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# NOVEL EXPERIMENTAL STUDIES FOR COAL LIQUEFACTION: QUARTERLY PROGRESS REPORT, JANUARY 1, 1987 TO MARCH 31, 1987

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Quarterly Progress Report

#### NOVEL EXPERIMENTAL STUDIES

#### FOR COAL LIQUEFACTION

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#### TASK 1: THE USE OF SLURRY REACTORS 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 use of a slurry reactor for indirect coal liquefaction is 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 via methyl formate.

#### **Results and Highlights**

Work during the quarter was devoted primarily to investigating the kinetics of the two-step process for conversion of synthesis gas to methanol. The synthesis consists of two sequential reactions. The first is the carbonylation of methanol to methyl formate and the second is the hydrogenation of methyl formate to two molecules of methanol, thus regenerating the methanol used in the carbonylation step and producing one molecule of product. The reactions can be carried outseparately or they can occur simultaneously in the same reactor. Each method has advantages and disadvantages. Carrying out the reactions in separate reactors allows the use of optimum reaction conditions for each reaction, but does require more equipment and the purification of products between stages. Carrying out the reactions simultaneously requires less equipment and there is no intermediate purification required, but both reactions must take place at the same temperature and pressure, and there can be deleterious interactions between the reactions. In particular, carbon monoxide which is present for the carbonylation step is a poison for the hydrogenation catalyst.

In previous reports, the kinetics of the individual reactions when carried out separately were reported. During the last quarter, the rate of reaction for the simultaneous two-step reaction was measured. Three temperatures were used -140°C, 160°C, and 180°C. Other parameters were kept constant at the values shown in Table 1-1. The experiments were conducted with a continuous feed of CO and  $H_2$  at a rate substantially greater than the rate of reaction and with an excess of hydrogen. Unreacted gas was removed continuously. The rate of consumption of CO and H<sub>2</sub> could thus be measured. Hydrogen consumption is directly proportional to methanol production (assuming no hydrogen consumption in any byproducts), so the vertical axis in Figures 1-1 and 1-2 is labeled as rate of methanol production. The fraction of CO converted is shown in Figures 1-3 and 1-4. The initial reactor contents were pure methanol, and during the first 20 - 40 hours the composition slowly changed. After about 40 hours, the liquid composition remained constant with the mole fraction of methyl formate varying from 0.02 to 0.06. No liquid products were removed, and the liquid level in the reactor slowly rose during the run. Runs were continued for more than 200 hours to evaluate performance over an extended period.

Table 1-1: Operating Conditions Used for Simultaneous Two-Step Reaction <u>Study</u>

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Variables	Values	
Pressure	62.2	atm
Feed H <sub>2</sub> /CO ratio	3	
Space Velocity	360	1/hr
Initial MeOH	500	сс
Initial MeF	0	СС
Potassium Methoxide	15	gram
(Carbonlyation Catalyst)		
G-89 (Hydrogenation Catalyst)	20	gram
Stirrer Speed	1800	rpm

A decrease in reaction rate with time for simultaneous reactions was noted in the last report and can be seen also in the data in Figure 1-1 through 1-4. There is a steady decrease in reaction rate with time at all three temperatures studied. Since the limiting reaction rate is hydrogenation, it is evident that the hydrogenation catalyst is losing activity with time. The rate of decrease of reaction rate (dR/dT) is greatest at 140°C and lowest at 180°C. One explanation for this trend is that the deactivation is caused by a chemisorbed poison which forms strong bonds with the active sites or changes the electronic nature of the surface. Since desorption rates increase faster with temperature than adsorption rates, the net effect would be a decrease in adsorbed poison with temperature.<sup>1</sup>







Figure 1-2: Rate of Methanol Production for Duplicate Runs at 180<sup>0</sup>C

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Figure 1-3. Fraction of CO Converted at 140 and  $160^{\circ}$ C ( $\Delta$  = 140, x = 160)

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Figure 1-4. Fraction of CO Converted for Duplicate runs at 180°C

The most likely source for a poison would be a by-product of the reaction which is produced in small amounts. The analysis of the effluent gases from the reactor using gas chromotography yielded three unidentified by-products. The mole fractions of these products in the effluent gas from the reactor are shown in Figures 1-5, 1-6, and 1-7. Samples are being analyzed by mass spectrometer, but the results are not available as yet. While one of these might be responsible for the observed deactivation, it seems unlikely because in each case the rate of production increases substantially with temperature. If the deactivation is caused by a poison, it is probably a small amount of an undetected by-product.

It can be seen in Figures 1-1 and 1-2 that the rate of hydrogenation increased to a maximum and then slowly decreased for runs made at 140°C and 160°C. However, at 180°C there is a very sharp decrease in rate between 20 and 40 hours, followed by a slow decrease. This indicates a substantial difference in catalyst performance at 180°C during the first 40 hours of operation. It was also observed that there was a significant production of methane during this period for the run made at 180°C. No methane was found for the runs at 140°C and 160°C, and none was found for the run at 180°C after the first forty hours. It seems probable that these observations are related. The effect is being studied further.

In another run, the effect of total pressure on methancl production was studied at  $140^{\circ}$ C, a feed H<sub>2</sub>/CO ratio of 6, and a space velocity of 260 hr<sup>-1</sup>. The pressure was initially 62.2 atm, and after 210 hours, the methanol production rate was constant. The pressure was then lowered and after ten hours, the reaction rate was measured. The pressure was lowered again, and the rate measured. The results are shown in Figure 1-8. As expected, higher methanol production rates were obtained at higher total pressures.



Figure 1-5. Mole Fraction of By-Product lin Effluent Gas From Reactor  $(\Delta = 140 \text{ C}; X = 160 \text{ C}; a, a = 180 \text{ C})$ 

Q



1.5





Figure 1-7. Mole Fraction of By-Product 3 in Effluent Gas from Reactor ( $\Delta$  = 140 C; X = 160 C;  $\square$  ,  $\blacksquare$  = 180 C)



Figure 1-8. Effect of Pressure on Rate of Methanol Production at 140 C

#### **Future Work**

During the next quarter, analysis will continue of the data obtained for the simultaneous two-step process, and experimental measurements will be made where appropriate. Attention will be concentrated on determining the effect of  $H_2/CO$  ratio, the explanation for catalyst deactivation, and the effect of temperature on the reaction. The analysis of by-products will also continue.

#### **References Cited**

1. Rase, H.F., "Chemical Reactor Design for Process Plants," Volume 1, John Wiley & Sons (1977).

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#### 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 liquidlike 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.

In this report, the entire program for evaluating mass transfer coefficients under supercritical conditions is described and a review of current knowledge and planned correlational appraoches is given.

#### BACKGROUND

Historically, interest in supercritical fluids was initially related to the observation that such fluids were often excellent solvents. This fact was discovered over 100 years ago by Hannay<sup>12</sup> and by Hannay and Hogarth.<sup>13,14</sup> Prior to that time, it was generally thought that materials above their critical temperatures would be gaseous in nature and thus poor solvents.

Studies of solubilities in supercritical fluids have been continued<sup>15,16</sup> and in most instances, they concentrated on developing phase diagrams for binary mixtures, particularly pressure-temperature projections. Vapor-liquid equilibrium data on binary hydrocarbon systems at elevated pressure became available in the 1930's<sup>17,18</sup> and the first patent for the practical application of supercritical extraction was made in 1943.<sup>19</sup> Later, Maddacks,<sup>20</sup> Tugrul<sup>21</sup> and Bartle et al.<sup>22</sup> described the extraction of components of low volatility from coal liquids using supercritical toluene. Barton and Fenske<sup>23</sup> suggested using C<sub>11</sub> and C<sub>12</sub> paraffinic fractions to desalinate sea water. Hubert and Vitzhu<sup>24</sup> studied on the removal of nicotine from tobacco leaves, of caffeine from green coffee beans, and the separation of a hop extract from commercial hops, in all cases using supercritical carbon dixoide. Modell et al.<sup>25,26</sup> discussed the regeneration of activated carbon by the use of supercritical carbon dioxide.

Critical data for a number of possible supercritical fluid solvents are listed in Table 2-1. These gases are suitable as a solvent either on their own or as components of mixtures. Because of their low critical temperatures, several of them can be used to extract heat-labile substances. Particularly, supercritical carbon dioxide is a very attractive solvent for practical applications because it is nonflammable, nontoxic, environmentally acceptable and relatively inexpensive. The critical temperature of carbon dioxide is only  $304^{\circ}K$  ( $31^{\circ}C$ ) and thus it can be used at moderate temperature for the extraction of heat sensitive substances without degradation. One good example of using supercritical carbon dioxide is shown in selective extraction of caffeine from green coffee beans.

Substance	Critical Temperature K	Critical Pressure MPa	Critical Density g cm <sup>-1</sup>
Methane	191	4.60	0.162
Ethylene	282	5.03	0.218
Chlorotrifluoro methane	302	3.92	0.579
Carbon dioxide	304	7.38	0 <b>.468</b>
Ethane a	305	4.88	0.203
Propylene	365	4.62	0.233
Propane	370	4.24	0.217
Ammonia	406	11.3	0.235
Diethyl ether	467	3.64	0.265
n. Pentane	470	3.37	0.237
Acetone	508	4.70	0.278
Methanol	513	8.09	0.272
Benzene	562	4.89	0.302
Toluene	592	4.11	0.292
Pyridine	620	5.63	0.312
Water	647	22.0	0.322

Table 2-1: Critical Data for Some Supercritical Solvents<sup>79</sup>

The supercritical fluid (SCF) region is not defined rigorously, but for the practical considerations, the SCF region is usually defined at conditions bounded approximately by  $0.9 < T_r < 1.2$  and  $P_r > 1.0$  where the SCF is very compressible as illustrated in Figure 2-1. For example, at a constant  $T_r$  of 1.0, increasing pressure from  $P_r = 0.8$  to  $P_r = 1.2$  significantly increases the density from gas-like densities to liquid-like densities. At higher reduced temperature, the pressure increase required to increase an equivalent density becomes greater. This practical



Figure 2-1: Reduced density-reduced pressure diagram for carbon dioxide at various reduced temperatures (T) in the vicinity of the critical point(CP) 35

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consideration sets the upper bound on temperature. At higher pressures, the density is less sensitive to temperature changes. In the vicinity of the critical point, large density changes can be obtained with either relatively small pressure or temperature changes.

The effect of SCF solvent density on solubilities is shown directly in Figure 2-2 in the naphthalene-ethylene system.<sup>27,28</sup> Solubilities increase with increasing ethylene densities along each isotherm due to increasing solvent power, and with increasing temperature at constant density due to increasing volatility of naphthalene. These solvent properties vary continuously with solvent density and thus control solvent power and enhance the selectivity of the solvent. Also solvent and solute can be easily separated, and we can fractionate multiple solutes by stepwise reductions in solvent density.

In addition, SCF has better physiocochemical properties than do gases and liquids. The order-of-magnitude comparison shown in Table 2-2 indicates that, while SCF has liquid-like densities, its viscosities and diffusivities are intermediate to those properties for liquids and gases. Thus SCF has the solvent power of liquids with better mass-transfer properties.

#### Table 2-2: Order of Magnitude Comparison of Gas, SCF and Liquid Phases<sup>35</sup>

Property	<u>Gas</u>	Phase <u>SCF*</u>	Liguid
Density (kg/m <sup>3</sup> )	1	700	1000
Viscosity (Ns/M <sup>2</sup> )	10-5	10-4	10-3
Diffusion coefficient (cm <sup>2</sup> /s)	10-1	10-4	10-5

\* At  $T_r = 1$  and  $P_r = 2$ 

**\*\***  $10^3$  centipoise = 1 Ns/m<sup>2</sup>



Figure 2-2: Solid solubilities of naphthalene in compressed ethylene as a function of ethylene density

#### **DIFFUSION COEFFICIENT AND VISCOSITY**

The development of mass-transfer models requires knowledge of the diffusion coefficient of the solute, the viscosity, and the density of the fluid phase which can be used to correlate mass transfer coefficients.

Experimental data on diffusion coefficients in supercritical condition are scarce. Most studies on diffusion coefficient in the high pressure had been limited to the measurement of self diffusion coefficients, and binary diffusion coefficients in simple systems such as  $H_2$ - $N_2$ , He- $N_2$  and  $H_2$ -Ar.<sup>32</sup> But recently, several experiments has been done to measure the diffusivities in systems such as naphthalene- $CO_2$ ,<sup>33,34</sup> benzene- $CO_2$  and caffeine- $CO_2$ .<sup>33</sup> As a result of this work, it has been found that the viscosities and diffusivities of supercritical fluids were strongly dependent upon pressure and temperature in the vicinity of the critical point, and the ratios  $(D_{VP})/(D_{VP})^{O}$  were 0.8 to 1.2.  $(D_{VP})^{O}$  is the value calculated on the basis of the low density theory for a gas at the given temperature. In the recent review article,<sup>35</sup> diffusion coefficient for the several systems were shown as a function of reduced pressure in Figure 2-3.

The viscosity of compressed fluids have been studied quite extensively. In Figure 2-4, the typical data of the viscosities of supercritical carbon dioxide is given as a function of pressure.<sup>36</sup> At the low pressure, the viscosities of carbon dioxide are essentially independent of pressure, but above the critical pressure, the viscosities increase rapidly with pressure.



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Symbol	т, °с	Syilla	Reference
•	20	CO <sub>2</sub> -Naphtheiene	56, 57
x	·30		
+	40		
4	35	CO <sub>2</sub> -Naphthalene	58
V	\$\$		
	12	Ethylcos-Naphthalsos	58
and the second s	35	•	-
ł	40	CO2-Benzene	60
-	40	CO2-Propylbenzens	34
٥	40	CO2-1,2,3-Trimethylbenzens	34

Table 2-3: Ke	y for f	ligure	2-3.
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Figure 2-4: Viscosity of supercritical carbon dicxide 35

#### MODELS FOR FLOW SYSTEM IN A PACKED BED

The packed bed reactor is applicable in many operations, such as extraction, adsorption, leaching, ion exchange and catalytic processes. Therefore, masstransfer coefficients in packed beds is the focus of the current research. First models for determining mass transfer from our experiments (past 38) will be developed and then these coefficients will be correlated.

The simplest flow model for the packed bed is the ideal plug flow model with no longitudinal mixing but complete radial mixing. Although no actual reactors can be fully represented by an ideal model, the plug flow model can be used in a number of packed bed reactors which behave close to the ideal.

However, flow behavior of most of the actual packed bed reactors deviates from ideal conditions. The deviation may be caused by nonuniform velocity profile, velocity fluctuation due to molecular or turbulent diffusion, by short-circuiting, by-passing and channeling of fluid, and by the presence of stagnant regions of fluid caused by the reactor shape and internals. Many flow models considering the nonideality of the flow pattern in packed reactor have been proposed.<sup>37-41</sup> Among them, the cell model or compartment model<sup>49,41</sup> is one of the most widely used models owing to its advantages over other models as decribed below. We used these two models (ideal plug flow model and cell model) to get mass-transfer coefficients and estimate nonideality.

#### The Ideal Plug Flow Model

Flow patterns in packed bed reactors with small ratios of the tube and particle diameter to length can be closely approximated by plug flow. The measurement of mass-transfer coefficients is based upon the following equation:

$$dN_{A} = d(V_{T}y_{A}) = k_{y}(y_{A}^{*} - y_{A})dA = k_{y}(y_{A}^{*} - y_{A})a_{S}SdL \qquad (2-1)$$

Here,

$$V_{T} = \frac{1'}{1 - y_{A}}$$
 (2-2)

where V is molal flow rate of inert component in moles per unit time. Therefore,

$$d(V_{T}y_{A}) = V'd(\frac{y_{A}}{1-y_{A}}) = v'\frac{dy_{A}}{(1-y_{A})^{2}} = V_{T}\frac{dy_{A}}{(1-y_{A})}$$
(2-3)

From equations (2-1) and (2-2)

where  $\bar{G}_{My}$  is the average molal mass velocity of the gas in moles per unit area per unit time. For dilute gas (i.e.,  $1 - y_A = 1$ ),

$$\int_{a}^{y} \frac{dy_{A}}{y_{A}^{*} - y_{A}} = \left(\frac{k_{y}aS}{G_{My}}\right)L_{T}$$
(2-5)

By integration and rearrangement,

$$k_y a_s = (\frac{G_{My}}{L_T}) \ln (\frac{y_A^*}{y_A^*} - y_{A,out})$$

#### Axial Dispersion in a Packed Bed

Several models have been used to analyze and correlate experimental data on mixing in a packed bed. They introduced radial and/or axial diffusion coefficients  $E_r$  and/or  $E_a$ , independent of solute concentration, to take into account the mixing effect in the radial and/or axial directions respectively, for packed beds. These diffusion coefficients can be realted to flow parameters, fluid properties and the geometry of the bed and the packing.

In a packed bed catalytic reactor, a chemical reaction takes place in a bed and heat flows through the tube wall and therefore, the radial heat and mass transfer are not negligible. However, radial dispersion can usually be neglected compared with axial dispersion when the ratio of column diameter to length is small and the flow is in the turbulent regime. Many investigators have found that the mixing effect in packed beds could be well described in an axial dispersion coefficient  $E_a$  alone even though there was some radial dispersion effect.

Dankwerts<sup>41</sup> first published the results on axial dispersion in a packed bed. Wen and Fan<sup>42</sup> summarized the results of previous investigations on the axial dispersion of liquids (Figure 2-5) and gases (Figure 2-6) in packed beds and have developed empirical correlations (shown below) based on about 500 data points for liquids and gases, respectively. The axial Peclet number  $P_{e,a}$  is defined as  $d_p u/E_a$ . These equations can be used to determine the axial diffusion coefficient  $E_a$  for liquids and gases, respectively.



Figure 2-5: A Correlation of longitudinal dispersion coefficient of liquid phase fixed beds and fluidized beds in terms of peclet number



Figure 2-6: Correlation of axial dispersion coefficient for gases flowing through fixed beds

Liquids:

$$\epsilon P_{e,a} \approx 0.2 \div 0.11 \text{ Re}^{0.48}$$
 (2-7)

Gases:

$$\frac{1}{P_{e,a}} = \frac{0.3}{ScRe} + \frac{0.5}{1 + 3.8(ReSc)^{-1}}$$
(2-8)

:

for 0.008 < Re < 400 and 0.28 < Se < 2.2

The general correlation of existing data of the axial dispersion coefficient for liquids and gases respectively<sup>43</sup> is shown in Figure 2-7. The dashed lines represent the molecular-diffusion asymptotes, for  $Pe = (Re)(Sc)T_{\epsilon}/\epsilon$ . The lines shown are for  $T_{\epsilon} = \sqrt{2}$  and  $\epsilon = 0.4$ . In the case of gases,  $P_{e,a}$  remains approximately constant,

:



Figure 2-7: Approximate representation of a large amount of published data on radial and axial dispersion in randomly packed beds of uniform spheres: flow of a single phase 43

decreasing little from its value of 2 until molecular diffusion is important at Re around 1.0. Molecular diffusion in liquids, however, is so slow that  $E_a$  increases as Re is reduced below 500. But as Re is decreased from 300 to 10,  $P_{e,a}$  remains approximately proportional to Re indicating that  $E_a$  is roughly constant in this region. The correction of  $P_{e,a}$  with Re is greatly dependent on the magnitude of the molecular diffusion coefficient  $D_v$ , that is, Schmidt number Sc =  $\mu/\rho D_v$ .

Even though no experimental data on axial dispersion have been published for supercritical fluids, we can approximate its effect as described below. For supercritical systems, the value of the Schmidt number, around 10, is intermediate to the values for gases (Sc  $\approx$  1.0) and liquids (Sc  $\approx$  1000). By comparing the order of magnitude of Schmidt number for gases, supercritical fluids and liquids, we can assume that the value of P<sub>e,a</sub> for SCF is so close to the value of P<sub>e,a</sub> for gas and is approximately equal to 2.0 when Re is greater than 1.0.

Kramers and Alberda<sup>44</sup> first discussed an analogy between a packed bed and a series of mixing vessels. By an analogy between the mechanism of imperfect mixing and Einstein's kinetic diffusion model, Carberry<sup>37</sup> showed that the number of perfect mixing tanks, n is given by:

$$n = \frac{Lu}{2E_a} = \frac{L}{d_p} \frac{P_{e,a}}{2}$$
(2-9)

As  $E_a + \infty$  for n = 1.0, then for a small number of mixers less than 10:44

$$n - 1 = \frac{Lu}{2E_a}$$
(2-10)

These equations are used for determining the number of perfect mixers to be used in the cell model below.

#### Mass-Transfer Coefficient from the Cell Model

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. The common characteristic of this model is that the basic mixing unit is a completely mixed or stirred tank. This model has been employed extensively from early days of chemical engineering to the present.<sup>40,41,45-48</sup> This cell model has the following practical advantages over other models:

- The transition mixing behavior of such model can be presented by a set of linear first-order ordinary differential equations instead of partial differential equations.
- 2. The steady-state reaction in such a model can be represented by a set of finite difference equations rather than differential equations.

Since complete mixing is assumed in a cell, the mole fraction of a solute in out-going stream from the ith cell is  $y_i$ . If the bed is viewed as a series of n perfect mixing cells each having surface area of pellets  $A_T/n$  and constant mass-transfer coefficient  $k_y$ , then for the steady-state mass-transfer the material balance around the first cell gives

$$k_{y}(A_{T}/n)(y^{*} - y_{1}) = V_{T}(y_{1} - y_{0})$$
(2-11)

Finally, we can obtain the following expression for n cells by using the similarity for each cell (its derivation is not given here)

$$k_{y}a_{S} = \frac{nV_{T}}{SL_{T}} \left[ \left( \frac{y^{*} - y_{o}}{y^{*} - y_{n}} \right)^{1/n} - 1 \right]$$
(2-12)

As mentioned above, we can assume that the value of  $P_{e,a}$  for SCF is approximately equal to 2.0 when Re is greater than 1.0. Then, the number of perfect mixers in a packed bed can be determined by equation (2-9) or (2-10) depending upon the number of layers of the pellets in a packed bed (L/d<sub>p</sub>). Finally, the mass-transfer coefficient under supercritical conditions can be obtained by equation (2-6) and/or (2-12) using the plug flow and/or cell models, respectively.

#### MASS-TRANSFER CORRELATIONS

After mass-transfer coefficients under supercritical conditions are determined, they need to be correlated as a function of the significant independent variables. Data on the rate of transfer between beds or particles and a flowing fluid are needed in the design of many industrial devices used for extraction, adsorption, leaching, ion exchange and chromatography. Numerous studies for packed beds have been carried out with the object of measuring mass-transfer coefficients and correlating the results under standard conditions, usually at 1 atm and 25°C. As far as we know, no data have been published on the mass-transfer coefficients under supercritical conditions. As several researchers pointed out, 10,11 under supercritical conditions we expect correlations for mass-transfer coefficients to differ from those for mass-transfer coefficients of solid-gas or solid-liquid systems under standard conditions. In general, mass-transfer between a fluid and a packed bed of solid can be described by correlations of the following form by the similarity to the relationships obtained for heat transfer:

$$Sh = f(Re, Sc, Gr)$$
(2-13)

where Sh, Re, Sc, and Gr are respectively the Sherwood number, Reynolds, Schmidt, and Grashof numbers for the mass-transfer. Such a relationship has been obtained theoretically by  $Eckert^{49}$  from a consideration of the boundary conditions.

Below we describe several existing correlations, developed under nonsupercritical conditions, which may serve as guides for the correlations to be developed in this work.

#### Natural Convection

Recently, Debenedetti and Reid<sup>50</sup> pointed out that, in the case of supercritical fluids, buoyant effects had to be considered because supercritical fluids showed extremely small kinematic viscosities as a result of their high densitites and low viscosities. The comparison of the properties of air, water, and mercury was given in Figure 2-8 to show the relative importance of buoyant forces at constant Reynolds number. From the last column in Figure 2-8, we can find that the effect of buoyant forces is more than two orders of magnitude higher in supercritical fluid than in normal liquids.

For transfer under natural convection condition, where the Reynolds number is unimportant, general expression reduces to

$$Sh = g(Sc,Gr)$$

(2-14)



Figure 2-8: Comparison of physical properties of air, water, and mercury, and CO<sub>2</sub>, showing relative importance of natural convection

at constant Reynolds numbers: air, H<sub>2</sub>O, Hg at 298°K and 1 bar, CO<sub>2</sub> at 310°K and 150 bar<sup>50</sup> For large Schmidt number (usually liquid system) Karabeal et al.<sup>51</sup> proposed the following typical form of relationship for this natural convection condition by the use of asymptotic relations.

$$Sh = 0.46(GrSc)^{1/4}$$
 (2-15)

for laminar natural convection

$$Sh = G.112(GrSc)^{1/3}$$
 (2-16)

for turbulent natural convection.

If natural convection is dominant, the correlations like those above are likely to be appropriate for modeling the mass-transfer coefficient data. Its main difference is that it is independent of Reynolds number Re.

#### **Forced Convection**

Under forced convection conditions, where the Grashof number is unimportant, the general expression becomes

$$Sh = h(Re,Sc)$$
(2-17)

The most convenient method of correlating mass-transfer data under forced convection conditions is to plot the  $j_d$  factor as a function of Reynolds number as suggested by Colburn<sup>5</sup> and Chilton and Colburn<sup>6</sup> who, from theoretical consideration of flow and from dimensional analysis, defined  $j_d$  as follows:

$$j_{d} = \frac{Sh}{ReSc^{1/3}} = \frac{k_{y}M_{av}}{G} (\frac{\mu}{\rho D_{v}})^{2/3}$$
(2-18)

In calculating the Schmidt nubmer,  $\mu/\rho D_v$ , the viscosity and density of carbon dioxide will be used since the amount of naphthalene in carbon dioixde has a negligible effect on these properties.

The functional dependence of  $j_d$  on Reynolds number Re has been the subject of study by many investigators. A variety of equations have been proposed to represent their experimental data. Many of these correlations also employ the bed porosity  $\varepsilon$  as an additional correlating parameter. The porosity is the ratio of the void volume between pellets to the total bed volume. Two typical correlations for solid-gas and solid-liquid systems are as follows:

1. Solid - Gas System:<sup>52</sup>

$$\epsilon_{jd} = 0.357 \text{ Re}^{-0.359}$$
 3< Re < 2000 (2-19)

2. Solid-Liquid System:<sup>8</sup>

$$\epsilon_{jd} = 0.25 \text{ Re}^{-0.31}$$
 55 < Re < 1500 (2-20)  
 $\epsilon_{jd} = 1.09 \text{ Re}^{-2/3}$  0.0016 < Re < 55 (2-21)

Other proposed correlations of mass-transfer data are shown in Rable 2-4.51

#### **Combined Natural and Forced Convection**

In the intermediate region where natural and forced convection happen simultaneously, neither the Reynolds number nor the Grashof number can be neglected. Garner and Grafton<sup>53</sup> suggested that the transfers due to the two processes are simply additive. Karabelas et al.<sup>51</sup> proposed the following correlations using an asymptotic method which are shown in Figure 2-9.

Sh = 
$$[\{0.46(GrSc)^{1/4}\}^6 + \{4.58 \text{ pe}^{1/3}\}^6]^{1/6}$$
 (2-22)

for 1 in, and 1/2 in, speheres (GrSc <  $1.31 \times 10^8$ )

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Sh = 
$$[\{0.112(GrSc)^{1/3}\}^2 + \{2.39 \text{ Re}^{0.56}Sc^{1/3}\}^2]^{1/2}$$
 (2.23)

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For 3 in, sphere (GrSc =  $3.2 \times 10^9$ )

## Table 2-4: Correlations of mass-transfer data 51

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Reference	Type of packing	Correlation	Re	Sc
él	Spherical and cylindrical pellets	$j_d = 16.8Rc^{-1}$ < 40		0.61-0.62
		$j_d = 0.989 Rc^{-9.41}$	> 350	
62	Same as above	$j_d = 1.82Rc^{-9.51}$	< 350	~ 0.615
á3	Granular solid	$S_{1}S_{1}C^{**} = 0.45R_{1}C^{-0.50}$	< 10	~ 1000
		$S_{1}S_{1}^{\mu\nu} = 0.20Re^{-\nu 2\mu}$	> 50	
Ď-i	Soheres and cylinders	$i_{4} = 1.251 Re^{-10.41}$	$Re_{m} > 620$	~ 0.61
		$i_{*} = 2.44 R c_{-0.51}$	$Re_{-} < 620$	
	Spherical and fishe	$i = 1.675 R_{e} - 1.507$	< 170	1200-1500
83	shund particles	$i = 0.687 R_{-9.327}$	> 170	1-111 10-11
44	Porous sobariand	$J_{4} = 0.0000000000000000000000000000000000$	0-10 000	776
40	numbers synchronic to the	$-0.015 \log R = 0.0817$	0-10,000	and
	particles source in an	-0.71210g KC + 0.0017		865
	adagons solution	liof Kal-		0.1.
		R 111	Re - 200	150-13.000
67	Pellets of succinic	$S_{1}S_{\ell} = 1.97 = 1.97$		
	and sulicylic acids		<b>D</b> -	Ú.
		$StSc^{-0.36} = 0.29 \frac{Rc}{C}$	$\frac{RP}{2}$ > 200	
		Le J	E	
		$\frac{150(1-\epsilon)}{100} R = 15 = 100$	wide range	wide range
6X	Various particle	Ja 66 NE SC	wide tange	#100 Tunge
	geometries	•		
		$+\frac{1.75}{5}Sc^{-13}$		•
		6e		
		16G1-+++	6 <b>G</b>	
69	Spheres	$j_d = 1.46 \left  \frac{1}{100} \right  \qquad (1 - \epsilon)^{1/2}$	$\frac{1}{2} > 100$	wide range
		[0/c] [6/c]=[	60	
		$j_{e} = 17 \left  \frac{30}{1 - \epsilon} \right ^{0.2}$	$\frac{00}{10} < 10$	
	Den at a		а <u>н</u> - 50	lanı
73	Porous spheres	$j_d = 10Re^{-t}$	. < 30	100
		$j_d = 1.30Re^{-0.5}$	> 150	
71	Benzoic acid	$j_a = 1.48 Re^{-0.32}$	1-70	~ 1000
••	granulas	-		
	-	[ Ro ]-474	Re	
72	Various particle types	$j_{\alpha} = 5.7 \left  \frac{1}{1 - 1} \right $	$1 < \frac{1}{1-1} < 30$ .	0-6-10,000
		[]=[]		
		$i_1 = 1.77$	$30 < \frac{\kappa e}{10^4} < 10^4$	
		20 [1−ε]	1 <i>~~€</i>	•
73	Spherical particles	$j_{\rm eff} = 0.667 Re^{-9.24}$	20-200	
	6	0.725		0.000
74	Porous spheres	$J_d = \frac{1}{Rc^{p-41} - 1.5}$	13-11-0	0.006
		0.863		
7	Fixed and fluidized	$\epsilon_{j_{\text{ell}}} = 0.010 + \frac{R_{i}}{R_{i}} = 0.483$	>1	wide range
	beds of spheres	101 - O-40,0		
75	Fixed and fluidized			
	heds of particles with	$\epsilon_{j_d} = 0.30$	$R_{\ell_{m}} > 50$	wide range
	various geometries	$f Re_{m} = 1.90$		
	various fromettics	Г.Р.,- <b>1-6-6</b> С	Ra	
76	Spherical particles	SIScos = 2.40	$0.08 < \frac{MC}{2} < 125$	~ 1000 ·
			€ D	
		$StSt^{+3+} = 0.442 \frac{Re}{2}$	$125 < \frac{\kappa r}{2} < 5000$	
		[ <i>€</i> ]	E	
77	Porous spherical and	5 C 2 1 3-050		
	cylindrical	$j_a = 2.25 \left  \frac{0.4}{1} \right $	wide range	0-60

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Figure 2-9: Asymptotic correlations for the combined natural and forced convection<sup>51</sup>

#### EXPERIMENTAL

The schematic diagram of the experimental apparatus used in this study is shown in Figure 2-10. Liquid carbon dioxide is pumped into the system via a highpressure Milton-Roy liquid pump. Pressure is controlled by using a back pressure regulator and pressure fluctuation is 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 171 cm<sup>3</sup> in volume, 14.6 cm in length and 3.87 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 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. 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 is found as described below. With this value and total amount of gas flow through wet-test meter, the mole fraction of solids in the supercritical fluid can be readily determined. The temperature and pressure in wet-test meter are also measured.

The sample collectors are high pressure bombs which are kept at room temperature by two 200 watt resistance heaters. Each vessel contains toluene



Figure 2-10: Schematic diagram of the experimental apparatus of SCFE

which will help dissolve the extract (naphthalene) from the carbon dioxide. These vessels are operated at 300 to 400 psi where the solubility of the solid in the carbon dioxide 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) is weighed. A sample of the toluene-extract solution is then injected into a gas chromatograph to determine what portion of the solution is extract. Finally, the bypass, from valve 12 to 16, is designed to insure steady-state flow through the extraction vessel 11.

The whole apparatus is rated for a pressure of 5000 psi. All measured temperatures and pressures are recorded on a data logger at regular time intervals. The parameters that are being studied are:

- Effect of flow rate on solubility of naphthalene in carbon dioxide at different pressures and temperatures.
- Effect of bed height on the mass-transfer coefficient under supercritical conditions.
- Effect of flow rate on the mass-transfer coefficient under supercritical conditions.
- Effect of pressure on the mass-transfer coefficient under supercritical conditions.

The experimental conditions are as follows:

System: Naphthalene - Carbon Dioxide

**Pellet Characteristics:** 

Material: Naphthalene

Shape: Cylindrical

Size: Length (mm) = 4.76 Diameter (mm) = 4.76 Height of Bed (mm): 4.76 - 19.04 Temperature of Bed (<sup>O</sup>K): 308, 318, 328 Pressure (psi): 1470, 2205, 2940, 3675 Flow Rates (STD. liter/min at 0<sup>o</sup>C and 1 atm): 4 - 30 Reynolds Number: 10 < Re < 250 Schmidt Number: 5 < Sc < 12 Grashof Number: 1.69x10<sup>6</sup> < Gr < 2.13x10<sup>7</sup>

#### **RESULTS AND PLANS**

This work is divided into two major parts. The first part is to measure masstransfer coefficients, while the second one is concerned with establishing the masstransfer correlations under supercritical conditions.

Mass-transfer coefficients in packed beds under standard conditions have been measured using various flow models. However, no study has yet been carried out to estimate the mass-transfer coefficient under supercritical conditions and no masstransfer correlations under these conditions have been developed.

For this fundamental mass-transfer study under supercritical conditions, naphthalene-CO<sub>2</sub> systems have been chosen due to convenience of getting the values of transport properties such as binary diffusion coefficient, viscosity and density of carbon dioixde from the literature. Experiments will be carried out to investigate the effect of the flow rate of CO<sub>2</sub> on solubility of naphthalene in CO<sub>2</sub>. The effect of flow rate on CO<sub>2</sub>, temperature, and pressure on mass-transfer coefficients will be determined using the plug flow model and cell model. Then, these mass-transfer coefficient data will be used to developed mass-transfer correlations analogous to those shown in the previous section which would be useful in designing separation units. Finally, these correlations for solid-supercritical fluid will be compared with mass-transfer correlations for solid-gas and/or solidliquid systems, depending upon three different flow conditions, respectively (natural, forced, and combined natural and forced convection).

#### **Preliminary Measurements**

In recent months, mass-transfer coefficients were obtained for different flow rates of carbon dioxide at 100 atm and  $35^{\circ}$ C by cell model and are shown in Table 2-5.

Run No.	Superficial Flow Rate (2/min) at O <sup>O</sup> C 1 atm	Exit Mole Fraction x10 <sup>3</sup>	k <sub>c</sub> a (sec <sup>-1</sup> )	Molar Mass Velocity (gmole/cm <sup>2</sup> sec) x10 <sup>4</sup>
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 -:

Table 2-5: Preliminary Results for Mass-Transfer Coefficients at 100 atm and 35°C

Comparison of our data with those of ordinary systems such as  $CO_2(g)$ naphthalene<sup>54</sup> and water-naphthalene<sup>55</sup> under standard conditions (usually 1 atm and 25°C) is shown in Figure 2-11. It shows that the mass-transfer rates under supercritical conditions were high (same order-of-magnitude as  $CO_2(g)$ - naphthalene system), and their numerical values lay in between those of solid-gas and solid-liquid as expected.



Figure 2-11. Comparison of supercritical condition with G-S and L-S system

#### NOMENCLATURE

а	:	System parameter in Peng-Robinson equation of state
as	:	Surface area of pellets per unit volume of extractor $[cm^2/cm^3]$
Ap	:	Surface area of single particle [cm <sup>2</sup> ]
AT	:	Total surface area of pellets in extractor $[cm^2]$
b	:	System parameter in Peng-Robinson equation of state
с	:	Concentration of solute [gmole/cm <sup>3</sup> ]
ďp	:	Diameter of sphere possessing the same surface area as a piece of
		packing [cm]
Dv	:	Molecular diffusivity [cm <sup>2</sup> /sec]
Ea	:	Axial dispersion coefficient [cm <sup>2</sup> /sec]
Er	:	Radial dispersion coefficient [cm <sup>2</sup> /sec]
$f_1^6$	:	Fugacity of component i in solid phase [atm]
$f_1^y$	:	Fugacity of component i in vapor phase [atm]
g	:	Gravitational acceleration [cm/s
G	:	Mass velocity [g/cm <sup>2</sup> sec]
₫ <sub>My</sub>	:	Average molal mass velocity [gmole/cm <sup>2</sup> sec]
G <sub>My</sub>	:	Molal mass velocity [gmole/cm <sup>2</sup> sec]
Gr	:	Grashof number = $d^3g_{\rho}\Delta\rho/\mu^2$
ja	:	Mass transfer factor = $ShRe^{-1}Se^{-1/3}$
k <sub>e</sub>	:	Mass transfer coefficient = kyC [cm/sec]
k <sub>ij</sub>	:	Binary interaction parameter
<sup>k</sup> y	:	Mass transfer coefficient [gmole/cm <sup>2</sup> sec mole-fraction]
$L_{T}$	:	Total height of bed [cm]
Mav	:	Average molecular weight [g/gmole]

n	:	Number of perfect mixers
NA	:	Molal flux of solute [gmole/cm <sup>2</sup> sec]
P	:	Total pressure [atm]
Pe	:	Critical pressure [atm]
Ре	:	Peclet number = $u_s d_p / D_v$
P <sub>e,a</sub>	:	Axial peclet number = $ud_p/E_a$
$P_1^S$	:	Saturation (Vapor) pressure of pure solid [atm]
R	:	Gas constant = 0.08205 [atm liter/gmole <sup>o</sup> K]
Re	:	Reynolds number = $\rho d_p u_s / \mu$
S	:	Cross section area of packed bed $[cm^2]$
Se	:	Schmidt number = $\mu/\rho D_V$
Sh	:	Sherwood number = $k_e d_p / D_v$
Т	:	Absolute temperature
Тe	:	Critical temperature [ <sup>0</sup> K]
Tr	:	Reduced temperature
Τ <sub>ε</sub>	:	Tortuosity of bed
บ	:	Interstitial velocity [cm/sec]
<sup>u</sup> s	:	Superficial velocity [cm/sec]
VT	:	Total molal flow rate [gmole/sec]
v	:	Molal flow rate of inert component [gmole/sec]
УА	:	Mole fraction of component A
y <b>*</b> A	:	Equilibrium mole fraction of component of A
Уі	:	Mole fraction of component A in stream outgoing from ith cell
Z	:	Compressibility factor

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#### Greek Letters

E	:	Void fraction
₽īv	:	Fugacity coefficient of component i in vapor phase
¢S IS	:	Fugacity coefficient of component i in solid phase at saturaction
		pressure P <sup>S</sup> <sub>1</sub>
Ϋ́	:	Activity coefficient at infinite dilution
μ	:	Viscosity [g/cm sec]
ρ	:	Density [g/cm <sup>3</sup> ]

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