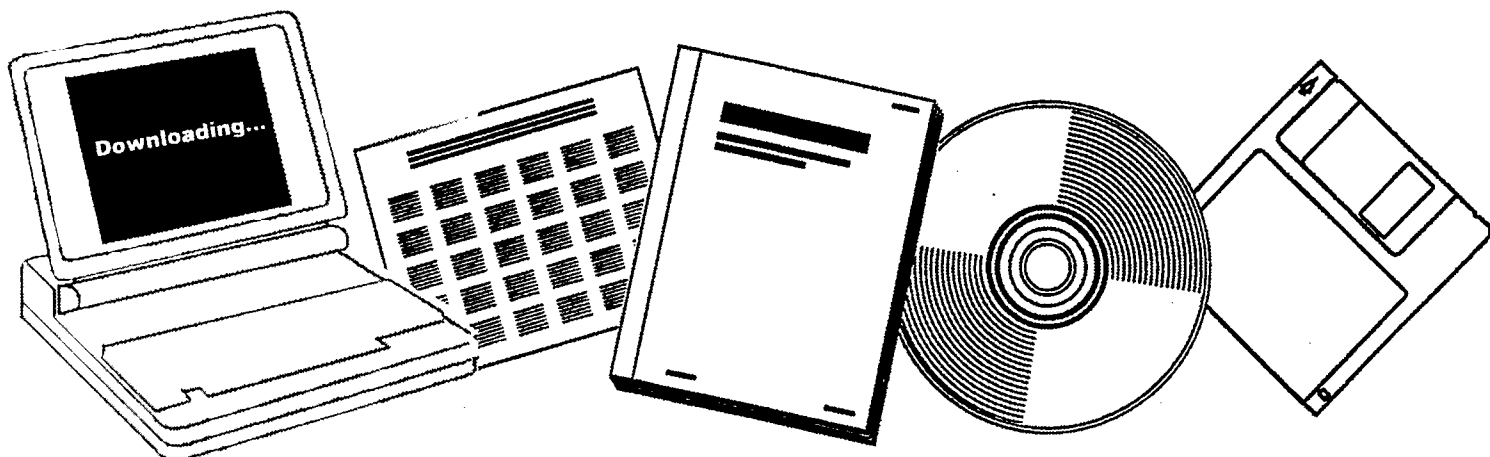# NOVEL EXPERIMENTAL STUDIES FOR COAL LIQUEFACTION: QUARTERLY PROGRESS REPORT, OCTOBER 1, 1986 TO DECEMBER 31, 1986

PITTSBURGH UNIV., PA

1986

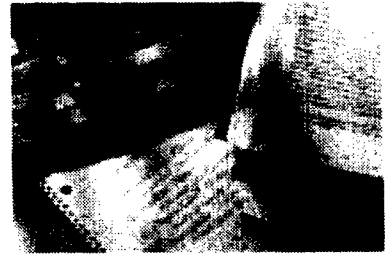# One Source. One Search. One Solution.

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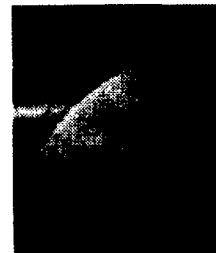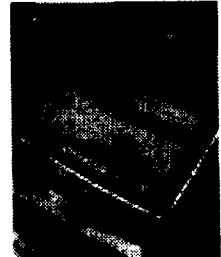
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Quarterly Progress Report

Novel Experimental Studies
for Coal Liquefaction

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Prepared for the Department of Energy
Contract No. DE-FG22-84PC71257

October 1, 1986 to December 31, 1986

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 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 coversion to methanol, and the two-step conversion to methanol.

Results and Highlights

A paper entitled "Kinetics of Two-Step Methanol Synthesis in the Slurry Phase" was submitted to Fuel Processing Technology. A copy is included with this report as an appendix. The paper summarizes the kinetic data measured for the two step process when each step is carried out independently. We are now experimentally investigating the kinetics of the two step process in which

the reactions are carried out simultaneously in one reactor. Some experimental measurements were made during the last quarter and are described below.

The selection of operating conditions for the reactor is complicated by the fact that there are two reactions occurring. Experimental data for the individual reactions carried out independently have shown that the carbonylation of methanol is reversible and faster than the hydrogenolysis of methyl formate at the experimental conditions. We can assume then that the carbonylation reaction is in equilibrium and the hydrogenolysis reaction is rate limiting. The rate equations were reported in the last quarterly report and are given in the appendix. Equating the forward and backward reaction rates for carbonylation gives:

$$r_1 = 4.11 \times 10^7 \exp(-10126/T) C_{Catal,1} C_{MeOH} P_{CO}$$

$$-1.70 \times 10^{17} \exp(-16788/T) C_{Catal,1} C_{MeF} = 0 \qquad (1)$$

and substituting C_{MeF} into the hydrogenolysis rate equation

$$r_2 = \frac{1871.5 \exp(-8348./T) C_{MeF} P_{H2} C_{Catal,2}}{1 + \sqrt{0.039 \ C_{MeF}} + 0.096 \ P_{CO}} \qquad (2)$$

the methanol production rate can be written as

$$r_{MeOH} = \frac{4.49 \times 10^{-7} \exp(-1686/T) C_{Catal,2} C_{MeOH} P_{CO} P_{H2}}{1 + 0.096 \ P_{CO}} \qquad (3)$$

The term $0.039 \ C_{MeF}$ in the denominator of equation 2 is small and can be neglected. It is clear from equation 3 that the methanol production rate will

increase with increasing pressure and with increasing temperature, although the temperature effect is small. We have used pressures from 35-63 atm and temperatures from 120-180°C. The temperatures are higher than those used in the only other results reported for this reaction by Aker Engineering (Petrole Informations, 34, 13 May, 1982).

The rates of reaction for the carbonylation and hydrogenolysis reactions are shown in Figure 1 for a run of about 10 days. Reactor conditions are noted on the figure. The liquid composition reached a steady composition after about 10 hours in which the methanol mole fraction was 0.957 and the methyl formate mole fraction 0.037. These values are close to those predicted assuming that the carbonylation reaction is in equilibrium.

For the first 60 hours, the reaction rates for both hydrogenolysis and carbonylation are significantly higher than those calculated from equations 1 and 2. After that the rates are lower than predicted. The unexpectedly high initial reaction rate may be a synergistic effect due to the carrying out of both reactions simultaneously. The decrease in reaction rate with time, however, is evidence that a catalyst aging or deactivation mechanism is taking place. Further experimental data are needed.

The temperature was varied from 120 to 160, and the reaction rate was found to increase as predicted by Equation 3. At 180°C, however, the rate dropped off very rapidly. Small amounts (less than 1.5%) of reaction products other than methanol or methyl formate were found. These are being analyzed.

Future Work

Work in the next quarter will continue on the experimental study of the simultaneous two step mehtanol synthesis.
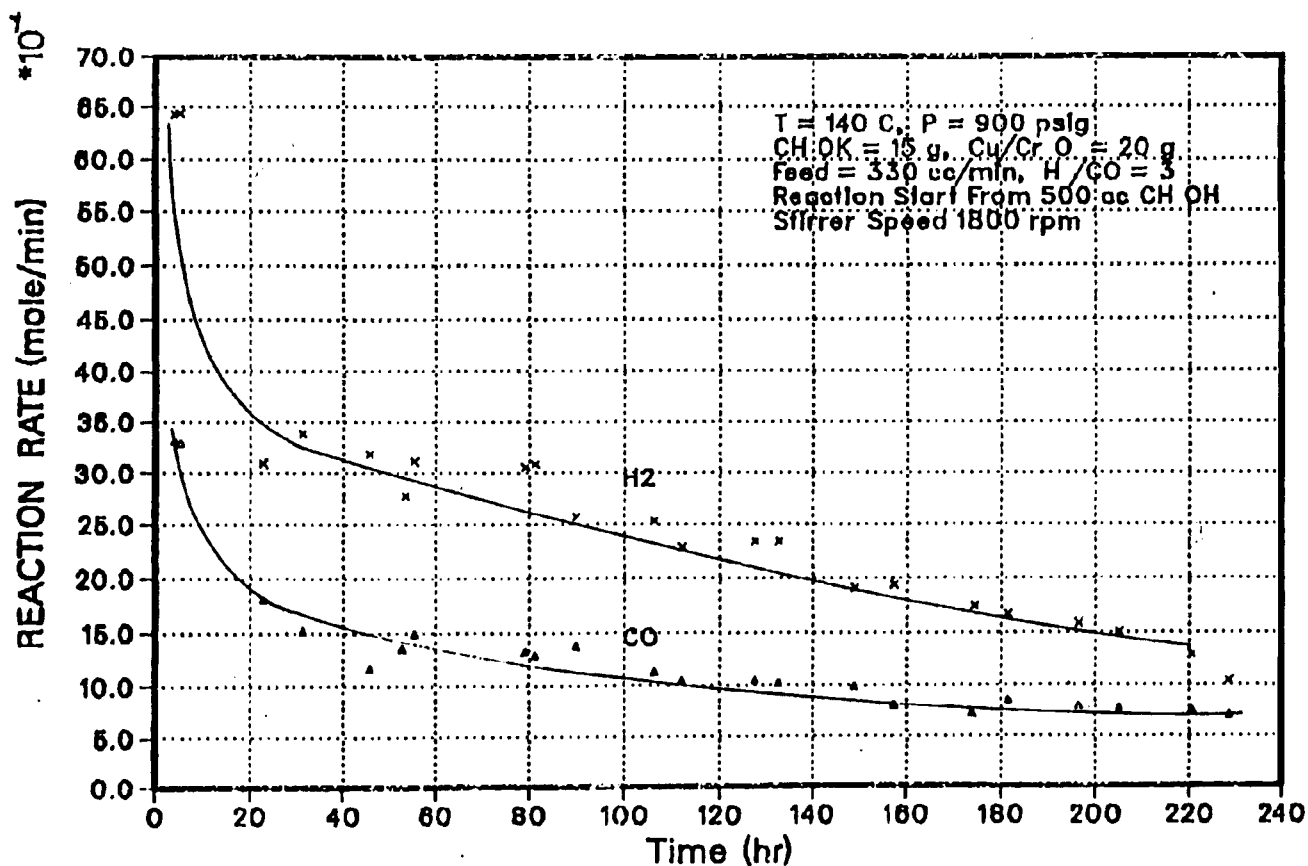
Figure 1. Rate of consumption of hydrogen and carbon monoxide for two-step methanol synthesis in one reactor.

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. 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 measurements 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 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 coefficient 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 comparable extraction 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 2 where diffusion coefficient are plotted as a function of reduced pressure of the solvent gases for the systems CO_2-napthalene, CO_2-benzene, and ethylene-napthalene. The low-pressure data show D_{AB} to be inversely proportional to pressure, but, approxiamtely, $D_{AB} \propto P^{1/2}$. The range of reduced temperatures shown in Figure 2 is 0.97 to 1.,09. At higher temperature, D_{AB} would increase.

There is an interesting discontinuity in Figure 2 for the system CO_2-napthalene at $35^{\circ}C$. At a pressure of about $80 \sim 81$ bar (Pr ~ 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 coefficient 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^2/s for Pr values of $1 \sim 5$ and Tr values of $1 \sim 1.2$.

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, liquids 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 coefficients can be determined.
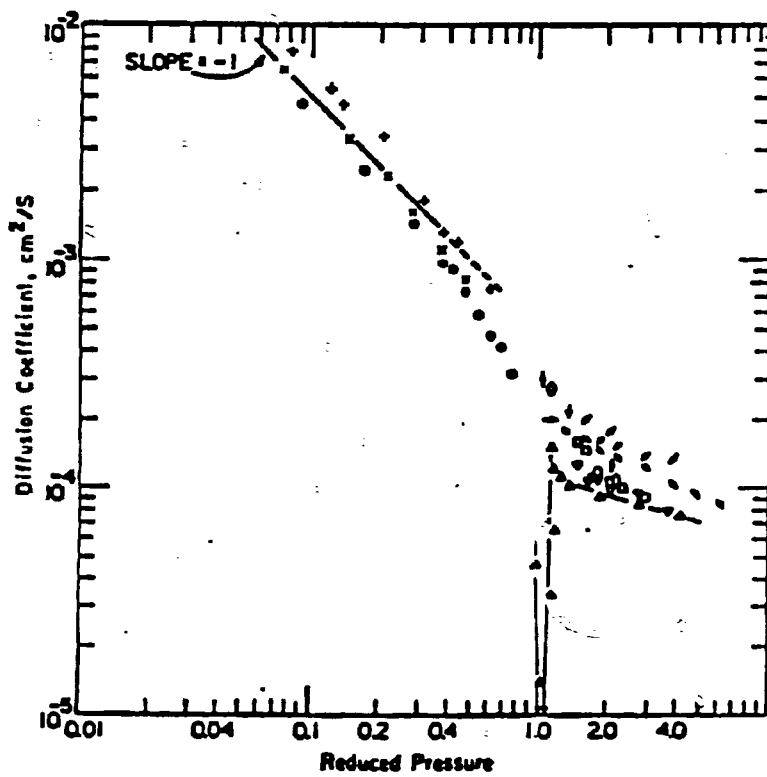
Fig. 2 The Diffusion Coefficients in Supercritical Fluids

Experimental Design

The schmatic diagram of the revised experimental apparatus used in the past quarter is shown in Figure 3. 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^3 in volume, 26.67 cm in length and 3.87 cm in diameter. The extraction vessel is packed with napthalene pellets which have been made from pure napthalene 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 is being used in glass beads with 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.

The fluid mixture coming out of the extractor is depressurized to atmospheric pressure by passing it through a heated metering valve and a back pressure regulator (4). The instantaneous flow meter reate 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. During this quarter, the bypass line has been modified as explained below.

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.

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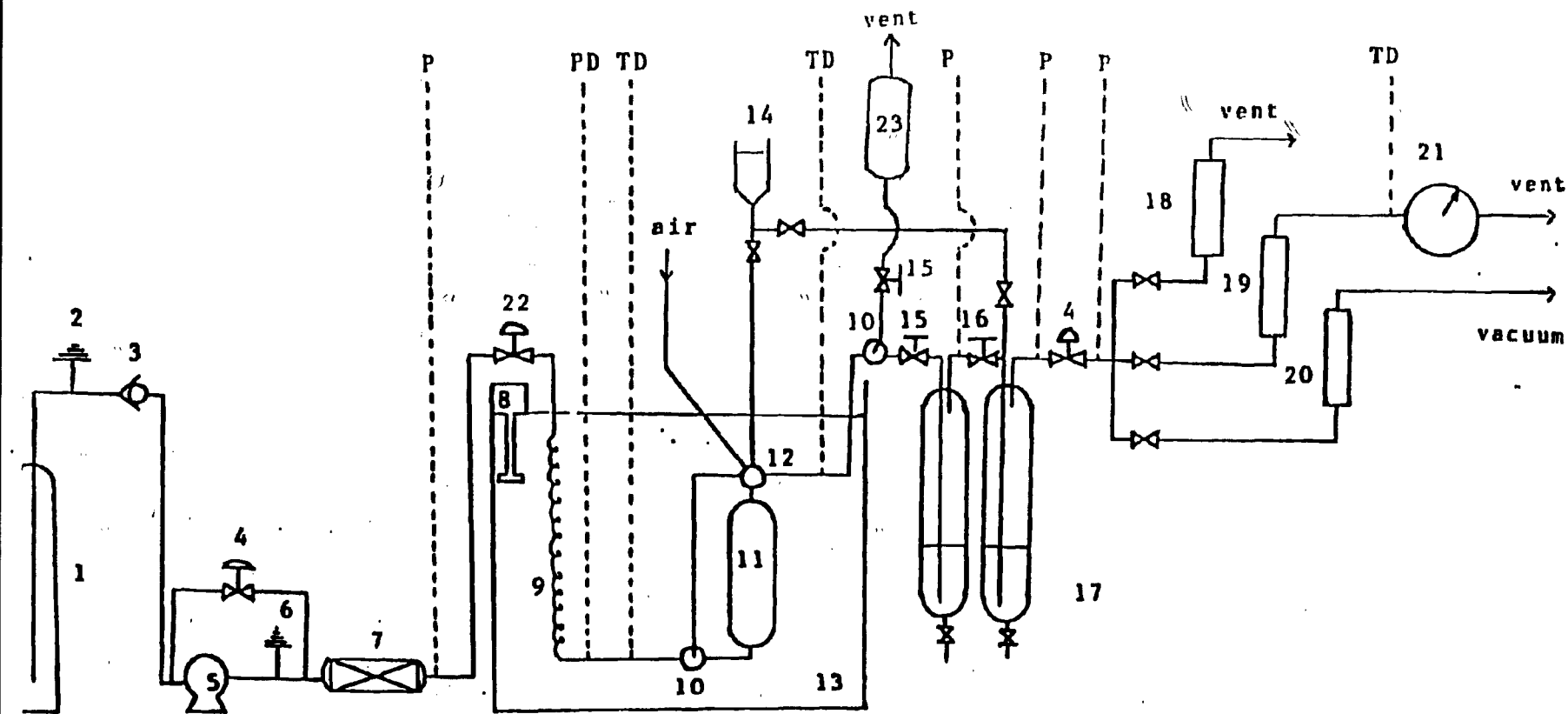
1. Cylinder
2. Relief valve
3. Check valve
4. Back pressure regulator
5. Liquid pump
6. Relief valve
7. Surge tank

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

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 whihc will help dissolve the extract (napthalene) from the CO_2. These vessels are operated at 300 to 400 psia where the solubility of the solid in the CO_2 is at a minimum. The second vessel is redundant and is used to guarantee taht all of the extract is collected and to reduce entrainment losses. No napthalene was found in these vessels during current experiments.

To determne 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 same cylinder, valve 12 was converted to a five-way alve 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_2 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 napthalene 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): 308, 328

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

    Flow rate (Std. Lit/Min at 70°F and 1 atm): 4 ~ 40

Calculation of Mass Transfer Coefficients

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

1) Plug flow model withou axial dispersion

The mass transfer coefficient is calculated as:

$$Ky = \left(\frac{\overline{G_{My}}}{a\ Z_T}\right)\ \ln\left(\frac{Y^*_A}{Y^*_A - Y_{out}}\right) \tag{1}$$

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 are per unit volume.

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2) Cell model or compartments model.

Flow patterns in a packed bed reactor with very small ratios of the tube particle diameter to length can be closely approximated by plug-flow, but in other cases, we should take account of axial dispersion effect on mass transfer rate.

The cell model is a generalization of a class of models such as the completely mixed tanks-in-series model and the back-flow mixed tanks-in series model. Since complete mixing is assumed in a cell, the concentration of an extractant (naphthalene) in the outgoing stream from the ith cell is also C_i. The material balance around the ith cell gives

$$v\, C_i + K_c A\, (C^* - C_i) - v\, C_i$$

$$= V_i\, \frac{dC_i}{dt}$$

For the steady-state and n cells

1st cell: $v\, C_{in} + k_c A\, (C^* - C_1) - vC_1 = 0$

2nd cell: $v\, C_1 + k_c A\, (C^* - C_1) - vC_2 = 0$

nth cell: $v\, C_{n-1} + k_c A\, (C^* - C_n) - v\, C_n = 0$

Therefore,

$$\sum_{i-1}^{n} k_c A\, (C^* - C_i) - vC_n = 0$$

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For one layer of napthalene pellets,

$$k_c A = v \left(\frac{C}{C^* - C} \right)$$

$$k_c A = \frac{v}{S Z_T} \left(\frac{C}{C^* - C} \right)$$

$$= \frac{v}{C \, S Z_T} \left(\frac{y}{y^* - y} \right)$$

$$= \frac{m y}{C \, AT} \left(\frac{y}{y^* - Y} \right)$$

$$= \frac{k_y a}{C}$$

where

C_{in}:   the concentration of component A at the inlet

C_{i-1}:   the concentration of component A outgoing from the (i-1)th cell

C_i: the concentration of component A outgoing from the ith cell

V_i: the volume of ith cell

v: the volumetric flow rate of the gas phase

G_{my}:   the total model mass velocity of the gas in the moles per unit area per unit time.

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

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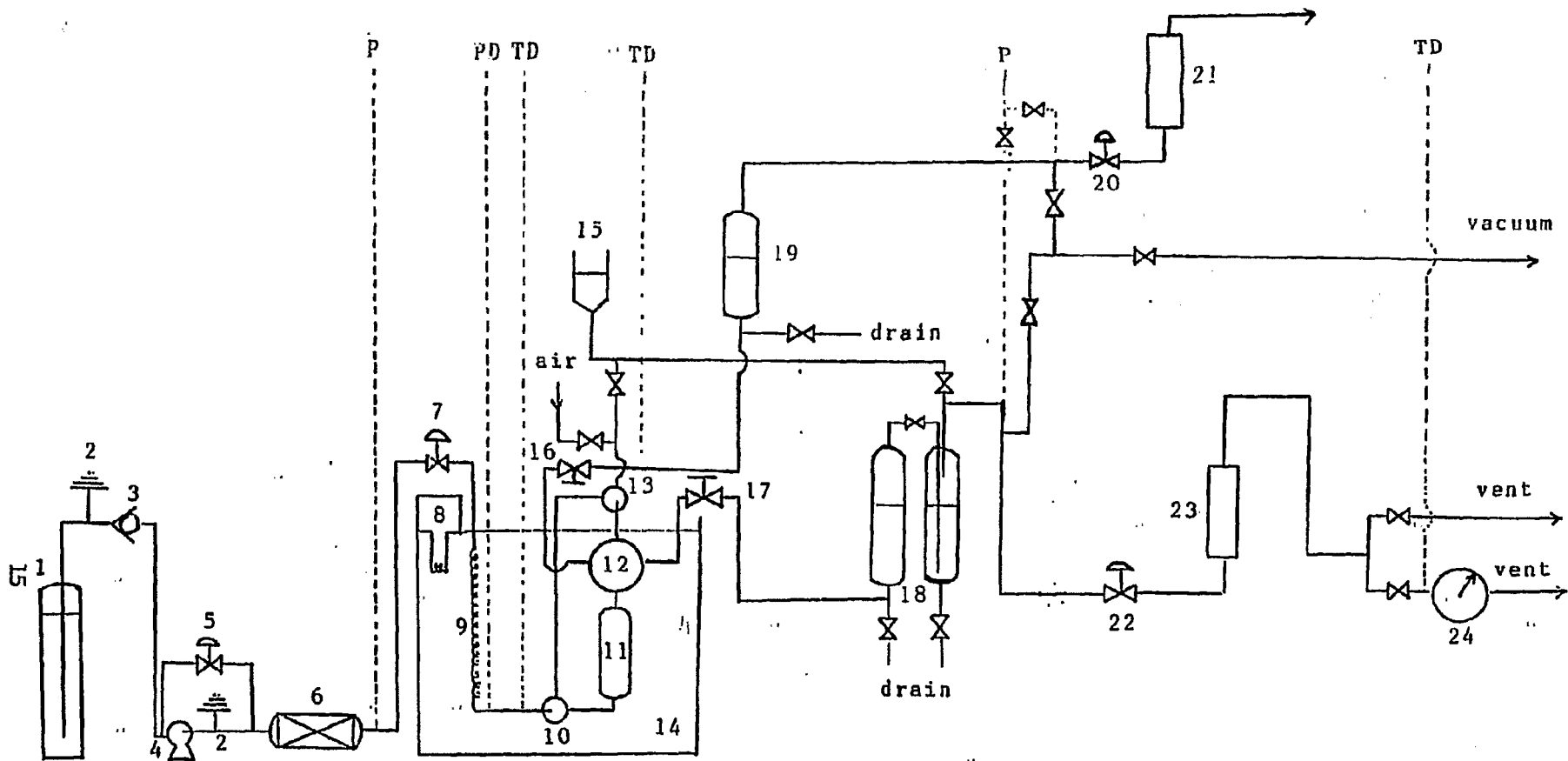
1. Cylinder	9. Preheater
2. Relief valve	10. Three-way valve
3. Check valve	11. Extractor
4. Liquid pump	12. Four-way valve
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6. Surge tank	14. Water bath
7. Pressure regulator	15. Solvent tank
8. Temperature controller	16. Metering valve

17. Metering valve
18. Sample tanks
19. Solid trap
20. Back pressure regulator
21. Rotameter
22. Back pressure regulator
23. Rotameter
24. Wet test meter

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

Fig. 4 Schematic Diagram of the Experimental Apparatus for Supercritical Fluid Extraction

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

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

Work for Current Period (October 1 - December 31)

The schematic diagram in Figure 3 was built and tested for supercritical conditions. In this experiment, we have found that some of the solid dissolved in vessel (11), under supercritical conditions, was precipitated in pipe between three-way valve (12) and four-way valve (16). This can cause error in estimating the amount of naphthalene dissolved into CO_2 gas in supercritical condition. During the operation of our system, we had to change the position of three valves (16, 21 and the valve in frot of the West-test meter (24)) simultaneously after the by-pass time (four-way valve (16) to solid trap (20)) reached steady state.

In the revised system Figure 4, we replaced the three-way valve by a four-way valve (12) and improved the washing system (four-way valve (12) to solven tank (15)) to get accurate data. Another back pressure regulator (20) and rotometer (21) were connected to the solid trap (19)) in by-pass line to make the operation of our system easier.

After revising our system, we operated it for 5 minutes at $308^\circ K$ and 100 atm for several flow rates. When we checked the amount of the residual naphthalene after each run and found that about 20% of original amount of naphthalene had dissolved into CO_2 in supercritical condition. So, we again decreased the running time to 2 minutes and found that only 5 to 10% of the original naphthalene dissolved into CO_2.
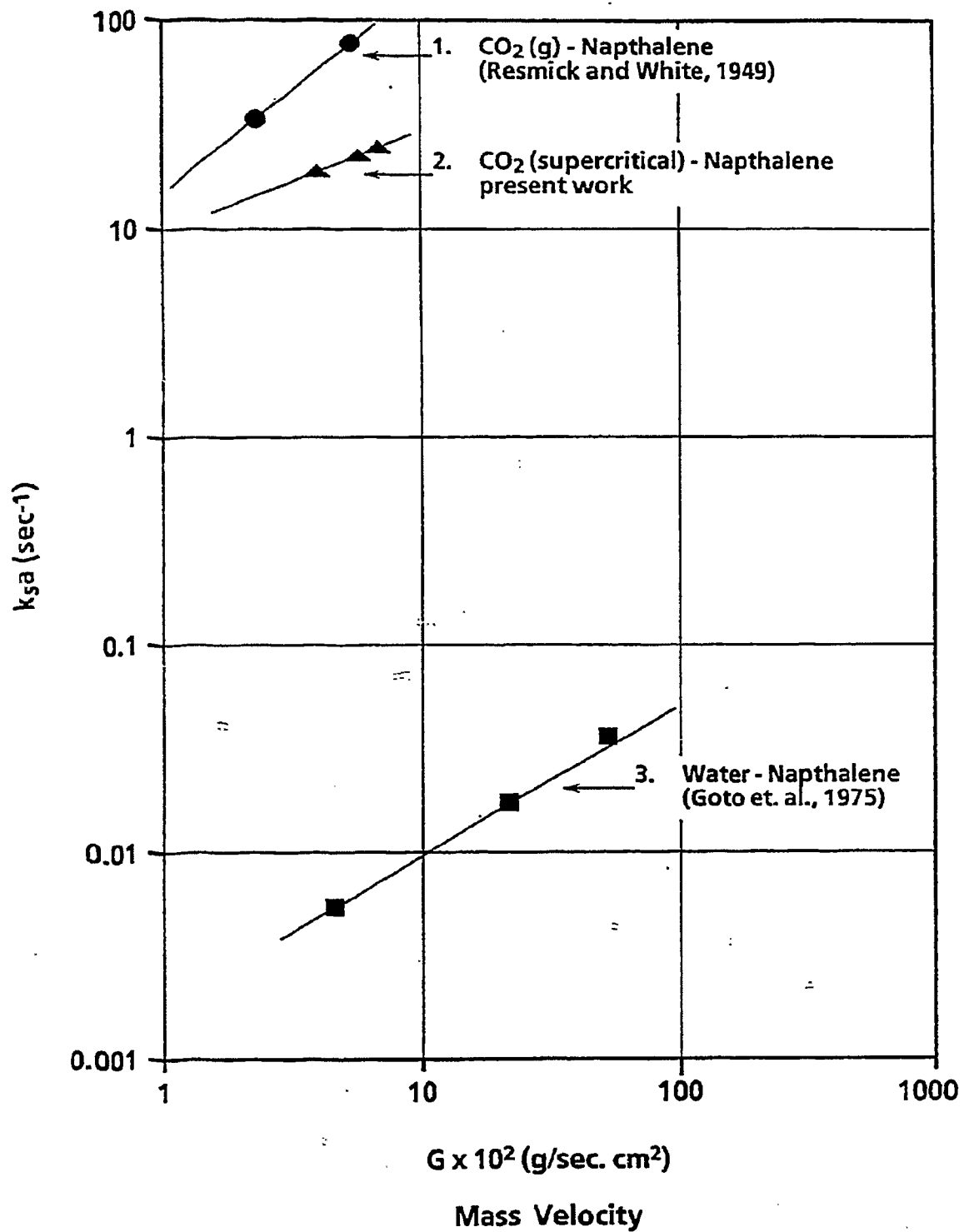
Figure 5. Comparison of supercritical condition with G-S & L-S systems.

In the following experiments, we operated our system for 2 minutes and used one layer of napthalene pellets in the extractor to keep it from reaching equilibrium solubility.

The mass transfer coefficients were obtained at 100 atm and 35°C by the cell model.

Table 1. Mass Transfer Coefficients

At 35°C, 100 atm

Run NO.	Superficial flow rate (l/min) at 0°C, 1 atm	Exit mole fraction $X10^3$	$k_c a$ (sec^{-1})	Molar Mass velocity (gmole/cm² sec) $X10^4$
2	19.324	3.4816	21.214	12.367
1	17.798	3.6256	20.794	11.392
3	14.009	4.3036	18.875	8.973
4	10.906	4.8020	16.036	6.989

In Figure 5, we compared our data with CO_2 (gas)-Naphthalene and water-naphthalene. It showed that the mass transfer rate at supercritical conditions lay between gas-solid and liquid-solid systems, but was the same order of magnitude as gas-solid systems.

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