designs are used.

Both routes mentioned above require synthesis gas of H_2/CO molar ratio greater than 2.0. In the case of methanol synthesis, this is required by stoichiometry. In the case of the conventional F-T technologies, the high H_2/CO ratio is required either for minimizing carbon formation from the carbon monoxide or avoiding formation of waxy hydrocarbons in fluidized bed systems, which causes the catalyst to lose fluidization characteristics.

In 1978, under DOE Contract No. EF-76-C-01-2447 (Schreiner, 1978), a research guidance study was carried out on coal-to-gasoline processes via both the MTG and SASOL-type Synthol route. It was found that the predominant cost of a complete plant is associated with the gasification of the coal. Consequently, a study to identify potentially lower-cost coal gasification systems was carried out in 1978 under DOE Contract No. EF-77-C-01-2766 (Shinnar and Kuo, 1978). The majority of the advanced coal gasification systems that have high thermal-efficiency (and thus potentially lower-cost) produce low H_2/CO ratio synthesis gas (ranged from 0.35 to 1.0). This is a

direct consequence of minimum steam usage during the gasification. Of course, those low H_2/CO ratio gases can be shifted to high H_2/CO ratios and then used as feed-gases to either methanol synthesis or conventional F-T units. However, the major cost advantage from the advanced coal gasification is then negated. To maintain this advantage, a synthesis process, that can directly use a low H_2/CO ratio gas is needed.

With Fe-based F-T catalysts which promote the water-gas shift reaction under synthesis conditions, the following reactions take place simultaneously (as illustrated by formation of $[-CH_2]$ hydrocarbons):

$$CO + 2H_2 = [-CH_2] + H_2O$$

$$H_2O + CO = H_2 + CO_2$$

The second reaction indicates that the Fe-based catalyst promotes "internal shift" by utilizing the water produced from the F-T reaction to make more H_2. By doing so, high single-pass synthesis gas conversion can be achieved with a low H_2/CO ratio synthesis gas. After this "internal shift" reaction, the overall F-T reaction becomes

$$2\ CO + H_2 = [-CH_2] + CO_2$$

This reaction is highly exothermic and strict temperature control is vessential. A slurry reactor provides excellent reaction temperature control and prevents excessive carbon formation by the following reaction.

$$2\ CO = CO_2 + C$$

The rate of this undesirable reaction increases drastically with increasing temperature.

The products from F-T process, however, are highly nonselective. They include a wide range of hydrocarbons and oxygenates and require expensive refinery steps to upgrade them to marketable products.

MRDC has, however, developed a process using ZSM-5 which converts the F-T products into high-quality gasoline in a single step. In this way, the conversion of coal derived synthesis gas to gasoline can be made more attractive economically. The potential of this two-stage technology is being assessed in this study.

IV. Design of Two-Stage Bench-Scale Pilot Plant

A. Simplified Flow Diagram and Design Basis

A simplified flow diagram of the bench-scale unit is shown in Figure 1. The unit consists of four sections:

- Gas feed
- Slurry F-T reactor
- Fixed-bed ZSM-5 reactor and product recovery
- Liquid hydrocarbon product distillation

The design basis of the BSU defines the normal operating conditions and the design ranges of all major variables of the pilot plant (Table 1). At normal operating conditions, the synthesis gas feed rate is 1.87 Nm^3/hr with a 0.67 H_2/CO ratio.

B. Engineering Flow, and Piping and Instrumentation Diagrams

The Engineering Flow, and Piping and Instrumentation diagrams for all sections, shown as Figures A-1 through A-4 in Appendix A, are based on the design basis defined in Table 1.

In the gas feed section (Figure A-1), the in-house H_2, and CO from a high pressure tank (13.9 MPa or 2000 psig) are filtered, purified over activated charcoal to remove any carbonyls, regulated and metered to give a simulated synthesis gas with a desired H_2/CO ratio. A desired quantity of high pressure N_2 or any other gas (e.g., methane) can also be mixed with the H_2 and CO stream. The mixed gaseous stream passes through a preheater before entering the slurry reactor. For safe handling of poisonous CO and flammable H_2 gas, solenoid valves coupled to the leak detectors are employed to shut the gases off in the event of any leak in the system.

Also shown in the diagram is an air supply for the regeneration of the second-stage reactor. Filtered, regulated, and metered air and nitrogen are fed to a compressor (E 50). The compressed mixture is then combined with the regeneration recycle gas and fed to the reactor.

Figure A-2 is the Engineering Flow, and Piping and Instrumentation diagram of the slurry F-T reactor section. The slurry reactor (5.1 cm ID x 762 cm height) consists of one 150 and two 305 cm sections of schedule 40 stainless steel pipe connected together with flange joints. The sectioning of the reactor into 305 cm and 710 cm levels offers the flexibility of design modifications, if warranted.

FIGURE 1

SIMPLIFIED FLOW DIAGRAM OF TWO-STAGE PILOT PLANT FOR SYNTHESIS GAS CONVERSION

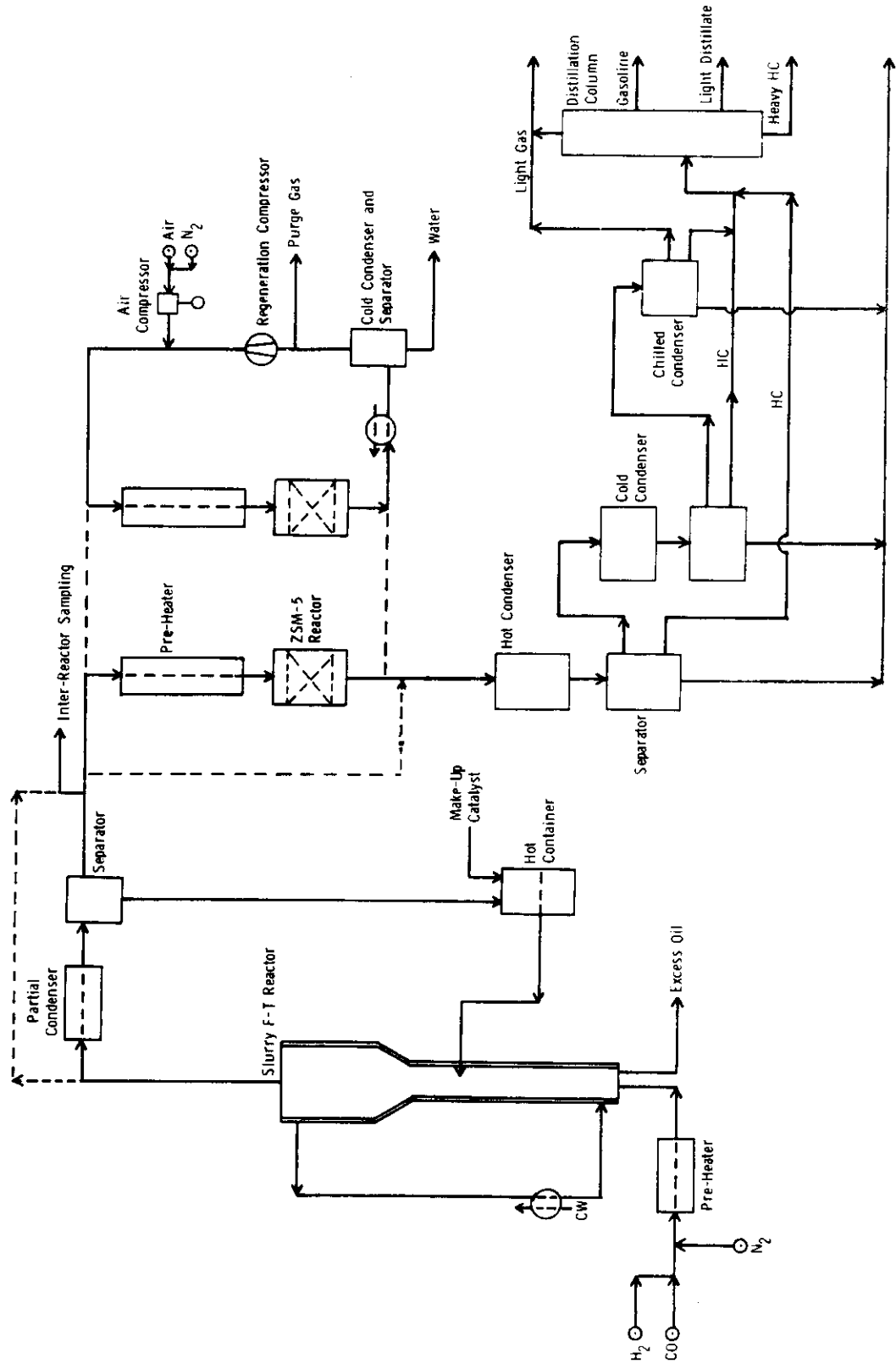


Table 1

Design Basis of the Two-Stage Synthesis Gas Conversion Bench-Scale Unit

		Normal	Design Range
I.	**Reactor Dimensions**		
	Slurry F-T Catalyst Bed, cm	5.08(ID)x305(L)	5.08(ID)x305 762(L)
	ZSM-5 Catalyst Bed, cm	5.08(ID)x20.3(L)	5.08(ID)x10.2-45.7(L)
II.	**Material Balance Basis**		
	Normal Operation		
	Syngas Feed Rate, Nm^3/hr	1.87	0.94-3.75
	H_2/CO Mole Ratio	0.67	0.5-2
	H_2+CO Conversion, Mol %	90	50-97
	ZSM-5 Reactor Regeneration		
	Air+Recycle Gas Flow Rate, Nm^3/hr	1.39	0.70-3.21
	Oxygen Concentration, Mole %	0.7-21	-
III.	**Reactor Operation Conditions**		
	Slurry F-T Reactor		
	Inlet Temperature, °C	260	38-343
	Exit Temperature, °C	260	216-343
	Pressure, MPa	1.38	0.69-4.14
	GHSV (STP), 1/hr	128	64-256
	Catalyst Load, g	1544	1544-3859
	Reaction Heat Removal Rate, MJ/hr	4.8	1.4-10
	ZSM-5 Reactor		
	Inlet Temperature, °C	316-399	316-454
	Exit Temperature, °C	379-463	316-482
	Pressure, MPa	1.31	0.69-4.14
	WHSV Based on Hydrocarbons, 1/hr	1.5	-
	Catalyst Load, g	227	114-545
	ZSM-5 Reactor Regeneration		
	Inlet Temperature, °C	316-482	316-538
	Exit Temperature, °C	371-482	371-538
	Pressure, MPa	2.76	1.03-4.14

Table 1 (cont'd)

IV. ZSM-5 Reactor Preheater	Normal	Design Range
Normal Operation		
Inlet Temperature, °C	260	177-343
Exit Temperature, °C	316-399	316-427
Pressure, MPa	1.31	0.69-4.14
Regeneration Operation		
Inlet Temperature, °C	Room	-
Exit Temperature, °C	343-482	316-538
Pressure, MPa	2.76	1.03-4.14
V. Other Operation Conditions		
Slurry F-T Reactor Preheater		
Inlet Temperature, °C	Room	-
Exit Temperature, °C	260	216-343
Pressure, MPa	1.38	0.69-4.14
Partial Condenser After F-T Reactor		
Inlet Temperature, °C	260	216-343
Exit Temperature, °C	260	177-343
Pressure, MPa	1.31	0.69-4.14
Hot Condenser		
Inlet Temperature, °C	379-463	343-482
Exit Temperature, °C	100	-
Pressure, MPa	1.31	0.69-4.14
Cold Condenser		
Inlet Temperature, °C	100	-
Exit Temperature, °C	Room	Room-52
Pressure, MPa	1.31	0.69-4.14
Chilled Condenser		
Inlet Temperture, °C	Room	Room-52
Exit Temperature, °C	0	-
Pressure, MPa	1.31	0.69-4.14
Liquid Hydrocarbon Distillation Column		
Pressure, MPa	0.17	0.07-0.41
Overhead Product	C_{4-}	-
Bottom Product	C_{12+}	-

The hot synthesis gas (H_2+CO) from the Feed Preheater enters the bottom zone below a distributor which is clamped between the bottom flanges. A drain is provided in the zone below the distributor to drain any slurry seeping through the distributor.

At the top, a disengaging zone (12.7 cm ID x 183 cm height) is provided to separate outgoing gases from the gas-liquid suspension. Two inclined baffles are in this zone to break up any froth formed and to minimize any liquid entrained in the gas. The product vapors leave this zone through a fine filter which prevents any catalyst carryover.

A coolant, such as Mobiltherm-600[1], is circulated through a jacket surrounding the reactor either to remove the heat of reaction or to add heat as may be required. The cooling jacket is divided into many sections to facilitate the attachment of pipe couplings to the reactor at different levels. These pipe couplings are used for the insertion of different probes (e.g., temperature, pressure, and liquid-level probes) and lines for the addition or withdrawal of slurry. Four sample taps are provided at 30, 152, 305 and 610 cm above the feed-gas distributor to withdraw slurry into sample bombs.

The catalyst slurry is prepared in a 26,000 cm^3 Slurry Tank (E-48) and transferred to the reactor above the distributor by applying N_2-pressure in the slurry tank. The Slurry Transfer Vessel (E-49) is used to add small quantities of slurry, if needed, during the operation of the reactor.

In case of accumulation of liquid hydrocarbon products in the reactor, a small amount of the liquid can be withdrawn through a fine filter suspended at a level of approximately 213 cm. The withdrawn liquid is collected in the Spent-Wax Receiver (E-23). The fresh liquid without catalyst is stored in the Fresh-Wax Reservoir (E-22). The wax from these two tanks can be pumped into the reactor in the case of a loss of the slurry.

A partial condenser (E-8, Liquid Drop-Out Pot) is employed on the product line before the products are sent to the second-stage reactor. If a drop in slurry level occurs within the bubble-column, this condenser can be used to recover some of the heavier hydrocarbons from the F-T reactor effluent and returned to the F-T reactor.

To analyze first-stage F-T reactor products, a small side-stream can be diverted from the effluent stream. The hot and cold condensers (E-93, 94) separate this sample stream into heavy and light liquid hydrocarbons, aqueous phase, and light gases. These four streams can then be analyzed separately.

In the fixed-bed ZSM-5 reactor and product recovery

[1]A registered trade mark.

section (shown in Figure A-3), two fixed-bed adiabatic reactors (5.08 cm ID x 10-46 cm height) are used; one in normal operation and the other in regeneration. The reactor containing the coked catalyst is regenerated under pressure with a controlled supply of O_2 (0.7 - 21 mol %).

The product stream from the reactor passes through hot (100°C), cold (about 38°C), and chilled (0°C) condensers. Each condenser is followed by a separator where liquid hydrocarbons and aqueous phases are separated and subsequently collected. The uncondensed light gases containing mostly CO_2 are metered, analyzed, and finally vented off. The liquid hydrocarbon products collected from three separators are sent to a distillation column for further separation.

In the liquid hydrocarbon product distillation section (Figure A-4), the three liquid hydrocarbon streams from the hot, cold, and chilled condensers are separated into a light gas, a gasoline range product, and heavier fraction liquid products, if there are any. This separation serves two purposes:

- To make the analysis of the liquid hydrocarbon products easier.
- To obtain the proper gasoline stream for product evaluation.

The distillation column is divided into two separate sections to ease control and operation. The first section separates very heavy products (boiling above a certain temperature which can be controlled) as the bottoms. The top stream enters the second section at a desired temperature. The gasoline product is obtained as a side stream. A temperature-controlled valve monitors the withdrawal rate of the gasoline product. The top portion of the section, acting as a condenser, is maintained at 0°C by circulating chilled glycol. The reflux ratio can be adjusted by withdrawing various amounts of liquid from the top portion. The light gas from the top is combined with the light gas from the chilled condenser to be metered and analyzed. The bottoms of the second section are collected as a light distillate. Provisions are made so that this section can be completely bypassed, if necessary. In this case, light and heavy hydrocarbon liquid streams with largely overlapping hydrocarbon distributions will be obtained.

C. Detailed Engineering Design

Table 2 gives a list of thirty-nine detailed fabrication drawings for the important BSU components, such as distillation columns, preheaters, condensers, receivers, drop-out pots, and glycol flow measuring systems.

Table 2

List of Fabrication Drawings

Drawing Nos.	Description
RB-9074, 9075, 9076	Main Fractionation Column, E-43
RB-9093	Pre-fractionation Column, E-42
RB-9087	Feed Preheater, E-32
RC-4470	Hot Condenser, E-38
RC-4471	Ambient Water Condenser, E-39
RC-4472	Chilled Glycol Condenser, E-40
RC-4469	Regeneration Gas Condenser, E-35
RD-2694	Inter-reactor Sample (I.R.S.) Hot Condenser, E-93
RD-2695	I.R.S. Water Condenser, E-94
RD-2699	Heavy Fuel Oil Vent Condenser, E-100
RE-6229	Wax Drop-out Pot (Partial Condenser), E-8
RB-9095	Slurry Tank, E-48
RC-4467	Fresh Wax Reservoir, E-22
RC-4468	Spent Wax Receiver, E-23
RC-4473	Heavy Fuel Oil Reservoir, E-41
RC-4474	Two-gallon Distillate Receiver, E-44
RC-4475	One-gallon Distillate Receiver, E-45
RC-4476	Two-gallon Gasoline Receiver, E-46
RC-4477	One-gallon Gasoline Receiver, E-47
RE-6225	Slurry Sample Bombs, E-1, 2, 3, 4
RE-6236	Slurry Transfer Vessel, E-49
RD-2693	H. P. Drop-out Pot, E-26
RE-6234	Water Drop-out Pot, E-29
RE-6240	I.R.S. Hot Condenser Drop-Out Pot, E-87

Table 2 (cont'd)

Drawing Nos.	Description
RE-6241	I.R.S. Ambient Condenser Drop-out Pot, E-88
RE-6226	Chilled Drop-out Pot, E-5
RE-6227	Surge Pot, E-6
RE-6228	Surge Pot, E-7
RE-6231	Surge Pot, E-17, 18, & 19
RE-6233	Glycol Reservoir, E-24 & 25
RE-6235	Glycol Reservoir, E-30 & 31
RE-6232	Glycol Hold-up Vessel, E-20, 21, 27 & 28
RE-6230	Glycol Overflow Vessel, E-13 & 14
RE-6243	Glycol Overflow Vessel, E-15 & 16
RE-6238	Funnel, E-81, 82, 83, 84 & 96
RE-6239	Funnel, E-97
RE-6237	Gas Mixing Tube, E-55

The detailed designs of the six sections for the F-T bubble-column reactor are shown in Figures A-5 and A-6. Figure A-5 shows section 1, the top flange with a filter attachment; section 2, the disengager; and section 6, the bottom section below the distributor. Also shown in the drawing is the overall layout of the reactor. Figure A-6 shows sections 3, 4, and 5 of the reactor between 610-762 cm, 305-610 cm, and 0-305 cm levels, respectively. Both figures show cooling jackets and pipe couplings for the insertion of different probes as described in the previous subsection. Figure A-7 gives details of the fixed-bed ZSM-5 reactor. The reactor is 101.6 cm long with 5.1 cm inside diameter, with the top thirty-eight cm section acting as a preheater. The maximum catalyst bed height is fifty-eight cm (capacity - 1,100 cm^3). An automated traversing thermocouple probe inserted into the thermowell at the center of the reactor records the fixed-bed temperature along the reactor.

The liquid level and gas holdup in the slurry F-T reactor are important process variables. Considerable effort was spent to evaluate methods for such measurements, i.e.:

- Axial pressure-drop measurement using pneumatic differential-pressure (DP) cells.
- Axial pressure-drop measurement using piezo-resistive pressure transducers.
- Liquid level height measurement using a floating radioactive-source.

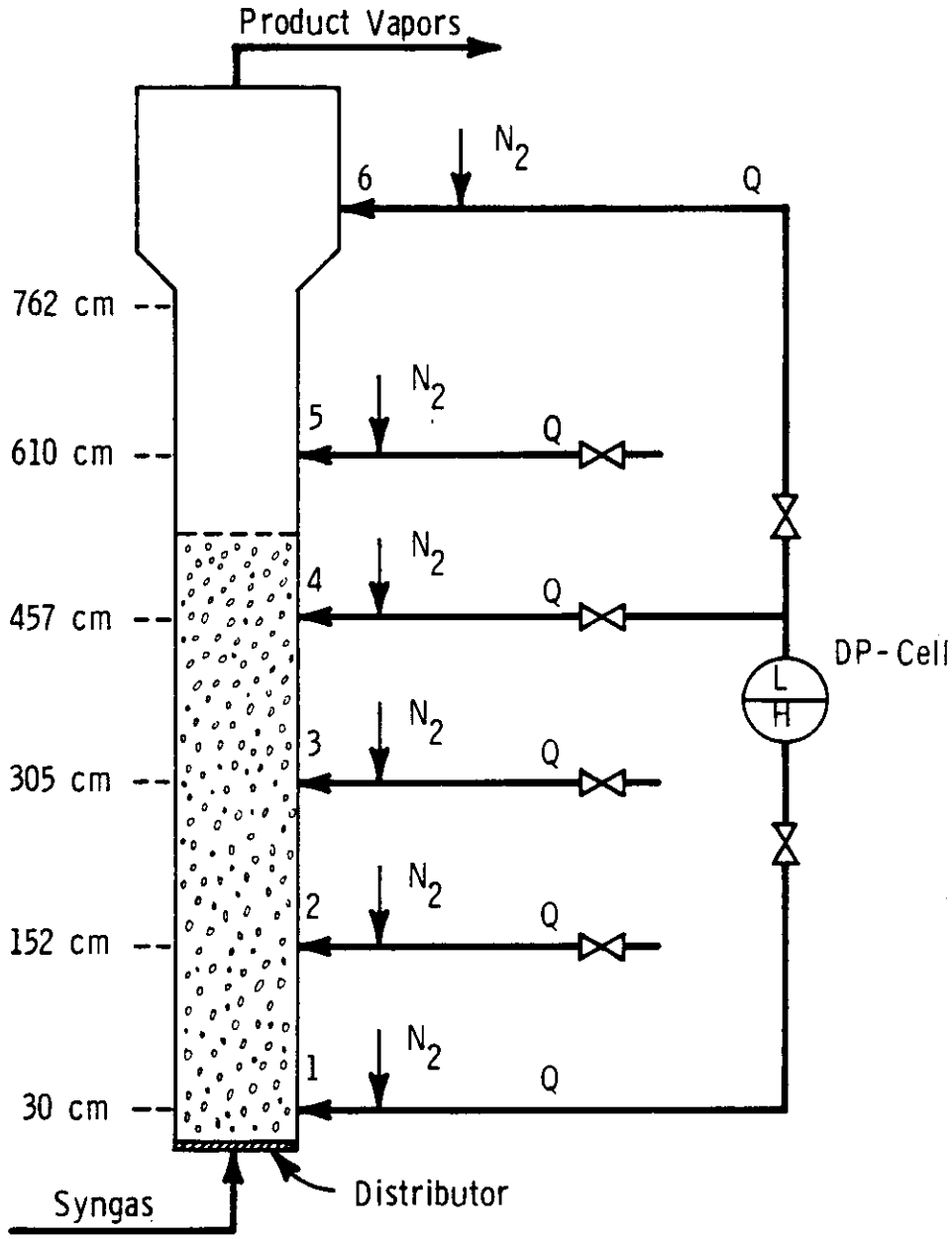
The decision was made to use the first method after thorough discussions with instrumentation experts and consultants. This method has the advantages of simplicity in both use and maintenance. The method of pressure-drop measurement using Peizo-resistive pressure transducers was ruled out because of difficulties with water-cooling to maintain the transducers at temperatures below a damaging 232°C. The method of measuring the liquid level height using a floating radioactive source in the bubble-column has been eliminated because the use of radioactive materials is cumbersome and does not give any indication of the axial profile of the gas holdup.

Figure 2 shows the schematic arrangement of a DP-cell with six N_2-purge lines along the reactor height to measure the pressure gradient. The pressure-drop between any two DP-cell lines, which gives the reactor pressure-drop between these two locations, can be measured by connecting these lines to a differential-pressure cell (DP-cell). In the figure, lines 1 and 6 are shown connected to the DP cell. Also shown is a pathway to connect lines 1 and 4 to the DP cell.

A continuous N_2-purging through the lines is necessary to keep them free of any slurry from the reactor which may plug them. Based on a laboratory experiment using hexadecane in a glass bubble-column, a purge rate of 12 cm^3/min (at actual

FIGURE 2

SCHEMATIC ARRANGEMENT OF DP-CELL FOR LIQUID LEVEL MEASUREMENT



Q: DP-Cell Lines

temperature and pressure) is sufficient. To be safe, a purge rate of 30 cm^3/min (actual) was used. The total N_2 purge rate was less than 4% of the flow rate of synthesis gas entering the reactor; thus, performance was not significantly affected.

Gas holdup is related to the densities of the slurry (ρ_{sl}), the expanded slurry (ρ_{esl}) and the gas (ρ_g) by the following equation:

$$\epsilon_g = (\rho_{sl}-\rho_{esl})/(\rho_{sl}-\rho_g) \quad (1)$$

ρ_g and ρ_{sl} can be easily calculated. ρ_{esl} can be estimated from the measured pressure-drop between any two locations within the expanded slurry. For example, if the slurry level is between 457 and 610 cm levels, the pressure drop between Locations 1 and 4 can be used to estimate the average ρ_{esl} between these two locations. In general, between Locations 1 and N:

$$\rho_{esl} = 70.38\ (P_N-P_1)/(z_N-z_1) \quad (2)$$

where 70.38 is the factor for converting pressure (psi) into a hydraulic head (cm of water), P_i is the pressure at location i (psi), z_i is the height of the reactor column at location i (cm), and ρ_{esl} is the average density of the expanded slurry (g/mL). An equation similar to Equation (2) can be used to calculate the average expanded slurry density between any two adjacent locations. An axial profile of the gas holdup can then be established. If the axial variation of the gas holdup is small, the density calculated from Equation (2) can be used for the whole slurry column; otherwise, the axial variation of the bed density must be taken into account. Using the same example, the liquid level in the slurry bubble-column can be calculated using the following equation:

$$z=z_4+(z_4-z_1)(P_6-P_4)/(P_4-P_1) \quad (3)$$

if the axial variation of the gas holdup is nil. With appreciable axial variation of the gas holdup, the axial profile can be taken into account to obtain a more accurate estimate of the liquid level.

Based on the information supplied by the DP cell vendor, the absolute error of pressure drop measurements is 0.3 kPa (0.05 psi) for range of 69 kPa (10 psi). This translates to a maximum error of 3% for the average gas holdup calculation when the liquid level is above 305 cm and a maximum error of 6% in the liquid level estimate.