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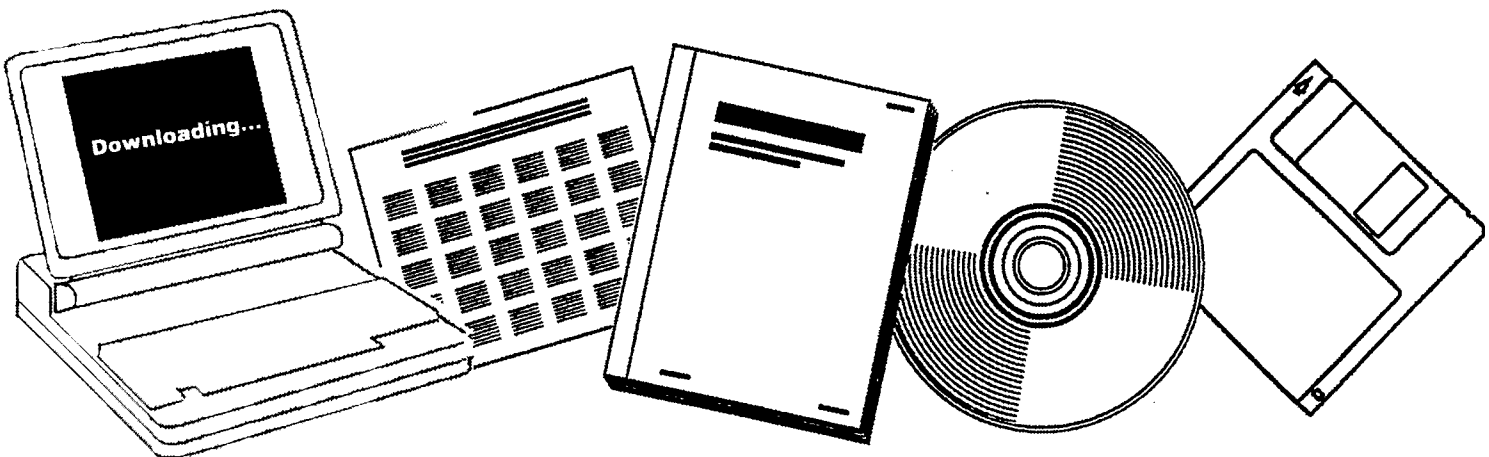
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**NOVEL EXPERIMENTAL STUDIES FOR COAL  
LIQUEFACTION. QUARTERLY PROGRESS REPORT,  
APRIL 1-JUNE 30, 1986**

PITTSBURGH UNIV., PA

1986



U.S. Department of Commerce  
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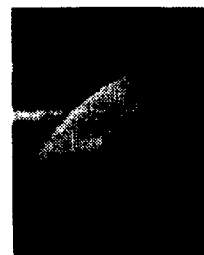
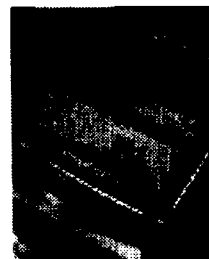
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NOVEL EXPERIMENTAL STUDIES  
FOR COAL LIQUEFACTION

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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 exothermic heat of reaction is difficult to remove, and care must be taken to prevent the catalyst from overheating 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 processes.

Scope of Work

In task 1 of this project, the thermal behavior of slurry reactors when used for indirect coal liquefaction is being studied. 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.

Work is being done using three indirect liquefaction routes involving synthesis gas -- the Fischer-Tropsch reaction, the one-step conversion to methanol, and the two-step conversion to methanol.

Results and Highlights

Experimental work during the last quarter was concentrated on examining the first step of the two-step process -- the carbonylation of alcohols using potassium alcoholates as the catalyst. The alcohol used was methanol; the catalyst used was potassium methoxide.

Carbonylation of methanol is a reversible reaction at the studied operating conditions. The reaction rate is assumed to follow the power law expression and can be expressed as:

$$r = k \exp(-E/RT) [\text{Cata}]^a [\text{MeOH}]^b P_{\text{CO}}^c - k' \exp(-E'/RT) [\text{Cata}]^d [\text{MeF}]^e \quad (1)$$

where

- k and k' : frequency factors
- E and E' : activation energies [kJ/mole]
- [Cata] : concentration of catalyst [gram/l]
- [MeOH] : concentration of methanol [moles/l]
- [MeF] : concentration of methyl formate [moles/l]
- P<sub>CO</sub> : pressure of CO [atm]

A batch reactor was used to evaluate the kinetic parameters in Equation 1. The initial reaction rate was measured and used to determine the kinetic parameters for the forward reaction since the concentration of methyl formate is zero initially. Equilibrium compositions were also measured. Then, using the equilibrium constants and analysis of experimental data, the parameters for the reverse reaction were determined.

The operating conditions are listed in Table 1.

Table 1. Operating Conditions

Operating Parameter	Unit	Operating Range
Temperature	C	60 - 112
Pressure	psig	400 - 1000
Catalyst Loading	gram/liter	7.0 - 28.0

The reaction system is shown in Figure 1. An auxiliary vessel was used to provide a reservoir for CO and ensure that the pressure drop would not be too fast. Initially, the reactor was filled with 500 cc methanol and the catalyst and then sealed. After the temperature of the reactor reached the desired value, the stirrer was turned off and CO was introduced into the reactor. The stirrer was turned on at 2,300 rpm after the reactor remained at the desired CO pressure for about 2 minutes. Equilibrium between the gas phase and the liquid phase was reached in less than 1 minute at 2,300 rpm. The pressure drop of the reactor was recorded against time, and the reaction rate was calculated from the pressure drop using the ideal gas law. Typical pressure drop curves are shown in Figure 2. The initial rate was obtained by extrapolating to zero time and was used for the forward reaction rate correlation.

The dependence of the forward reaction rate on the catalyst loading and temperature are shown in Figure 3 and Figure 4. The results of a multiple variable regression using MINITAB are listed in Table 2.

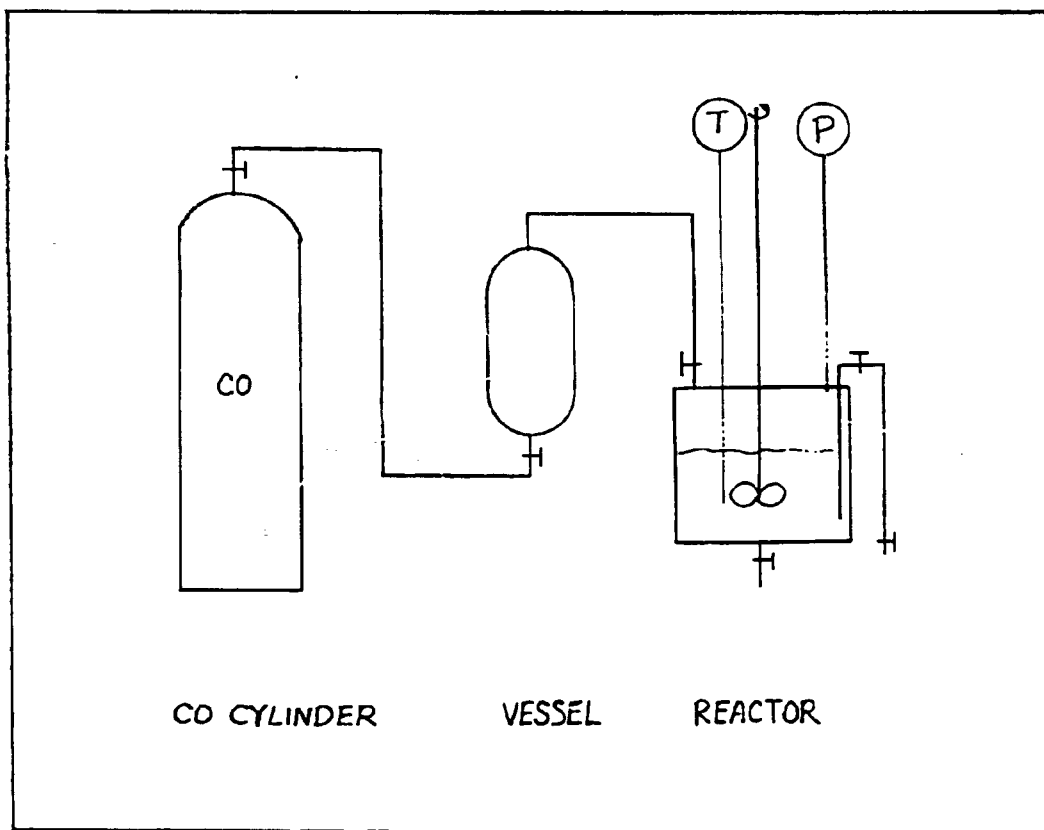


Figure 1. Process Flow Diagram



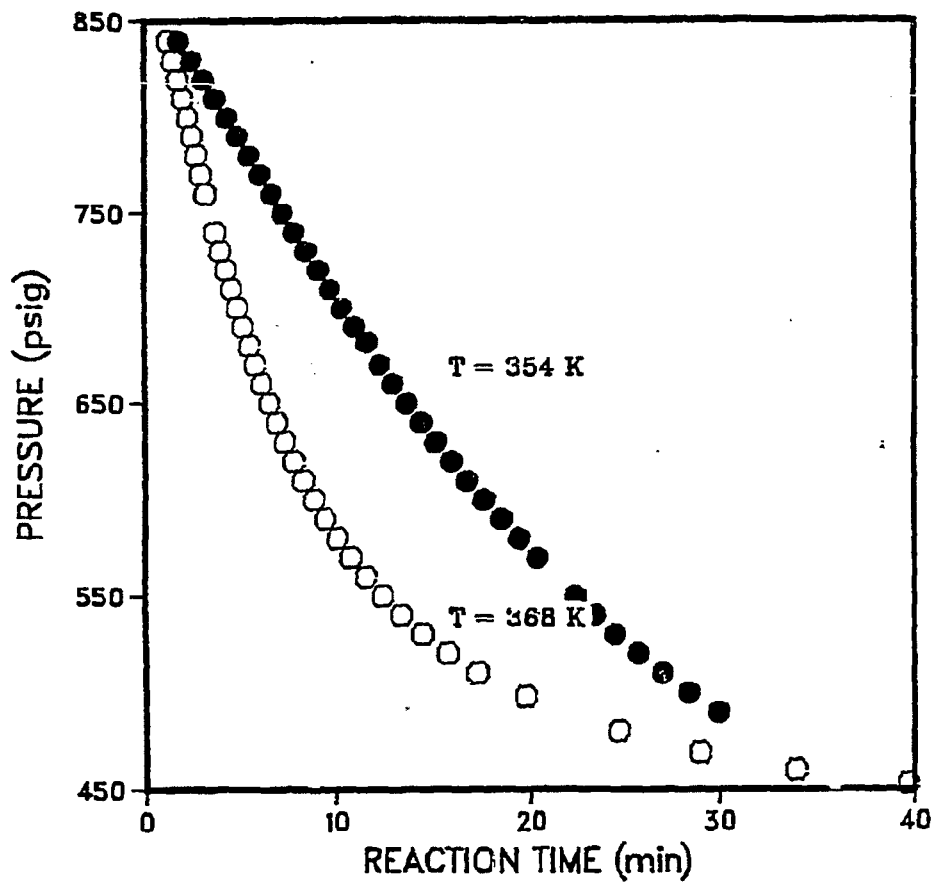


Figure 2. Typical plot of pressure drop versus time for carbonylation of methanol.

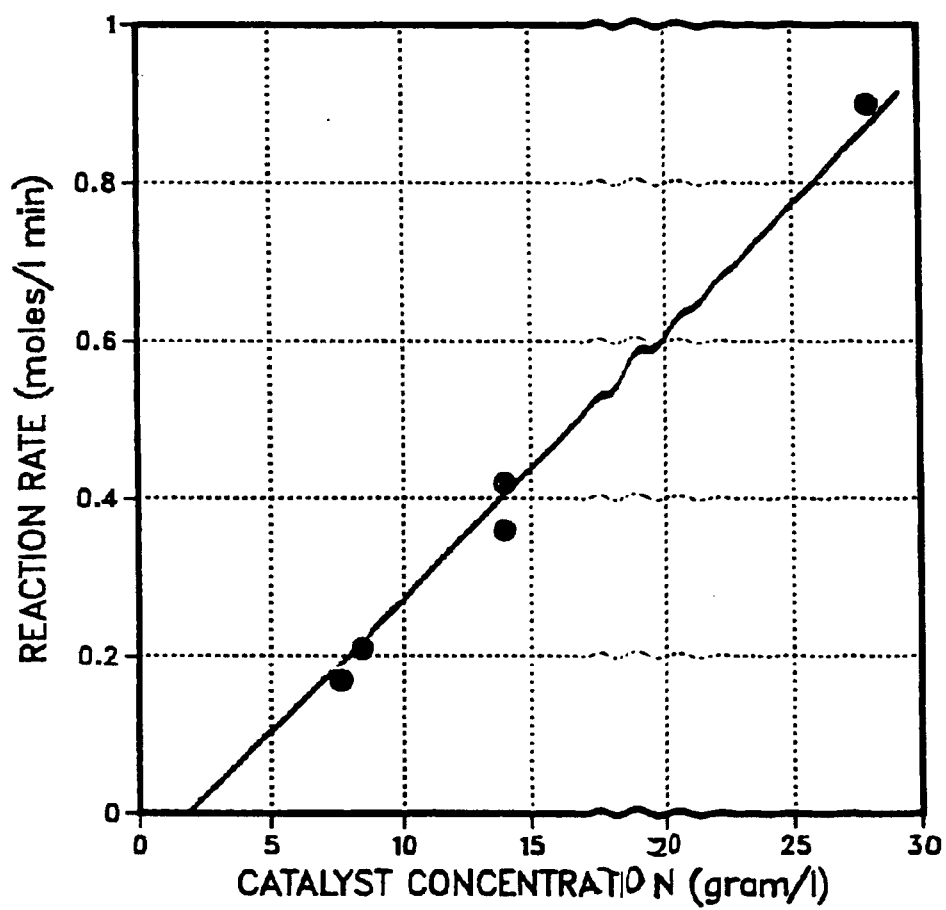


Figure 3. Effect of catalyst loading on carbonylation of methanol.

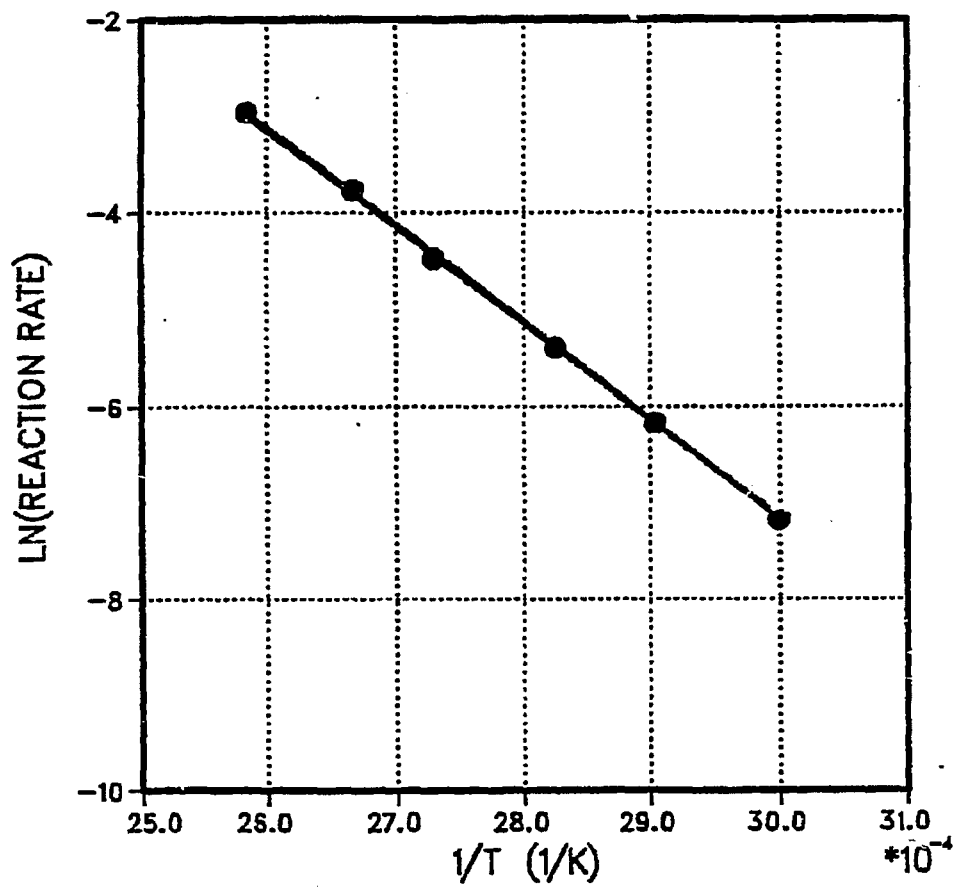


Figure 4. Effect of temperature on rate of carbonylation of methanol.

Table 2. Initial Estimation of Kinetic Parameters  
for Carbonylation of Methanol

Parameters	Value	Standard Deviation
$\ln(k [\text{MeOH}])$	20.13	0.754
E/R	10115.17	220.1
a	1.007	0.058
b	-	-
c	1.143	0.089
Correlation coefficient: .993		

Since pure methanol was used in the experiments, the dependence of the reaction rate on the methanol concentration was not obtained.

A first order dependence of the reaction rate on the catalyst concentration and on the CO pressure was reported by Trimm and his co-workers (Trimm 1983) for the temperature region of 50 - 70°C using sodium catalyst. It is clear from our data that the first order dependence of the reaction rate on catalyst concentration and on partial pressure of CO cannot be rejected at the 95% confidence level. By setting  $a = c = 1$ , a linear regression was carried out using MINTAB to determine the activation energy of the reaction. The corrected kinetic rate expression for the forward reaction is shown below:

$$r = 8.2238 \times 10^7 \exp(-10126./T) [\text{Cata}] [\text{MeOH}] P_{\text{CO}} \quad (2)$$

The t-ratio for  $\ln(k)$  is 39.9 and for E/R is -54.8. The activation energy is  $20.120 + 0.402[\text{kcal/mole}]$ . The correlation coefficient is .993.

The observed initial reaction rate is plotted against the predicted rate (calculated by using Equation 2) in Figure 5.

The dependence of the reverse reaction rate on the catalyst loading was assumed to be first order ( $d = 1$ ), which was checked by running the reaction at different catalyst loadings while keeping temperature and partial pressures of CO constant. If  $d = 1$ , Equation 3 is valid.

$$r_1 = r_2 ([\text{Cata}_1]/[\text{Cata}_2]) \quad (3)$$

where  $r_1$  and  $r_2$  are the reaction rates at the catalyst concentrations  $[\text{Cata}_1]$  and  $[\text{Cata}_2]$ , respectively. Figure 6 shows the pressure vs. time history for two different catalyst loadings, corrected for catalyst loading by Equation 3. A first order dependence on catalyst is indicated.

The activation energy  $E'$  for the reverse reaction was determined from calculated reaction equilibrium constants ( $K_e$ ). The equilibrium constant can be expressed as:

$$K_e = (k/k') \exp((E'-E)/RT) \quad (4)$$

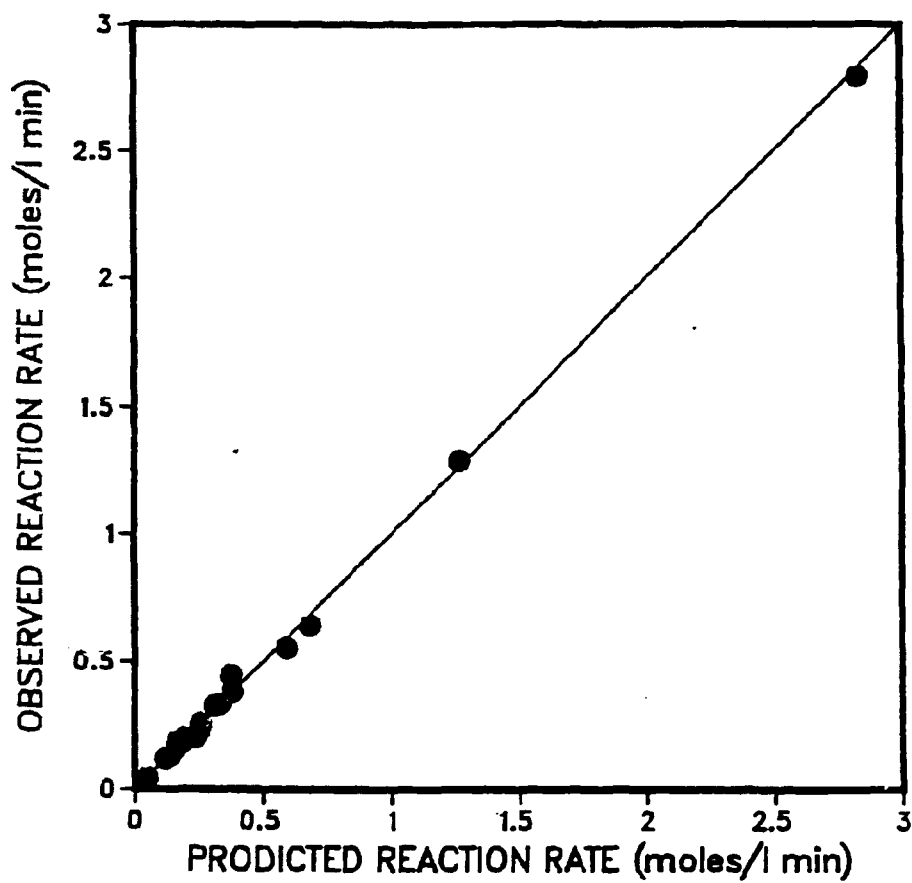


Figure 5. Comparison of experimental and predicted rates for the carbonylation of methanol (forward reaction only).

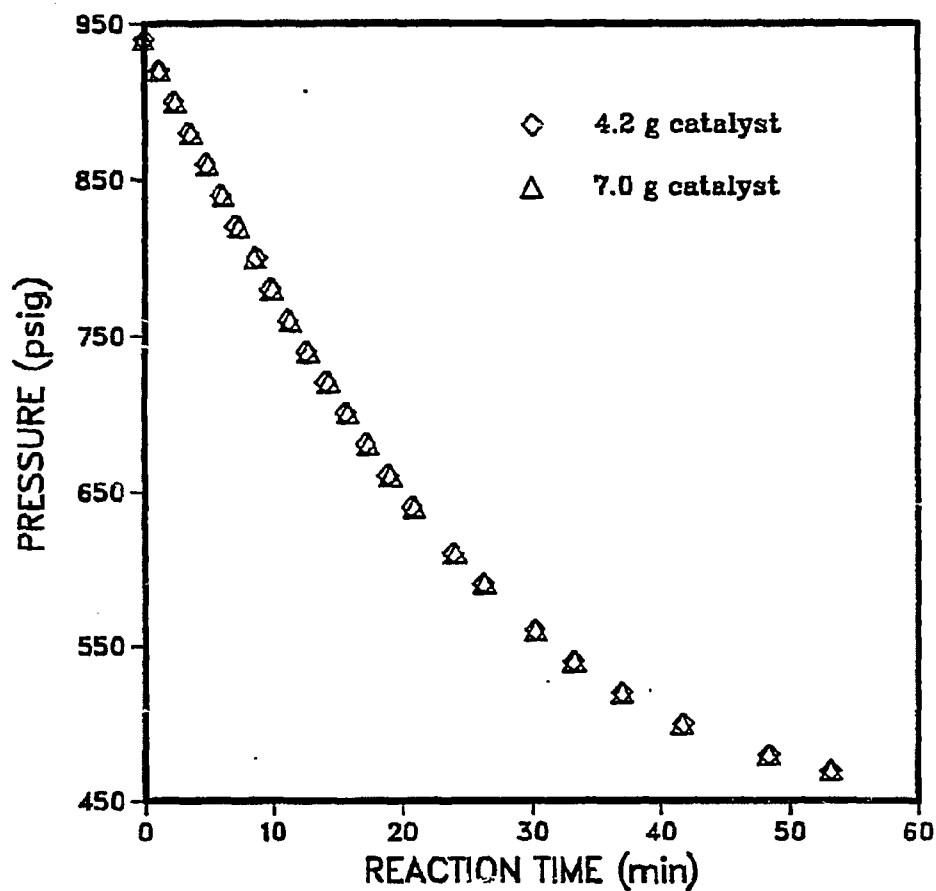


Figure 6. Pressure versus time for carbonylation of methanol corrected for catalyst loading by Equation 3. Results are for two runs made at identical conditions except for catalyst loading.

Since the term  $(k/k')$  can be assumed temperature independent, a plot of  $\ln(K_e)$  vs.  $(1/T)$  gives a straight line with a slope of  $(E'-E)/R$ . Using the measured value of the slope and the value of  $E$  for the forward reaction,  $E'$  is found to be 29.41 kcal/mole.

The reaction was very selective to methyl formate. The only observable by-products are a small amount of white precipitate and formaldehyde. We believe that the precipitate is potassium formate, which results from the reaction of  $H_2O$  and  $CH_3OK$  (catalyst), followed by the reaction of  $KOH$  and  $CH_3OOCH$  (product). The catalyst was consumed in the reaction. In Figure 3, a zero reaction rate is found at 2 [gram/liter] catalyst. A constant catalyst loss is of 2 is indicated.

The formaldehyde concentration increased with reaction time. The maximum amount was less than 0.5%.

#### Future Work

During the next quarter, work will be continued on analysis of the carbonylation data and determination of kinetic parameters of the reverse reaction. Carbonylation of n-butanol will also be started.



## 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 of 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. Two papers have resulted from this study.

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. Ultimately, such measurement will be extended to coal/supercritical fluid systems to help define the flow rates liquid/solvent ratios that would be appropriate for a supercritical system.

### Review of Mass Transfer/Equilibrium Under Supercritical Conditions

Over the past few years, significant interest has been expressed in a separation concept wherein a condensed phase (liquid or solid) is contacted with a fluid phase that is supercritical both in a temperature and pressure sense. Several industrial extraction processes have been developed such as deasphalting petroleum with supercritical propane (1) and decaffeinating coffee with supercritical carbon dioxide (2). Other examples would include deashing coal liquids (3) and regenerating activated carbon with carbon dioxide (4).

Supercritical carbon dioxide is a particularly attractive solvent for practical applications because it is nontoxic, nonflammable, environmentally acceptable, and relatively inexpensive. The critical temperature of carbon dioxide is only 304 K and thus extractions can be accomplished at moderate temperatures where thermal degradation of heat-labile extracts is minimal.

One of the cited advantages for using supercritical fluids as extractants is that the diffusion coefficients are significantly higher than for liquid systems while the viscosity more closely approximates that of a gas. Such trends would lead one to conclude that mass transfer characteristics of supercritical fluids may be better than for comparable extractions carried out in the normal liquid phase.

There are few experimental data for diffusion coefficients of solutes in supercritical fluids. Those available are shown in Figure 7 where diffusion coefficients are plotted as a function of reduced pressure of the solvent gases for the systems CO<sub>2</sub>-naphthalene, CO<sub>2</sub>-benzene, and ethylene-naphthalene. The low-pressure data show  $D_{AB}$  to be inversely proportional to pressure, but, approximately,  $D_{AB} \propto P^{1/2}$ . The range of reduced temperatures shown in Figure 7 is 0.97 to 1.09. At higher temperatures,  $D_{AB}$  would increase.

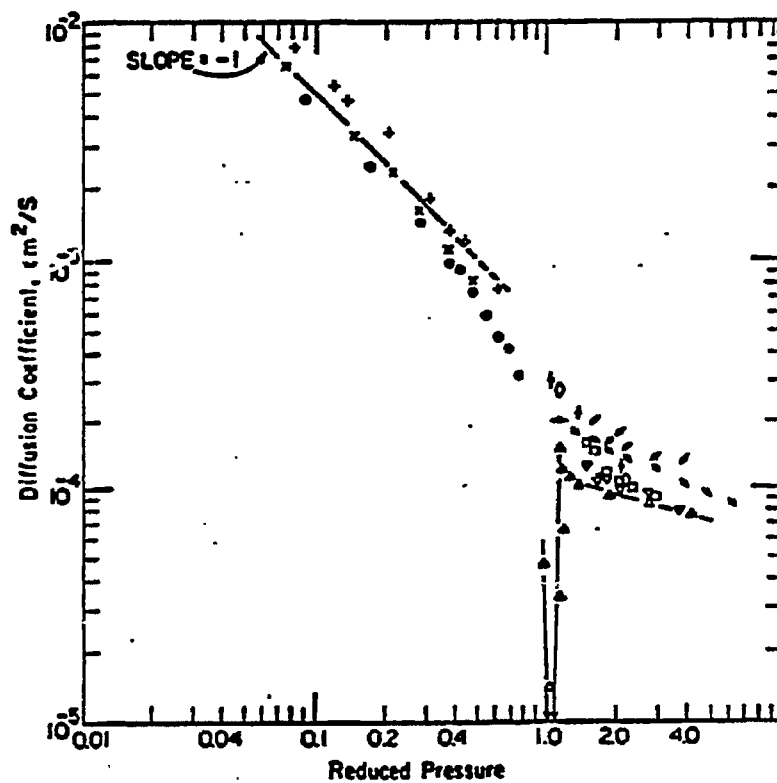


Fig. 7 The Diffusion Coefficients in Supercritical Fluids

There is an interesting discontinuity in Figure 7 for the system CO<sub>2</sub>-naphthalene at 35°C. At a pressure of about 80 ~ 81 bar ( $P_r \sim 1.09$ ), the lower critical end point is attained and the diffusion coefficient is essentially zero (5). The change in  $D_{AB}$ , as this critical point is approached, is very abrupt. Diffusion coefficients have not been reported for systems near the upper critical end points, but judging from the general trend of liquid-liquid systems near critical points (6, 7), it would be expected that diffusion coefficients would be very small in this region. In general, even though one has few data, it would appear that the binary diffusion coefficients for solutes in supercritical gases are around  $10^{-4}$  cm<sup>2</sup>/s for  $P_r$  values of 1 ~ 5 and  $T_r$  values of 1 ~ 1.2.

In the pressure and temperature range where most supercritical extractions would be operated, there are no generally accepted correlations for mass transfer coefficients. Storck and Coeuret (8) and Wilson and Geankoplis (9) have reviewed liquid phase relations while Gupta and Thodos (10) cover dilute gas phase systems. Both Bradshaw and Bennett (11) and Pfeffer (12) point out that due to the difference in Schmidt numbers, liquid and gases would be expected to have different correlations for the mass transfer coefficient.

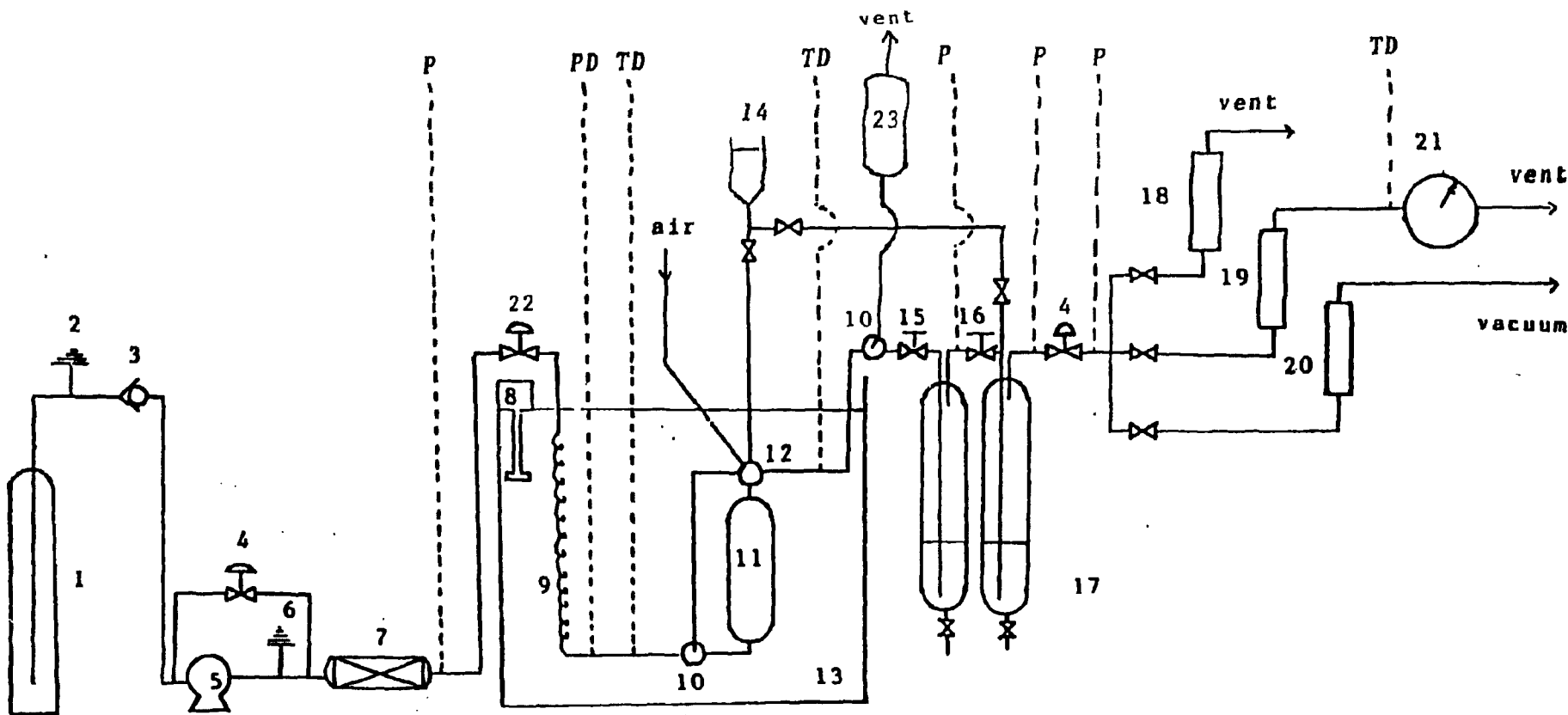
It is the purpose of this work to measure mass transfer coefficients and to compare their dependence on pressure and temperature to the corresponding dependence of diffusion coefficients. In this way, the relationship between diffusion coefficients and mass transfer coefficient can be determined.

### Experimental Design

The schematic diagram of the experimental apparatus used in the past quarter is shown in Figure 8. Liquid carbon dioxide is pumped into the system via a high-pressure Milton-Roy liquid pump. Pressure is controlled by using a back pressure regulator and pressure fluctuations are dampened with an on-line surge tank. The system consists of a preheater which allows the solvent to reach the desired temperature and the extraction vessel 313 cm<sup>3</sup> in volume, 26.67 cm in length and 3.87 cm in diameter. 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 and the top of the bed. The inert packing material being used is nylon rods with shape and size similar to that of the pellets. Another advantage in using the inert pellets is to get rid of end effects in the packed bed being used as the extractor. Pressure at the inlet of extractor is measured using a pressure transducer. The temperature of the extractor is measured at the inlet and outlet.

The fluid mixture coming out of the extractor is depressurized to atmospheric pressure by passing it through a heated metering valve. 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 mass of precipitated solid will be found as described below. With this value and total amount of gas flow from wet test meter, the mole fraction of solids in the supercritical fluid can be readily determined. The inlet stream temperature and pressure of wet test meter are also measured.



1. Cylinder
2. Relief valve
3. Check valve
4. Back pressure regulator
5. Liquid pump
6. Relief valve
7. Surge tank

8. Temperature controller
9. Preheater
10. Three-way valve
11. Extractor
12. Five-way valve
13. Water bath
14. Solvent(Toluene) tank

15. Metering valve
16. Metering valve
17. Sample tanks
18. Rotameter
19. Rotameter
20. Rotameter
21. Wet test meter
22. Pressure Regulator
23. Naphthalene trap

P: Pressure gauge  
 PD: Pressure transmitter to Data logger  
 TD: Thermocouple to Data logger

Fig. 8 Schematic Diagram of the Experimental Apparatus for Supercritical Fluid Extraction

In the present system, the sample collectors are high pressure bombs which are kept at room temperature by two 200 watt resistance heaters. Each vessel contains toluene which will help dissolve the extract (naphthalene) from the CO<sub>2</sub>. These vessels are operated at 300 to 400 psia where the solubility of the solid in the CO<sub>2</sub> is at a minimum. The second vessel is redundant and is used to guarantee that all of the extract is collected and to reduce entrainment losses. No naphthalene was found in these vessels during current experiments.

To determine the amount of extract collected, the amount of toluene (with dissolved extract) will be weighed. A sample of the toluene-extract solution will then be injected into a gas chromatograph to determine what portion of the solution is extract. To insure no extract remains in the line between valve 12 and the sample cylinder, valve 12 was converted to a five-way valve to allow washing of the line with toluene. Finally, the bypass, from valve 10 to 12, is designed to insure steady flow before allowing the CO<sub>2</sub> to pass through the extraction vessel (11).

The whole apparatus is rated for a pressure of 5,000 psi. All measured temperatures and pressures are recorded on a data logger.

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 experimental conditions are as follows:

System: Napthalene - Carbon dioxide

Pellet characteristics:

Material: Napthalene

Shape: Cylindrical

Size: Length (mm) = 10

Diameter (mm) = 4.5

Height of Bed (cm): 13.3, 8.9, 6.7

Temperature of Bed ( $^{\circ}$ K): 298, 308, 328

Pressure (psi): 1470, 2205, 2940, 3675

Flow rate (Std. Lit/Min at  $70^{\circ}$ F and 1 atm): 4 ~ 40

#### Calculation of Mass Transfer Coefficients

The measurement of mass transfer coefficients is based upon the following equation:

The mass transfer coefficient is calculated as:

$$K_y = \left( \frac{\overline{G}_{My}}{a Z_T} \right) \ln \left( \frac{Y_A^*}{Y_A^* - Y_{out}} \right) \quad (1)$$

where  $\overline{G}_{My}$  is the averaged molal mass velocity of the gas in moles per unit area per unit time.

where  $Y_A^*$  is equilibrium mole fraction and  $Z_T$  is the height of the packed section, and  $a$  is the interfacial gas/solid area per unit volume.



$Y_{out}$  can be determined by the amount of naphthalene precipitated and total amount of carbon dioxide passed through the experimental apparatus during the given time.

$$Y_{out} = \frac{N_{C_{10}H_8}}{N_{C_{10}H_8} + N_{CO_2}}$$

$$N_{C_{10}H_8} = \frac{W_{C_{10}H_8}}{\text{Mol. Wt. (128)}} \quad N_{CO_2} = \frac{PV}{ZRT} \quad (Z = 0.995)$$

#### Work for Current Period (April 1 - June 30)

This is the first quarter in which the new apparatus has been working effectively and mass transfer coefficients were obtained at 20 atm and 25°C (Table 3). These conditions are near-critical ( $T_R = .98$ ) rather than supercritical in order to have a comparison to the results obtained at supercritical conditions. The mass transfer coefficients are based upon an equilibrium solubility of  $1.82 \times 10^{-5}$  mole fraction ( $y_A^*$ ). As can be seen, the mass transfer coefficients generally increase with superficial gas flow rate and range from 0.3 to 6.5 lb-mole/(hr-ft<sup>2</sup>-mole fraction). This trend is as expected.

There is considerable (20 - 40%) uncertainty in these experiments because the equilibrium solubility is so low. Next quarter, the conditions at which we intend to operate will give equilibrium solubilities about 1000 times higher and the experimental error should be less than 5%, conservatively.

Because the experiment is now working well, we expect data collection to be rapid in the next quarter. We will obtain mass transfer coefficients at 308 K for several pressures and flow rates.

Table 3: Mass Transfer Coefficients at 20 atm and 25°C

Run No.	Superficial Flow Rate (l/min) at 0°C, 1 atm	Exit Mole Fraction $\times 10^5$	Mass Transfer Coeff. (lb-mole/hr.-ft. <sup>2</sup> mole fraction)	P (Psi)
10	1.465	1.6797	0.2869	≈294
8	7.277	1.1689	0.6609	294
1	9.330	1.4433	1.2922	294
7	9.670	0.9499	0.6304	294
2	13.229	1.7817	4.5189	294
3	15.266	1.9205		294
6	15.516	1.7034	3.7754	294
5	21.159	1.7652	6.5794	294
4	24.025	1.6068	4.5575	294
9	28.840	1.8189		294

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