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NOVEL EXPERIMENTAL STUDIES FOR COAL LIQUEFACTION. QUARTERLY PROGRESS REPORT, OCTOBER 1-DECEMBER 31, 1985

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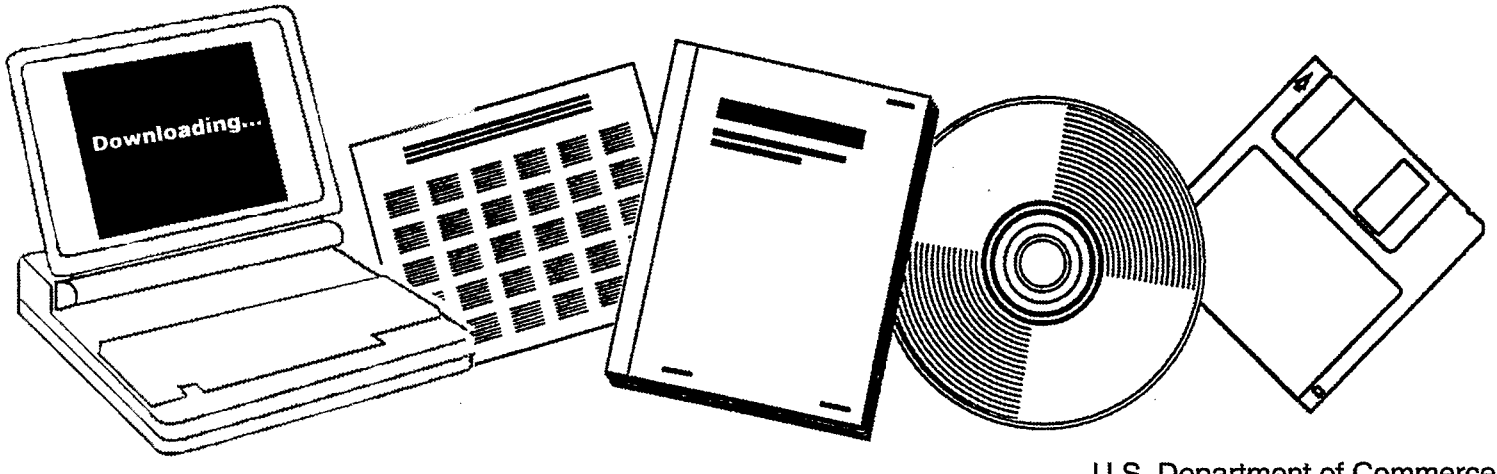

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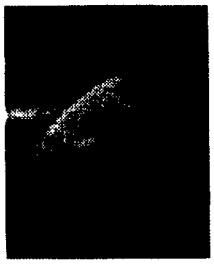

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DOE/PC/71257--T5

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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

MASTER

October 1, 1985 to December 31, 1985

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

Results and Highlights

Experimental work during the last quarter was concentrated on examining the second step of the two step process—the hydrogenolysis of the formate (in these experiments methyl formate) using a Cu-Cr (United Catalyst G-89) catalyst. Preliminary work indicated that the catalyst activation procedure was not producing uniformly active catalyst, and an improved control system for programming the temperature profile during activation was developed.

Some trial runs were made to determine approximate reaction rates. Results are shown in Table 1. At 100 C and 400 psig the reaction rate is low. Raising the pressure to 800 psig or the temperature to 120 C gives good reaction rates.

The conversion of methyl formate to methanol should be essentially complete at equilibrium according to calculations based on the equilibrium constant for the hydrogenolysis reaction. For example at 315 psig and 120 C the equilibrium liquid composition should be less that 0.01 mole fraction. This would imply that in analyzing the kinetics of the reaction, it is only necessary to consider the forward reaction. This was checked in the runs shown in Table 2. There was no increase in methyl formate over a long period when the starting solution contained 0.9997 mole fraction methanol and 0.0003 mole fraction methyl formate at 120 and 140 C. A mixture containing 0.9137 methyl formate was converted to 0.9987 methanol in 111 hours.

There has been some concern that when the hydrogenolysis reaction is carried out in the same reactor as the carbonylation reaction, the CO present may have a deleterious effect on the hydrogenation catalyst. A batch run was made to determine if this effect would significantly reduce the catalyst performance. The results are shown in Figures 1 and 2. Figure 1 shows a plot of the partial pressure of hydrogen versus time. The partial pressure decreases as the reaction proceeds and the rate of decrease is a measure of the rate of reaction as shown in Figure 2. For the first portion of the run ($t<85$) the reactor was initially pressured with pure hydrogen. At $t=85$, sufficient CO was added to make the CO/H_2 ratio 0.25. The total pressure, of course increased, but the hydrogen partial pressure did not. At $t=165$ and again at $t=330$ more CO was added. It can be see from Figure 1 that the decrease in hydrogen partial pressure changes smoothly and does not seem to be

Table 1

Rate of Hydrogenolysis of Methyl Formate

(Catalyst Loading: 16.7 g/liter)

Temp. (°C)	P (psig)	C_{meF} (mole/ℓ)	Rate (mole/min.ℓ)
100	400	14.8	0.0018
120	400	14.4	0.0049
120	800	9.5	0.0182

Table 2

Verification of Equilibruim Composition for Hydrogenolysis of Methyl Formate

Temp.	Pressure	Mole Fraction				Time
		Initial		Final		
(°C)	(psig)	MeF	MeOH	MeF	MeOH	(hrs.)
120	160	0.03	99.97	<0.03	>99.97	64
140	820	91.37	8.63	0.13	99.87	111
140	300	0.03	99.97	<0.03	>99.97	24

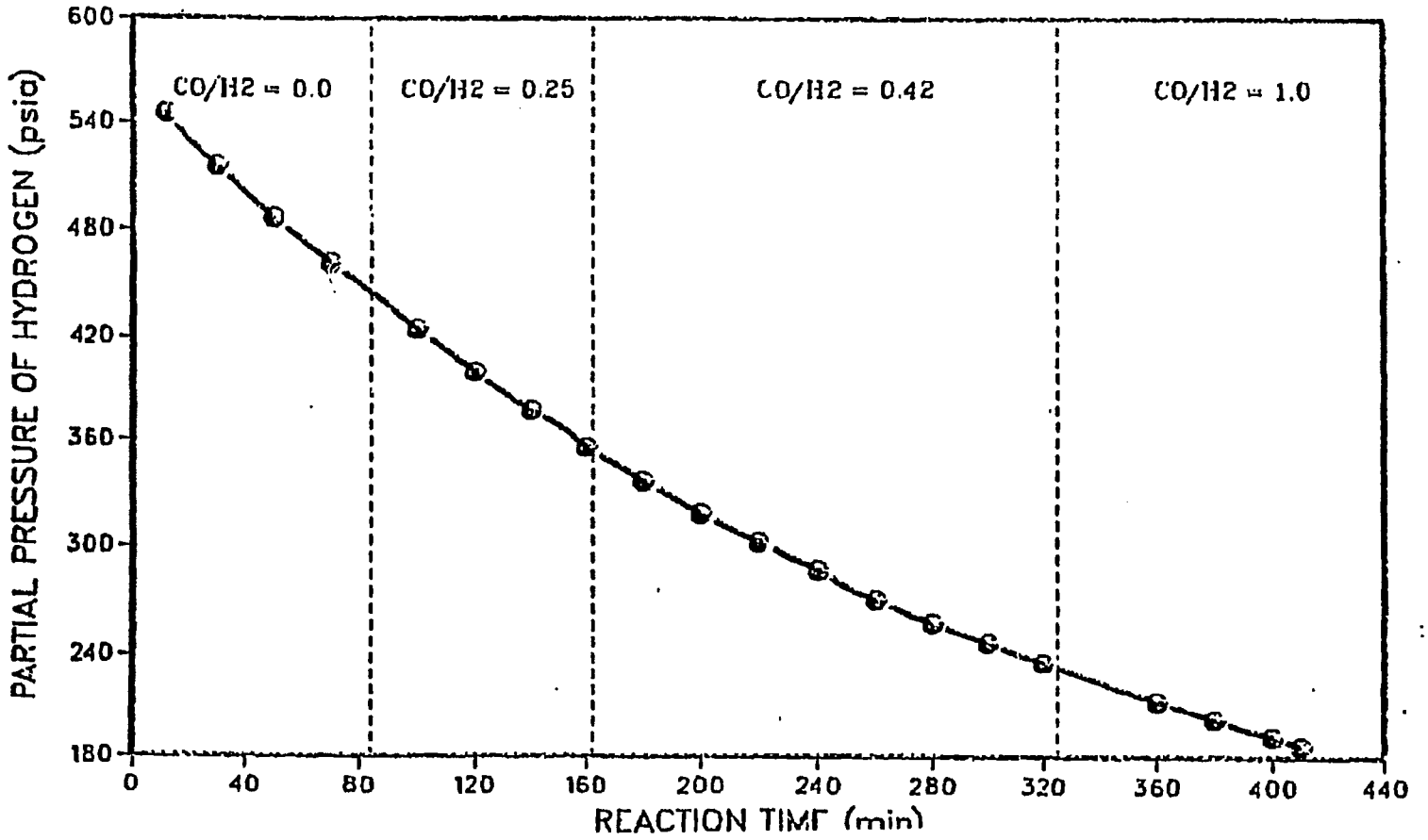


Figure 1

Partial pressure of hydrogen in batch reactor during hydrogenolysis of methyl formate with varying amounts of CO present.

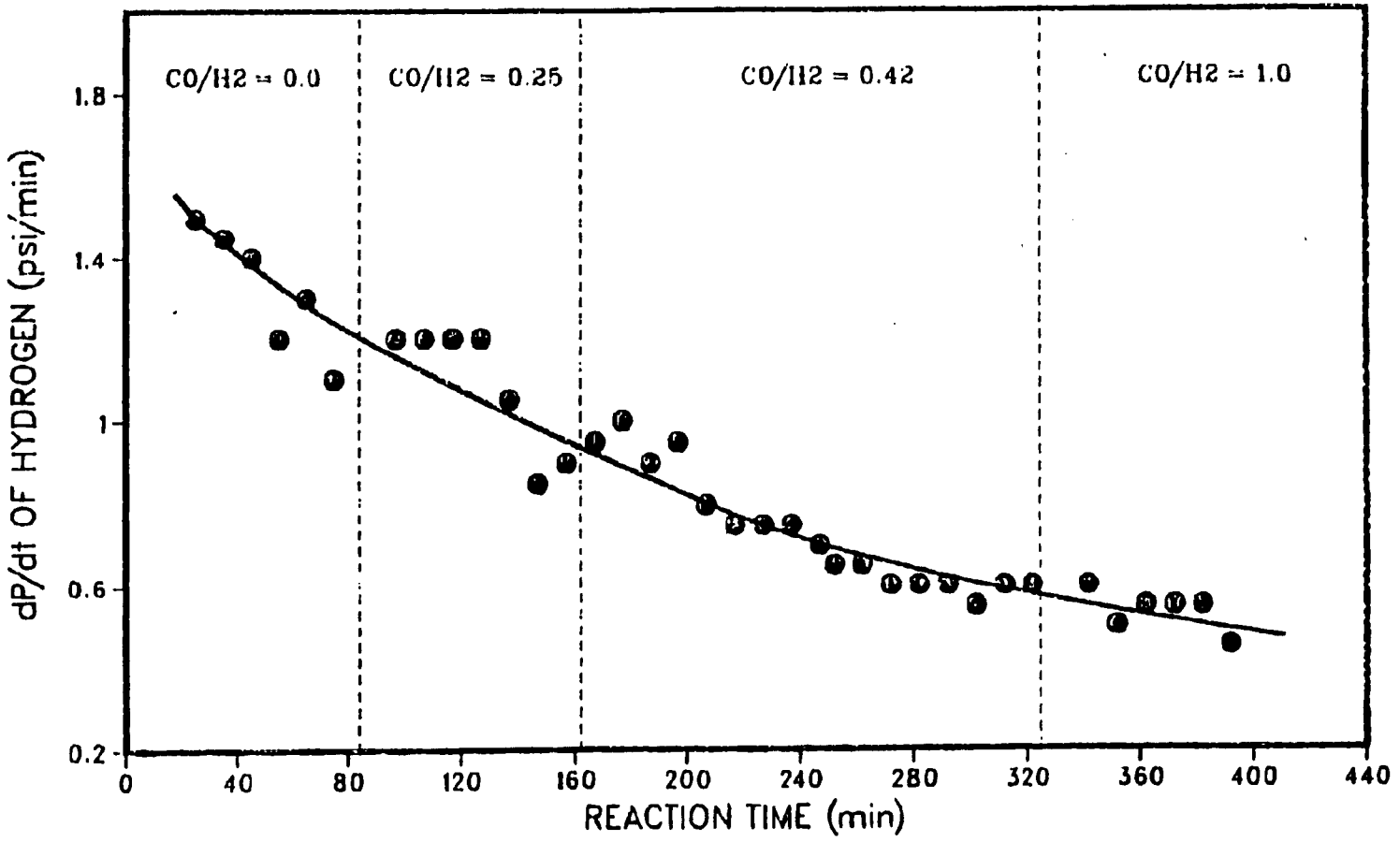


Figure 2
Rate of hydrogenolysis of methyl formate with varying amounts of CO_2 present.

affected by the CO present. The reaction rate in Figure 2 shows the same trend. It seems from these results that the presence of CO does not effect the the conversion of formate to methanol.

Future Work

During the next quarter work will be continued on the hydrogenolysis and carbonylation reactions for the two step process. Measurement of the thermal effects for the Fischer-Tropsch synthesis will be resumed using an $Fe/Cu/K_2CO_3$ catalyst which is being obtained.

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.

2. 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 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 3 where diffusion coefficients 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, approximately, $D_{AB} \alpha P^{1/2}$. The range of reduced temperatures shown in Figure 3 is 0.97 to 1.09. At higher temperatures, D_{AB} would increase.

There is an interesting discontinuity in Figure 3 for the system CO_2-napthalene at 35°C. At a pressure of about 80 ~ 81 bar(P_r ~ 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 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 system. Both Bradshaw and Bennett (11) and Pfeffer (12) point out that due to the difference in Schmidt numbers, liquids

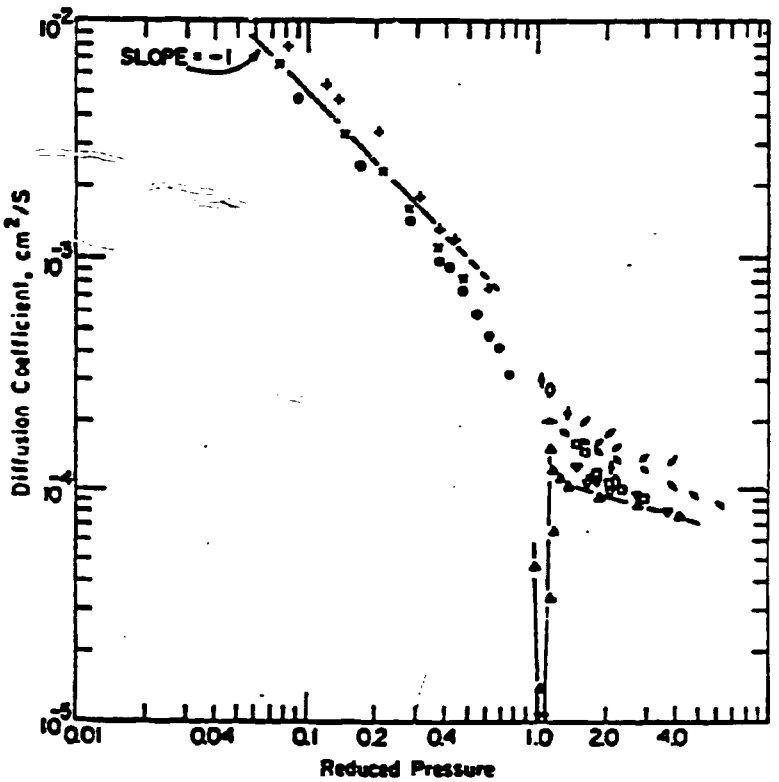


Fig.3 The Diffusion Coefficients in Supercritical Fluids

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.

Progress During the Past Quarter

Fourteen samples collected during the previous quarter were analyzed and showed no traces of napthalene which was to have been extracted. This is an impossible result and led to re-evaluation of the experimental design. A new configuration has been constructed with the emphasis on obtaining much larger flows than in the previous design. A new graduate student, G. B. Lim, has replaced the student previously working on this project and has completed the redesign of the apparatus. Several experimental runs will be conducted during the next quarter.

Experimental Design

The schematic diagram of the revised experimental apparatus is shown in Figure 4. Liquid carbon dioxide is pumped into the system via a high-pressure Milton-Roy liquid pump. Pressure is controlled to the desired pressure 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, 25.67 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 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 end effects in the packed bed being used as the extractor. Pressure at the inlet of extractor will be measured using a pressure transducer. The temperature of the extractor will be 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 dissolved solids precipitated in two U-tubes (ice temperature) in series following the valve. Both tubes are packed with glass wool at the outlet. 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.

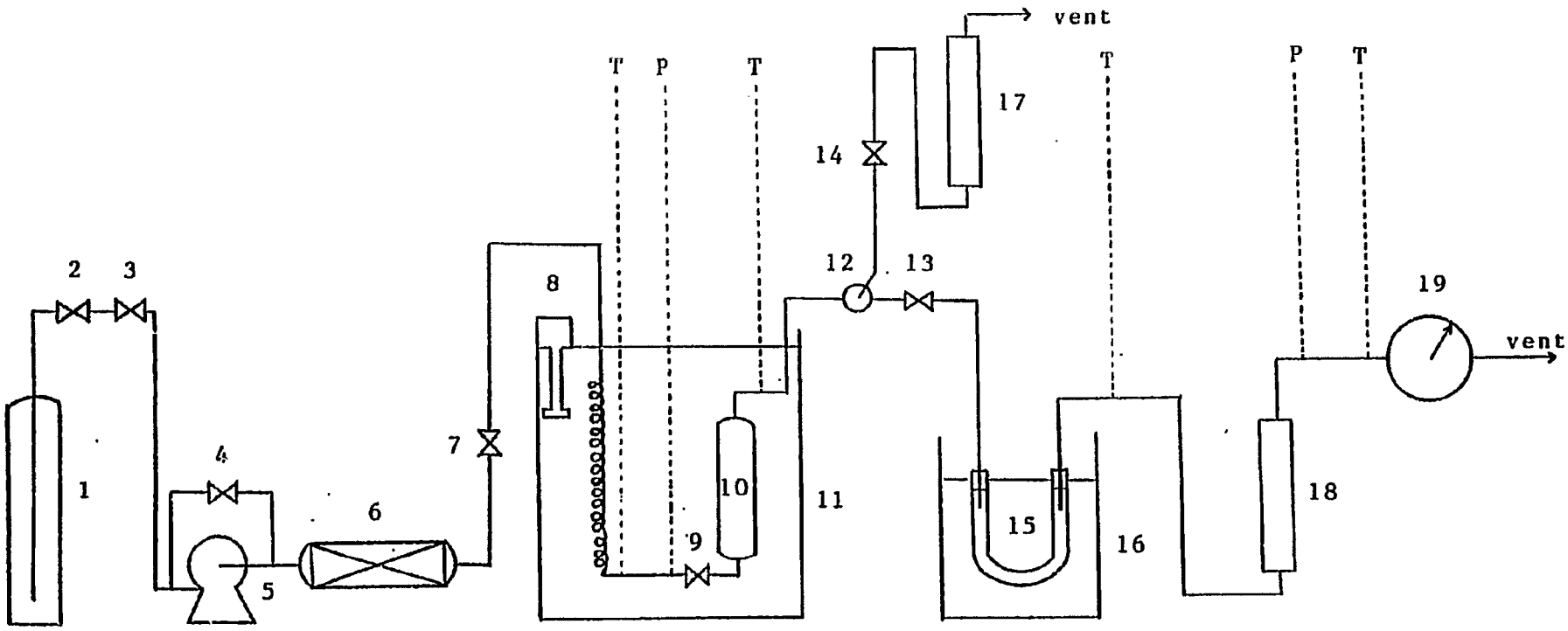
As the U-tubes will be initially tared, the mass of precipitated solid will be found by weighing the tubes after an experiment. With this value and total amount of gas flow from wet test meter, the mole fraction of solids in the supercritical fluid can be readily determined. The inlet stream temperature ad pressure of wet test meter will be also measured.

The whole apparatus is rated for a pressure of 5,000 psi. At the beginning of experiment, we use the upper vent line (valve 14 in Figure 4) in order to reach steady state for a given flow rate, temperature and pressure. After we get steady state, we can obtain data using the lower vent line (valve 13 in Figure 4). 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;



1.Cylinder
2.Relief valve
3.Check valve
4.Back pressure regulator
5.Liquid pump
6.Surge tank
7.Relief valve
8.Temperature controller
9.Valve
10.Extractor
11.Water bath
12.Three-way valve
13.Metering valve
14.Metering valve
15.U-tube
16.Ice bath
17.Rotameter
18.Rotameter
19.Wet test meter

P: Pressure gauge

Data logger

T: Temperature gauge

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

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 (^{o}K): 308, 328

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

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

Calculation of Mass Transfer Coefficients

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

$$dN_A = d(VY_A) = k_y (Y_{iA} - Y_A)\, dA = k_y (Y_{iA} - Y_A)\, aSdZ \quad (1)$$

where

N_A: the molal rate of transfer of component A in moles per unit time

V: the molal flow rate of the gas phase

k_y individual mass transfer coefficient in moles/area/time

Y_A: the mole fraction of component A in bulk of gas phase

Y_{iA}: the mole fraction of component A at gas side of interface (assume to be equilibrium)

A: the total area of interface for mass transfer (area of pellets in packed section)

a: the area of interface per unit volume of packed section

S: the total cross section area of column

Z: the height of packed section

Here,

$$V = \frac{V'}{1 - Y_A} \qquad (2)$$

where V′ is molal flow rate of inert component in moles per unit time

Therefore,

$$d(VY_A) = V'\, d\left(\frac{Y_A}{1-Y_A}\right) = V' \frac{dY_A}{(1-Y_A)^2} = V \frac{dY_A}{1-Y_A} \qquad (3)$$

From equations (1) and (3)

$$\int_{Y_{A,in}=0}^{Y_{out}} \frac{dY_A}{(1-Y_A)(Y_{iA} - Y_A)} = \frac{k_y a}{\overline{G_{My}}} \int_0^{Z_T} dZ$$

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

For dilute gas (i.e., $1 - Y_A \approx 1$)

$$\int_0^{Y_{out}} \frac{dY_A}{Y_A^* - Y_A} = \left(\frac{k_y a}{G_{My}}\right) Z_T$$

where Y^*_A is equilibrium mole fraction.

By integration and rearrangement

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

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.

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

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

4. References

(1) Zhuze, T.P.; Petroleum (London) (1960), 23, 298.

(2) Vitzthum, O.; Hubert, P. German Patent 23575P0, (1975).

(3) Baldwin, R.S.; Davis, R.E.; Wing, H.F. "Critical Solvent De-Ashing - A New Solids Separation Method for Coal Liquefaction Processes," presented at the 4th International Conference on Coal Gasification, Liquefaction, and Conversion to Electricity, University of Pittsburgh, Pittsburgh, PA, Aug. 1977.

(4) Modell, M.; deFillippi, R.P.; Krukomis, V.J. "Regeneration of Activated Carbon with Supercritical Carbon Dioxide," presented at the National Meeting of American Chemical Society, Miami, FL Sept. 14, 1978.

(5) Tsekhanskaya, Yu.V., Diffusion of Napthalene in Carbon Dioxide Near the Liquid-Gas Critical Point, Russ. J. Phys. Chem., 45, 744 (1971).

(6) Ramie, R.W. and Cussler, E.L., Fas Fluxes with Supercritical Sovlents, AIChE J., 20, 353-356 (1974).

(7) Tsekhanskaya, Yu.V., Diffusion in the System p-Nitrophenol-Water in the Critical Region, Russ. J. Phys. Chem. 42, 532-3 (1968).

(8) Storck, A. and Coeuret, F., Mass Transfer Between a Flowing Fluid and a Wall or Immersed Surface in Fixed and Fluidized Beds, Chem. Eng. J., 20, 149-56 (1980).

(9) Wilson, E.J. and Geankoplis, C.J., Liquid Mass Transfer at Very Low Reynolds Numbers in Packed Beds, Ind. Eng. Chem. Fund., 5, 9-14 (1966).

(10) Gupta, A.J. and Thodos, G., Mass and Heat Transfer in the Flow of Fluids Through Fixed and Fluidized Beds of Spherical Particles, AIChE J., 8, 608-10 (1962).

(11) Bradshaw, R.D. and Bennett, C.O., Fluid-Particle Mass Transfer in a Packed Bed, AIChE J. 7, 48-52 (1961).

(12) Pfeffer, R., Heat and Mass Transport in Multiparticle Systems, Ind. Eng. Chem. Fund., 3, 380-3 (1964).

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