EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN AN ADIABATIC COAL LIQUEFACTION REACTOR. PROGRESS REPORT, SEPTEMBER 1, 1982-FEBRUARY 28, 1983

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

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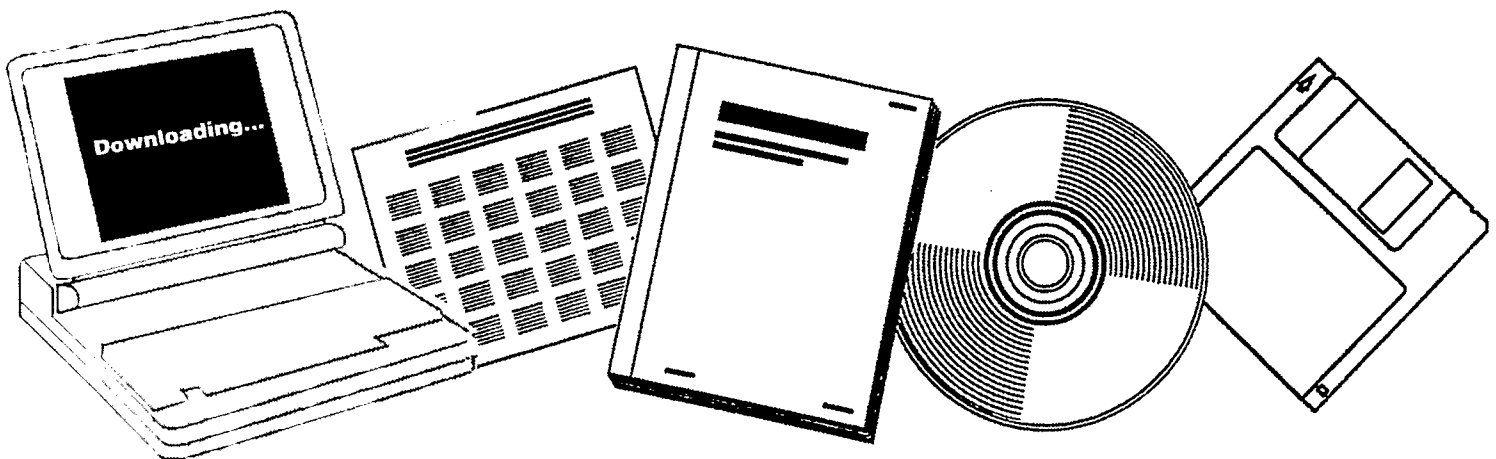

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Progress Report

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AN EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN AN ADIABATIC COAL LIQUEFACTION REACTOR

SUMMARY

Previous work on this project has demonstrated that a small scale batch reactor can be made to operate in an adiabatic mode by making proper compensation for heat losses. The reactor was constructed at Gulf Research and Development Laboratories and described in previous reports. A major difficulty with the reactor was the long times required to obtain steady state. A modified reactor which should come to steady state in much shorter times has been designed and built in the laboratories of the Chemical and Petroleum Engineering Department. The design of the reactor and the results of some preliminary experimental runs are presented.

INTRODUCTION

As described in previous reports for this project, there are substantial difficulties in designing and operating a small scale reactor under conditions for coal liquefaction in an adiabatic mode because of the high surface area to volume ratio in a small reactor. Yet, for large commercial reactors, the reverse is true, and adiabatic operation will result unless heat exchangers are provided. A small-scale reactor to achieve adiabatic operation was designed and operated at Gulf Research and Development and described in previous reports. The concept of adiabatic operation was demonstrated, but there were some serious drawbacks in the operation of the reactor: the only control on reactor temperature is the feed temperature, and this results in long times to reach equilibrium; the placement of thermocouples for measurement of the temperature gradient in the insulation surrounding the reactor is critical because of poor thermal conductivity of the insultion; and the use of a simple analog control system does not provide the versatility desired. Because of these and other limitations, an improved design for a bench scale reactor was undertaken. It has the following new features:

A cooling coil is provided for the reactor. This permits removal of large amounts of heats, and, more importantly, allows the heat removal to be accurately measured. Furthermore, the reactor can be operated in an isothermal mode by measuring and controlling the amount of heat removed. This should result in short times to achieve steady state.

The insulated reactor is placed in a thick copper vessel and a zero temperature gradient is maintained between the reactor wall and the copper vessel. Because of the high thermal condutivity of the copper, the thermocouple placement is much less critical.

A digital computer is incorporated in the system to record important process variables at frequent intervals, to provide control signals for the adiabatic heaters; and to control the flow of coolant. Since the computer has access to all important process variables, control algorithms can be complicated and easily changed.

A detailed description of the reactor is given in the next section. It has been built in the Chemical and Petroleum Engineering Department laboratories, and some preliminary test results are reported which indicate that it operates as planned. The digital control system has been essentially completed and is being tested.

REACTOR DESIGN

A standard "Autoclave Engineers" one liter stirred autoclave serves as the reaction vessel. The reactor is operated in a semi-batch fashion, with batch solid/liquid holdup and continuous gas flow. Gas is continuously sparged to the slurry phase via a dip tube. Thorough mixing is provided by a mechanical stirrer equipped with a single 1-1/4 in. blade impeller. The variable speed (2500 RPM maximum) stirrer is driven by a magnetic coupling. A 12 in. shaft extension is employed to allow for increased insulation and the positioning of heating elements above the reactor.

The reactor is operated with an initial slurry charge of 0.5 liters. Product gases are continuously removed via the effluent port in order to maintain a constant reactor pressure. Gas and slurry phase temperatures are constantly monitored via thermocouples, while reactor pressure is indicated on a pressure gage and a pressure tranducer. If accumulation of liquid products in the reactor at reactor conditions presents a problem, the reactor is operated full with continuous removal of excess liquid and gas. A sintered metal filter is employed to prevent loss of fine catalyst particles.

The reactor and its contents are heated to desired initial conditions by means of a 51 in., 1500 W "Chromalox" tubular heater. The heat of reaction is removed via an internal cooling coil assembly. House air is used as the cooling medium. The flow rate of air is measured and controlled by a "Brooks system" consisting of a mass flow meter, integral control valve and set point potentiometer.

Adiabatic operation is diffucult to attain in such a small scale reactor due to the high surface area to volume ratio inherent in the design. Therefore, special modifications have been added to the reaction system to insure adiabatic operation. The modifications are illustrated in Figure 1.

The reactor is placed inside an 11 in. diameter, $1/4$ in. thick copper cylinder with custom designed circular, $1/4$ in. thick top and bottom copper plates. The reactor rests on solid insulation board, and the volume between the reactor and the copper vessel is packed with "Fiberfrax" bulk fiber insulation. Four quarter-cylinder 1000 W ceramic heaters and four ring heaters (500-1000 W) are situated outside of the copper cylinder. Temperature at various points on the reactor skin, shaft extension and the copper vessel are monitored by means of thermocouples. The external heaters are operated so as to maintain a zero temperature gradient between the reactor skin and the copper cylinder. Therefore, direct heat losses from the reactor are minimized and adiabatic operation is attained.

The entire apparatus depicted in Figure 1 is mounted in a 20 in. diameter, 30 in. tall drum. Free internal volume is filled with more of the Fiberfrax bulk fiber. One inch thick "Durablanket" insulation is wrapped around the drum exterior to minimize overall heat losses and maintain laboratory safety.

Process Flow Diagram

The overall process flow diagram for the slurry unit is depicted in Figure 2. The design is presented for a CO/H_2 feed gas system. The unit can be used to study other low to medium pressure gas/solid, or gas/liquid/solid reactions with little modification.

Calibrated metering valves allow control of the overall feed gas composition. The gas feed temperature is set at desired levels by a preheater oven. As noted earlier, gas is continuously sparged to the reactor via a dip tube. The internal cooling coil assembly is again illustrated. House air at 100 psig enters through a pressure reducing valve and passes through a knockout drum and filter to remove extraneous liquid and solid material. The flow rate is measured and controlled by means of the mass flow meter and integral control valve.

Gaseous products are continuously removed so as to maintain a constant reactor pressure. The products are first passed through a high temperature, high pressure separator in which the heavier hydrocarbon fractions condense and are removed. The collection vessel and liquid transfer lines are heated to prevent wax solidification. The vapor overhead is then passed through a cold water condenser, where the lighter hydrocarbon fractions are condensed. The condensate is collected in a second high pressure separator. The product gas flow rate is monitored by a wet test meter. Gas samples are taken periodically and analyzed by gas chromatographic techniques. The hydrocarbon liquid fractions are weighed and analyzed by chromatographic techniques.

Reactor Digital Control System

A computer is employed in various control and data-logging operations for the slurry unit. The digital computer capabilities are provided by a Digital

Equipment Corporation (DEC) MINC/DECLAB 23 system. The primary functions of the digital system are:

1. Monitor reactor temperature and pressure and initiate emergency shutdown procedures in critical situations.
2. Provide direct digital control of external heater operation so as to maintain zero temperature gradient between the copper cylinder and reactor skin.
3. Provide supervisory control of the cooling air flow rate by establishing a set point for the integral control valve.
4. Provide data-logging capabilities by recording various temperatures, reactor pressure, heating rates, etc. at desired intervals.

Real time programming techniques are employed to maximize computer usage efficiency. A real time clock (MNCKW) is programmed to generate interrupts at a fixed frequency. Under an interrupt condition, the computer will exit from the current program and process a desired routine. Upon completion of the routine, the computer returns to the original program. The clock interrupts trigger sampling sweeps in which the analog thermocouple, pressure transducer and mass flow meter signals are digitized via an A/D converter (DT2764).

Since sampling sweeps are interrupt driven, the computer is not dedicated solely to A/D conversions. Therefore, the computer is free to update the external heater output and coolant flow set point via specified control subroutines. Essential data are also stored for analysis purposes.

Computer Equipment

As noted, the basic computer is a DEC MINC DECLAB/23 system. The system is extremely powerful and versatile, providing 128 K bytes of random access MOS memory. The system employed dual RL01 hard disk drives, with each disk allowed storage of 5.2 million bytes of data.

Five input/output modules are used to interface the computer with the experimental equipment. Real time clock capabilities are provided by a DEC MNCKW module, a programmable counter capable of generating interrupts upon an

overflow condition. The counter is driven by either external events or an internal oscillator.

A/D conversions are provided by a Data Translation DT2764 module. The input range is set at 0-16.425 mV with 12 bit resolution. Common mode noise is effectively cancelled through use of differential input connections. A Data Translation DT2774 multiplexer expander module is combined with the DT2764 to provide 32 differential input channels.

A DEC MNCDO module is used to interface the computer system with the external heaters. The desired heating rates are attained by periodically outputting 16 bit words to a series of relays. Each bit controls a separate relay. The relays inturn activate the external heaters to provide the desired heating pattern.

Supervisory control of the coolant flow rate is provided by adjusting the set point of the integral control valve. A Data Translation DT2767 D/A converter is employed to interface the computer system with the control valve. The module outputs analog signals in the range ± 10 V with eight bit resolution. Four individual channels are available for D/A conversions.

The computer is also used to maintain safe operating conditions. One of the relays is employed to control the operation of the gas feed solenoid valves. One solenoid controls the flow of H_2/CO and is normally open while the other controls the flow of inert N_2 and is normally closed. In emergency situations, the computer stops H_2/CO flow and allows flow of cold N_2 quench via the solenoid valves. Other emergency procedures are also enacted.

EXPERIMENTAL RESULTS

An initial test of the reactor was made to verify operability. The reactor temperature was kept constant, and adiabatic heater were not used. The reactor was initially charged with 350 ml. of solvent (synfluid obtained

from Gulf R&D, whose composition is listed in Table 1) and 30 gms. of -100 mesh catalyst particles (obtained from United Catalyst Inc., with the composition listed in Table 2). The system was then pressure tested with helium at 400 psig for approximately 15 hours. Cold hydrogen was then passed through the reactor at 10 atm and the temperature of the reactor was slowly increased with the tubular heater wrapped around the body of the reactor. The temperature was maintained constant at 200°C for approximately 20 hours and at 250°C for 50 hours in order to reduce the catalyst. Then a mixture of carbon monoxide and hydrogen was sent through the reactor. After about 24 hours of operation, steady state with respect to conversion of CO and H_2 was attained in the reactor. The feed and product gas compositions were analysed in a Sigma 1 (Perkin - Elmer) gas chromatograph. The process parameters during the reduction and reaction periods and the experimental results are tabulated and given in Table 3.

At steady state, the conversion of CO was 13.3% and H_2 was 11.6% and the combined (CO + H_2) conversion was 13.2%. The low conversion of both CO and H_2 may be attributed to very low H_2/CO ratio in the feed gas and comparatively large catalyst particle size. However, when our conversion data were matched with those reported by Huff (1982), we find that the agreement was fair, as shown in Figure 3.

FUTURE WORK

The digital control system and the reactor are being integrated and testing with a CO/H_2 feed will be carried out. The operability and accuracy of the reactor will be evaluated. If time permits, liquid feeds will also be used.

REFERENCES

Huff, G. A., "Ph.D. Thesis, Massachussetts, Institute of Technology (1982)"

Table - 1

Composition of Solvent

Component	wt%
C_{20}	0.06
C_{30}	28.04
C_{40}	53.22
C_{50}	15.58
C_{60}	3.11

Table - 2

Specification of the Iron Catalyst

Catalyst Type: - C-73-1-01

Composition (wt %): -		
	FeO	30-37
	Fe_2O_3	65-68
	Free Fe	< 0.5
	Total Fe	67-69
	Al_2O_3	2.0-3.0
	K_2O	0.5-0.8

Table 3

Experimental result for Isothermal Fischer-Tropsch reaction

SL#	Time (hrs.)	Temp (°C)	Pressure (psia)	Flow rate cc/min	Comments
1.	20	210	147.0	350.0(H_2)	Reduction
2.	50	250	147.0	400.0(H_2)	Reduction
3.	24	250	147.0	3900(H_2+CO) ($CO:H_2$ = 0.174)	Reaction*

* Liquid products condensed in the cold trap. No liquid product was obtained in the hot trap.

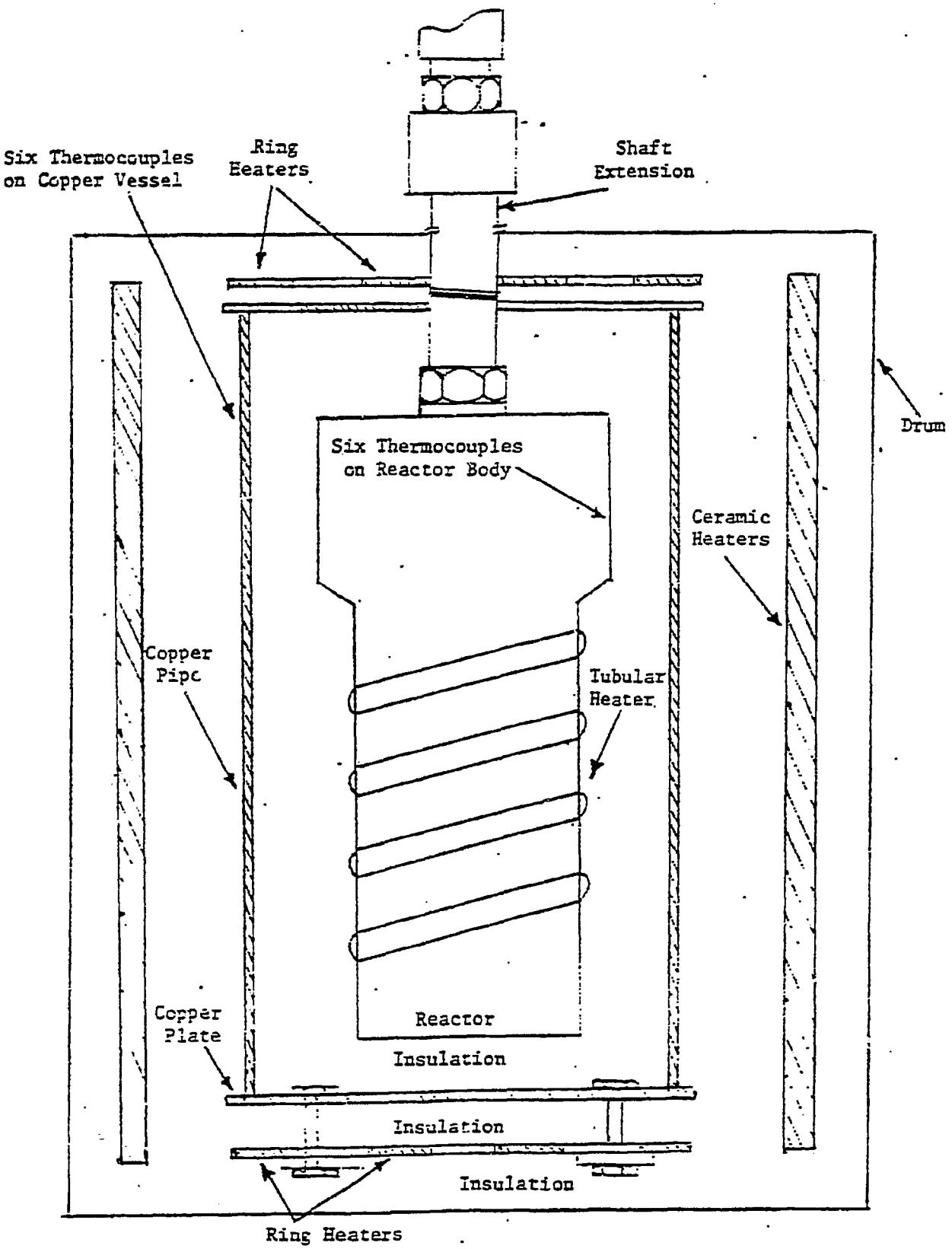

Figure 1. Cross Section of Adiabatic Container for Slurry Reactor.

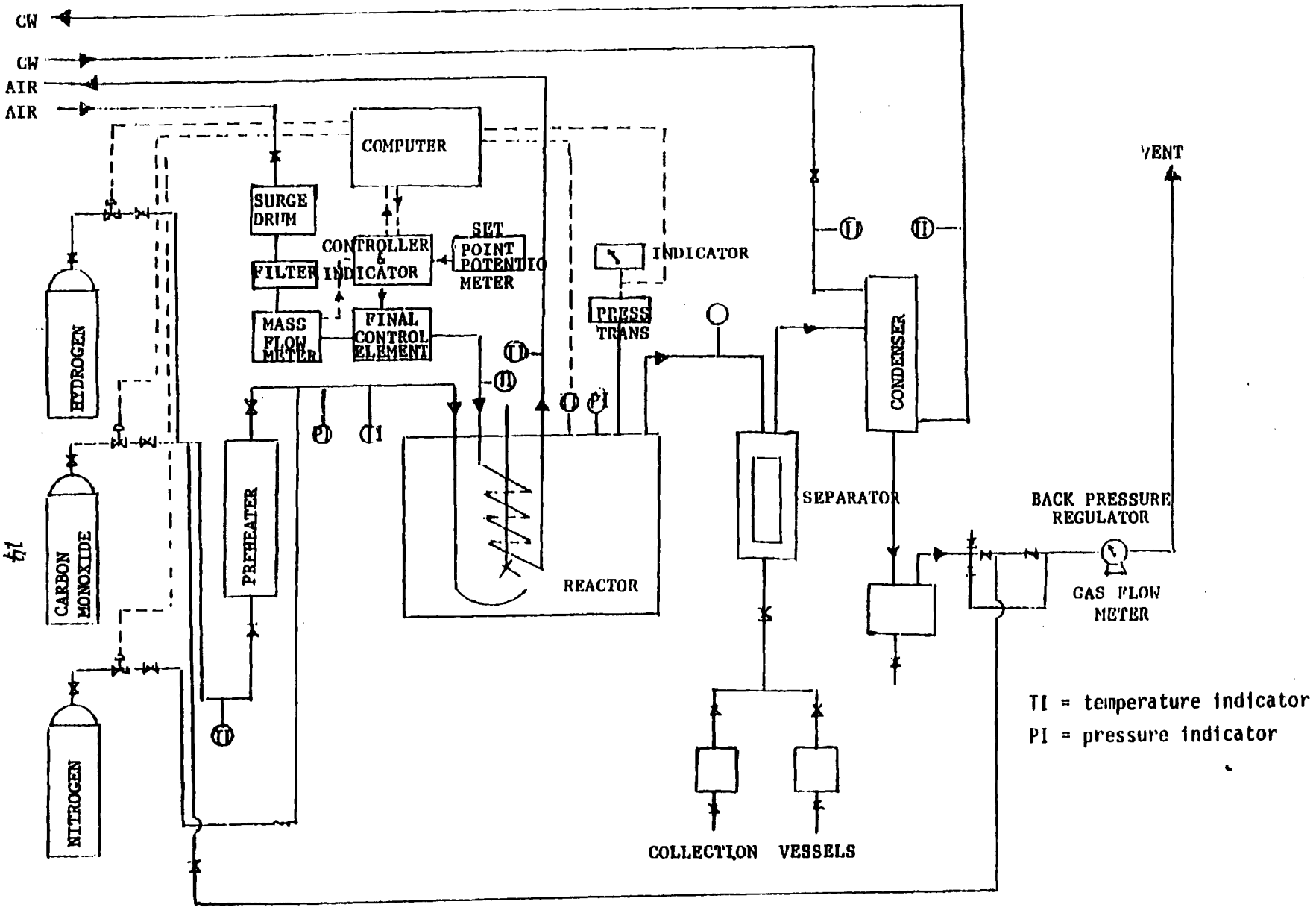

Figure 2. Flow Diagram for Adiabatic Slurry Reactor Unit

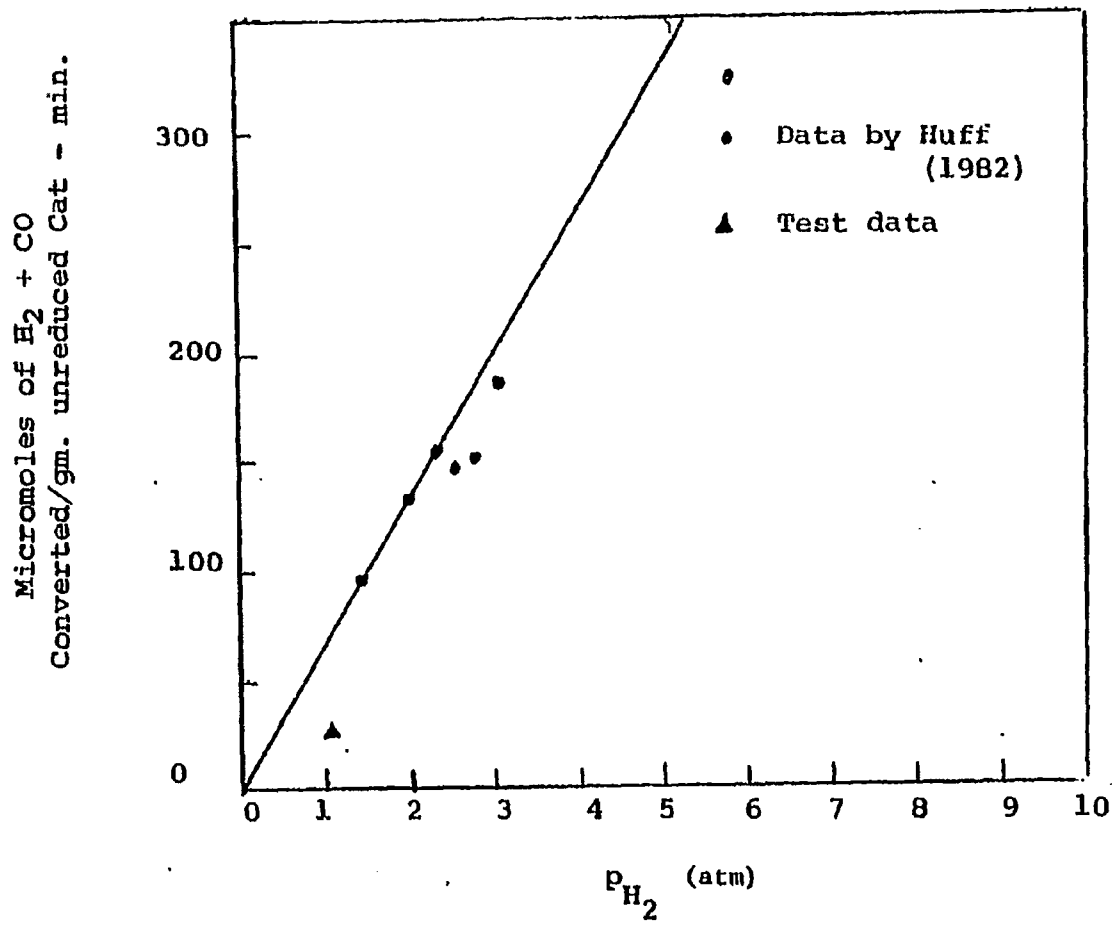

FIGURE 3: Rate of Synthesis Gas Conversion as a Function Hydrogen Partial Pressure

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