NOVEL EXPERIMENTAL STUDIES FOR COAL LIQUEFACTION. QUARTERLY PROGRESS REPORT, JULY 1-SEPTEMBER 30, 1985

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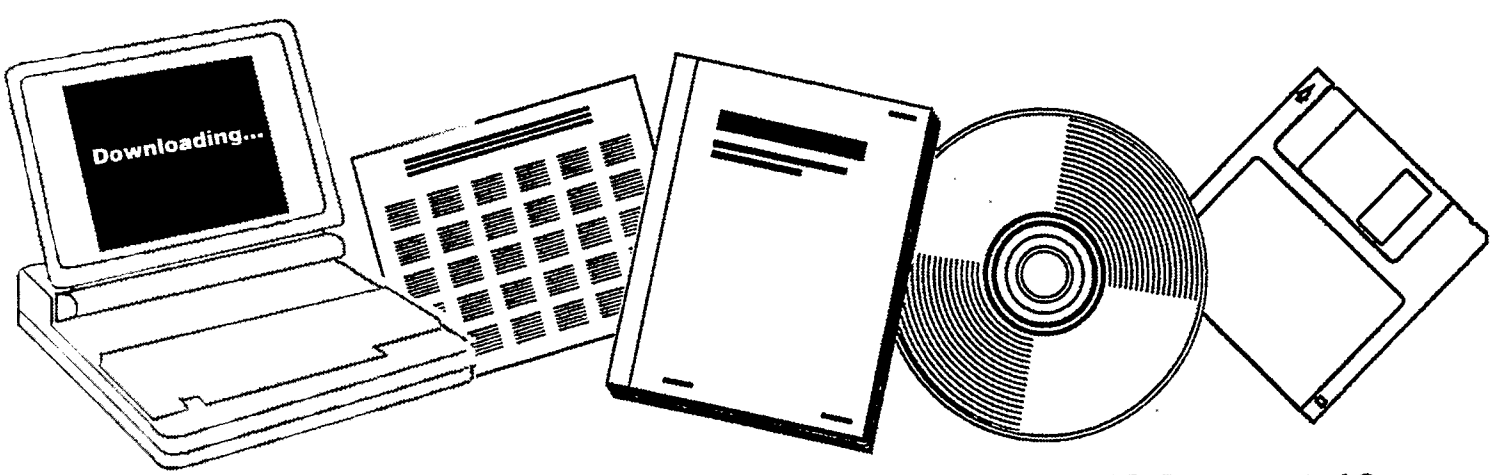
1985



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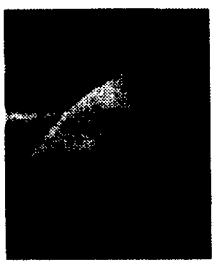

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Novel Experimental Studies for Coal Liquefaction

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DISCLAIMER

Task 1: Thermal Behavior of Slurry Reactors used for Indirect Coal Liquefaction

The conversion of synthesis gas to liquid products is usually carried out with the reactants in the gas phase and a solid catalyst. Because of relatively poor heat transfer from the gas to the solid, the reaction sites may overheat with loss of selectivity and activity. Slurry reactors in which the catalyst is suspended in a liquid medium and the gases are bubbled through the slurry have intrinsically better heat transfer characteristics and appear promising for indirect liquefaction.

In Task 1 the thermal behavior of slurry reactors is being studied. Of particular interest is the determination of multiple steady states if they exist. Previous work with a ruthenium catalyst has shown that two distinct steady states can be found for identical operating conditions. Other catalysts and operating conditions are being studied.

During the last quarter work on this task continued in three areas — Fischer-Tropsch synthesis, methanol synthesis via a formate, and methanol synthesis using a Cu-ZnO catalyst. Most attention was given to the synthesis of methanol using a formate intermediate. The reaction involves carbonylation of an alcohol to formate and then hydrogenation to produce methanol. This sequence has an advantage over conventional synthesis methods in that the reaction can be carried out at a lower temperature where higher conversions per pass can be obtained because of more favorable thermodynamics. By using a slurry reactor, both reactions can take place in the same vessel. The carbonylation step uses a homogeneous catalyst and the hydrogenation step uses a heterogeneous catalyst.

The feasibility of the reaction was demonstrated in an experiment

conducted during the quarter in which a mixture of 25% hydrogen, 75% CO was used as feed to the reactor which contained secondary butanol as the carrier alcohol. The use of an alcohol other than methanol as the carrier alcohol was done so that any methanol presented in the product could be definitely identified as a result of synthesis. Potassium butoxide was the carbonylation catalyst, and Cu-Cr (United Catalyst G-89) was the hydrogenation catalyst. The temperature was 100 C, and the pressure was 805 psig. Analysis of the effluent gases and reactor liquid after four hours of operation showed that methanol, methyl formate, and secondary butyl formate were present. No other products were detected. The methyl formate was formed by carbonylation of product methanol. The results of the experiment demonstrated that methanol can be synthesized in a single step and indicated that the carbonylation step is much faster than the hydrogenation step under the conditions of the experiment.

The first step in the two step synthesis was also investigated during the last quarter. Experiments were conducted using pure CO at pressures of 14-47 atm and mixtures of methanol and benzene and with potassium methoxide as catalyst. Benzene was added to reduce the mole fraction of methanol in the liquid phase. It was selected because it does not react with methanol, methyl formate, or CO at reaction conditions. The reaction was found to be very selective. The only product found in the gas and liquid was methyl formate. The methanol must be very dry because the presence of even small amounts of water results in removal of catalyst in the form of a white precipitate — potassium formate or carbonate. The rate of reaction was measured and results are shown in Table 1. Further measurements are being made to determine the solubility of CO in methanol-benzene mixtures so that a suitable kinetic expression can be derived.

During the quarter preparations were also made for additional runs using an iron Fischer-Tropsch catalyst. Previous runs with iron catalyst showed low conversion. The activation procedure was reviewed and modified. Delays were encountered in obtaining a liquid medium for the slurry reactor. Experimental data will be obtained in the next quarter. Analysis of the results obtained using the slurry reactor for the synthesis of methanol with a Cu-ZnO oxide catalyst is being carried out with the object of developing suitable kinetic expressions.

Table 1: Rate of reaction of CO to methyl formate using potassium methoxide catalyst

Temperature (c)	Pressure (atm)	Methanol Concentration (mole/l)	Concentration (mole/l)	Rate of Reaction Mole CO Consumed per min
106.000	41.560	25.000	0.300	0.1343
106.000	31.320	25.000	0.300	0.1093
105.600	19.350	25.000	0.300	0.0670
83.000	26.990	25.000	0.150	0.0323
82.000	14.850	18.750	0.150	0.0218
83.000	45.090	12.500	0.150	0.1065
85.000	30.770	6.250	0.150	0.1065
61.000	46.650	25.000	0.100	0.0056
111.000	24.800	25.000	0.050	0.0168

Task 2: Coal Liquefaction under Supercritical Conditions

Supercritical fluid extraction is an attractive process primarily because the density and solvent power of a fluid changes dramatically with pressure at near critical conditions and during the extraction of coal, the density of a supercritical fluid should also change the extractability of the coal. During earlier quarters a non-reacting supercritical fluid, toluene, was studied to determine the effect of density on the coal extraction/reaction process. Extractions were carried out for 2 to 60 minutes at reduced densities between 0.5 and 2.0 and at temperatures between 647 and 698 K. The data obtained can be explained by the hypothesis that coal dissolution is required preceding liquefaction reactions and that the degree of dissolution depends upon solvent density and temperature. A kinetic model shows that higher solvent densities result in faster conversion rates and in higher total conversions. A second factor that makes supercritical extraction attractive is high mass transfer rates. At high pressures, mass transfer rates in a supercritical fluid are much higher than in a liquid, despite the fact that the supercritical fluid has liquid-like solvent powers. The objective of this work is to measure mass transfer rates for naphthalene extraction by carbon dioxide to enable us to determine how mass transfer coefficients vary with pressure, flow rate, and bed height, since these parameters will influence the design of extraction or reaction processes which utilize supercritical fluids.

The schematic of the experimental set up which is being used for this purpose is shown in Figure 1. Liquid carbon dioxide is pumped into the system via a high pressure liquid pump. The system consists of a preheater which allows the solvent to reach the desired temperature and the extraction vessel containing the solid. The extraction vessel is packed with naphthalene pellets which have been made from pure naphthalene using a die. The height of

the packing in the bed can be changed by using inert packing at the bottom of the bed. The inert packing material being used is nylon rods of similar shape and size as the pellets. Another advantage in using the inert pellets is to get rid of entrance effects in the packed bed being used as the extractor. The fluid mixture coming out of the extractor is depressurized to atmospheric pressure by passing it through a heated valve. The fluid mixture is then passed through two gas washing bottles containing liquid toluene which dissolves the napthalene. The instantaneous flow rate of the gas leaving the extractor is measured using a rotameter and the total amount of gas flow is measured with a calibrated wet test meter. The whole apparatus is rated for a pressure of 5000 psi. The amount of naphthalene extracted by supercritical carbon dioxide is determined by chromatographic analysis of toluene/nathalene solution using a 5880A hP Gas Chromatograph with capillary column capability.

The parameters that are being studied are:

a) Effect of flow rate on solubility of naphthalene in carbon dioxide at different pressures and temperatures.

b) Effect of bed height on the mass transfer coefficient under supercritical conditions.

c) Effect of flow rate on the mass transfer coefficient under supercritical conditions.

d) Effect of pressure on the mass transfer coefficient under supercritical conditions.

The data obtained from above would then be correlated using the following expression:

$$Sh = a + b*Re^{c}*Sc^{d}$$

where Sh = Sherwood number

Re = Reynolds number

Sc = Schmidt number

and a, b, c, d are to be estimated from the data collected and the expression given above. The viscosity of carbon dioxide and the diffusivities of naphthalene in carbon dioxide at the experimental temperatures and pressures are obtained from the literature.

The data taken up until now encompasses mostly the study of the effect of flow rate on the solubility of naphthalene at different pressures and temperatures. The experimental conditions are as follows:

System: Naphthalene - Carbon dioxide

Pellet Characteristics:

Material: Naphthalene

Shape: Cylindrical

Size: Length (mm) = 10

Diameter (mm) = 5

Number of Pellets: 600

Height of Bed (ft): 0.667

Temperature of Bed (^{o}K): 304, 328

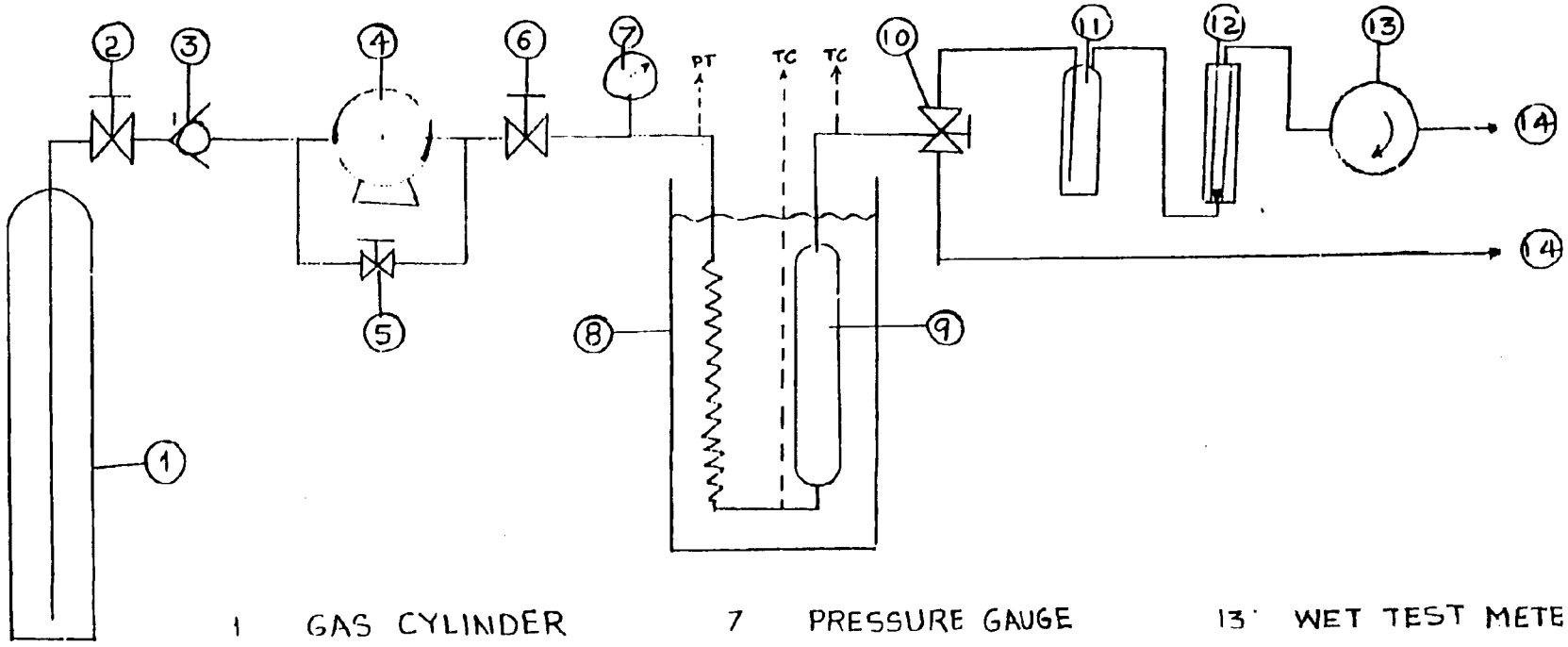
Pressure (Psi): 250, 500, 750

Flow rates (Std. Lit./Min at 70^{o}F and 1 Atm): 0.14,0.25, 0.36, 0.48, 0.58, 0.70

FIG: 1

SCHEMATIC DIAGRAM OF EXPERIMENTAL SET UP

(MASS TRANSFER IN SUPERCRITICAL EXTRACTION)



1	GAS CYLINDER	7	PRESSURE GAUGE	13	WET TEST METE
2	REGULATOR	8	WATER BATH	14	VENT
3	CHECK VALVE	9	EXTRACTOR	TC	THERMOCOUPLE
4	PUMP	10	3-WAY PRESSURE- -LET DOWN VALVE	PT	PRESSURE - TRANSDUCER
5	BACK PRESSURE- -REGULATOR	11	SAMPLE BOTTLE	TC, PT	TO DATA LOGGER
6	METERING VALVE	12	ROTAMETER		

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