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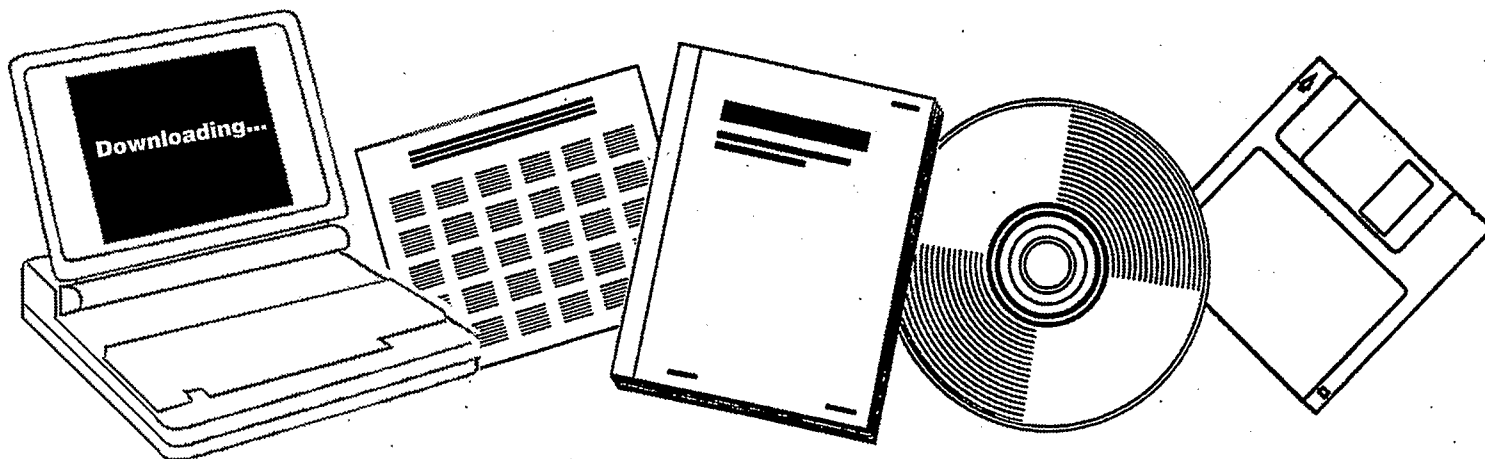
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**NOVEL EXPERIMENTAL STUDIES FOR COAL  
LIQUEFACTION: QUARTERLY PROGRESS REPORT,  
JANUARY 1, 1988-MARCH 31, 1988**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL  
AND PETROLEUM ENGINEERING**

1988



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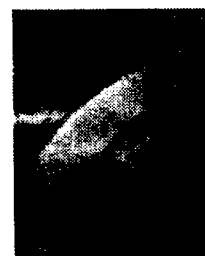
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**Quarterly Progress Report**

DOE/PC/71257--T15

DE88 010828

**NOVEL EXPERIMENTAL STUDIES  
FOR COAL LIQUEFACTION**

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

**January 1, 1988 to March 31, 1988**

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## **NOVEL EXPERIMENTAL STUDIES FOR COAL LIQUEFACTION**

Research is being carried out in this project in two areas which are of interest to ongoing investigations at the Pittsburgh Energy Technology Center (PETC). They are: (a) behavior of slurry reactors used for indirect coal liquefaction, and (b) coal liquefaction under supercritical conditions. The current status of each of these tasks is summarized in this report.

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## TASK 1: 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.

#### 1.1 Scope of Work

Experimental work is presently being concentrated on the synthesis of methanol from CO and H<sub>2</sub> via methyl formate. The process consists in the carbonylation of a molecule of methanol to methyl formate followed by hydrogenation to form two molecules of methanol. The kinetics of the individual reactions were first studied and the results have been included in previous progress reports. They are also presented in a paper which has been accepted for publication in Fuel Processing Technology. Subsequently, the two reactions were carried out concurrently -- both reactions taking place simultaneously in a single reactor. The concurrent reaction is very promising and we are concentrating experimental work in Task 1 on further elucidation of the effect of important design parameters.

A modeling study is also being carried out by Dr. Y. T. Shah at the University of Tulsa. He is investigating the non-isothermal unsteady state Fischer-Tropsch reaction. Experimental work which was begun on a previous project and which was

extended on this project demonstrated that multiple steady states can exist for this reaction.<sup>(1)</sup>

### 1.2 Results and Highlights

During the quarter experimental studies were conducted in three areas related to the concurrent reaction -- activation of the heterogeneous catalyst in-situ, further study of the effect of H<sub>2</sub>/CO ratio on reaction rate, and a thermodynamic evaluation of the conditions under which the concurrent reaction can be carried out. Work on modeling of the Fischer-Tropsch reaction also continued. Each of these activities is discussed below.

### 1.3 Future Work

Experimental work on the concurrent synthesis of methanol will continue. We plan to evaluate alternate homogeneous catalysts. A paper describing work on the concurrent synthesis is being prepared and should be submitted for publication during the next quarter. Modeling work will be finished during the quarter, and a paper describing the results is being prepared for publication.

### 1.4 In-Situ Activation of Copper-Chromite Catalysts

The hydrogenolysis catalyst used in our work is a copper-chromite catalyst with the analysis shown in Table 1. It was purchased from United Catalyst (G-89), who state that it does not have to be pre-activated for hydrogenation [1]. However, it has been reported that different activation methods result in different hydrogenolysis activities for this catalyst. Trimm et al. [2] studied the hydrogenolysis of methyl formate after reducing the catalyst in a 5% H<sub>2</sub> in N<sub>2</sub> gas mixture at 200°C for for hours and then raising the temperature to 250°C and



using pure H<sub>2</sub> for 12 hours. Sorum and Onsager [3] studied the same reaction and reduced the catalyst in the liquid phase overnight at reaction temperatures using pure H<sub>2</sub>. Trimm et al. reported lower reaction rates and attributed the difference to different methods used in catalyst reduction.

In our previous work, we reduced the catalyst in the gas phase in an H<sub>2</sub> atmosphere. The temperature was increased from room temperature to 170°C at the rate of 0.6 C/min and maintained at 170°C for 12 hours. The H<sub>2</sub> feed rate was 10 cc/min. The rate of hydrogenolysis of methyl formate was similar to that reported by Trimm et al., although we used a lower reduction temperature and pure H<sub>2</sub>.

A study was conducted to determine whether an in-situ method of catalyst preparation could be used for the concurrent reaction. In-situ methods have the obvious advantage that they eliminate the time-consuming external reduction step. Runs were made using three different treatments for the copper-chromite catalyst --reduction in-situ using methanol and H<sub>2</sub>; reduction in-situ using methanol and H<sub>2</sub> and with potassium methoxide present; and no reduction. Experiments were carried out in a 300 cc autoclave manufactured by Autoclave Engineers. The reactor is equipped with a variable speed mechanical stirrer which is driven by a magnetic coupling and has a cooling coil and two baffles. The reactor has five openings on the top. Two openings are for feed and effluent streams, one for temperature measurement, one for liquid sampling and one for a rupture disk. Reactor pressure measurement is made through the effluent line. The reactor was cleaned and charged with 150 cc of methanol and six grams of un-reduced catalyst. Homogeneous catalyst (CH<sub>3</sub>OK) was or was not charged in the reactor at this time depending upon the reduction method. The reactor was then sealed and pressurized with H<sub>2</sub> to test for possible leakage at a pressure higher than the

reaction pressure. If there was no leak, heater and stirrer were turned on. The reactor temperature was increased to 170°C and pressure was maintained at 62 atm. A constant H<sub>2</sub> flow of 30 cc/min was maintained for 15 hours. The reactor temperature was then lowered to reaction temperature (160°C). If CH<sub>3</sub>OK was not present in the reactor, the temperature was lowered to room temperature after the pre-reduction and the reactor was opened to add CH<sub>3</sub>OK and then sealed and heated to reaction temperature. The reaction was started by introducing a mixture of H<sub>2</sub> and CO to the reactor. The flow rates of H<sub>2</sub> and CO were monitored by two on-line mass flow controllers. The reactor operation and sampling were the same as those previously reported. Methanol formation rates are shown in Figure 1. It is clear that the hydrogenolysis rates of the runs using the in-situ pre-reduction are higher than the rates obtained in the runs using the gas phase pre-reduction and no pre-reduction. The rates using in-situ pre-reduction with and without CH<sub>3</sub>OK are similar.

H<sub>2</sub>O is a product of catalyst reduction when H<sub>2</sub> is used as a reducing agent. The H<sub>2</sub>O concentration of the slurry increased from 0.37 mol% before the pre-reduction to 0.53 mol% after the pre-reduction. It has been reported that H<sub>2</sub>O has a negative effect on the homogeneous catalyst (CH<sub>3</sub>OK in this study) [2,4,5]. However, the increased H<sub>2</sub>O concentration in the slurry after the catalyst pre-reduction did not reduce the methanol production rates in the concurrent reactions. One possible explanation is that the amount of CH<sub>3</sub>OK added in the reactor (0.43 ml/L = 1.8 mol%) may be more than enough for the concurrent reactions. Even if some of the CH<sub>3</sub>OK is lost by reacting with H<sub>2</sub>O to form potassium hydroxide and methanol, there is still enough left to catalyze the carbonylation reaction. Another explanation is that the H<sub>2</sub>O produced during the catalyst pre-reduction

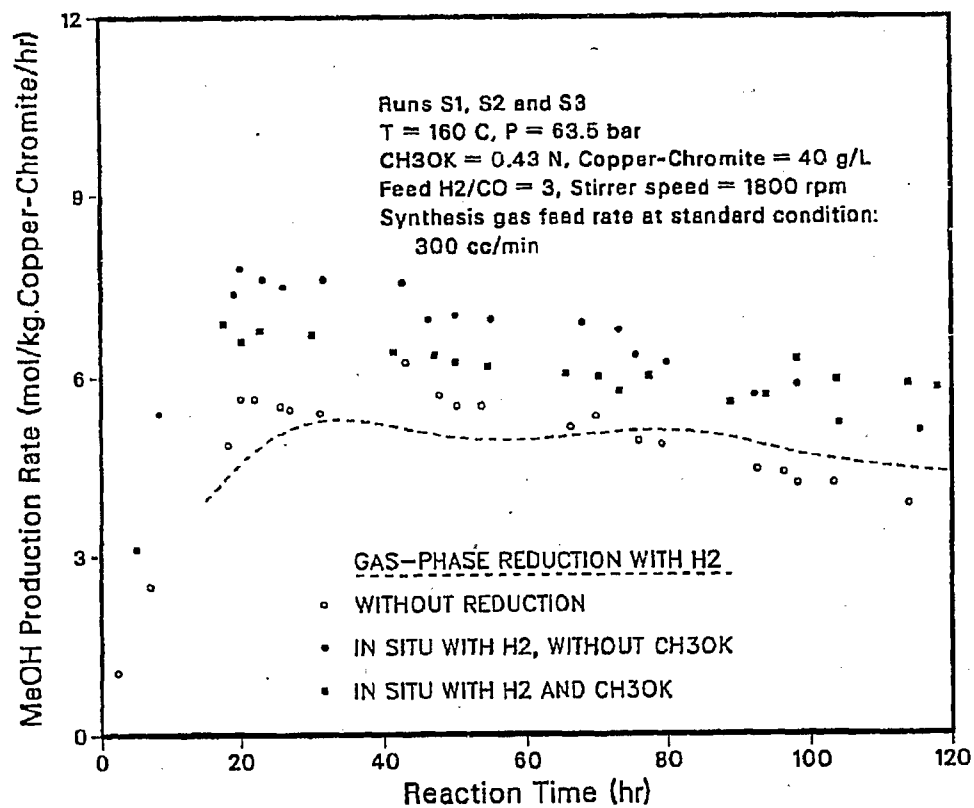


Figure 1: Effect of hydrogenolysis catalyst reduction method on MEOH production rate.

may be removed from the reactor by side-reaction(s). The latter is supported by analysis of reactor gas effluent. After the catalyst reduction, the reactor gas phase contained H<sub>2</sub> with a small amount of CO<sub>2</sub> and methanol. After synthesis gas was introduced into the reactor (CO was the only new chemical introduced), the CO<sub>2</sub> concentration in the gas phase started to increase with time, reached a maximum in 4 hours, and then decreased to a steady-state level. CO<sub>2</sub> formation rate in two runs is shown in Figure 2. The H<sub>2</sub>O concentration also decreased after synthesis gas was introduced to the reactor. These facts suggest that a water-gas shift reaction occurs in the reactor after CO is introduced into the reactor.



Thermodynamic calculations verify that at the reaction conditions used the above reaction will proceed to the right.

It can be concluded that in-situ copper-chromite pre-reduction in the presence of CH<sub>3</sub>OK can be used in the concurrent two-step methanol synthesis. It gives good catalyst activity and is simple in operation. Water, which has been reported to be a poison for the carbonylation catalyst does not seem to be a problem for the concurrent two-step reaction in a single reactor. The H<sub>2</sub>O concentration can be reduced by the reverse water-gas shift reaction and the CO<sub>2</sub> formed can be removed from the reactor.

#### 1.5 Effect of H<sub>2</sub>/CO Ratio on the Concurrent Two-Step Reactions

H<sub>2</sub>/CO ratio is an important operating parameter for the concurrent methanol synthesis. Some experiments were made to study the effect of H<sub>2</sub>/CO ratio on the methanol formation rate using gas phase catalyst pre-reduction and

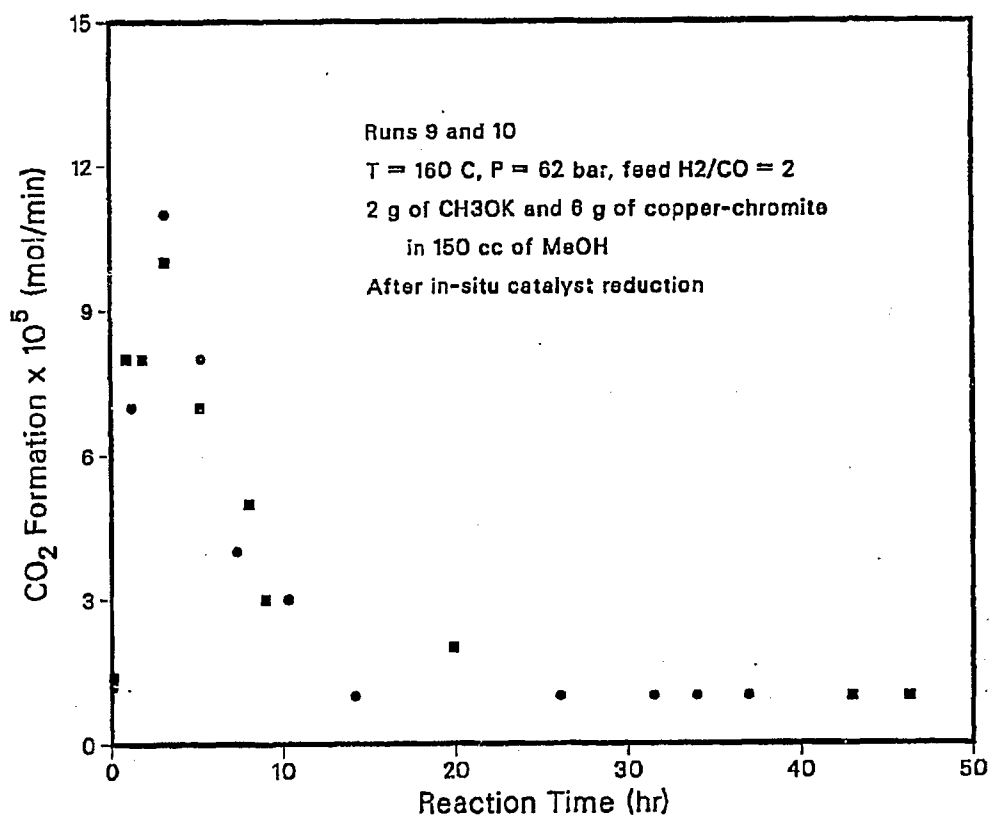


Figure 2: CO<sub>2</sub> formation in the transient period after in-situ catalyst reduction.

the results were reported previously. Further study on the effect of  $H_2/CO$  was made in the last quarter using in-situ reduction with  $H_2$  in the presence of  $CH_3OK$ . The experiments were carried out at  $160^\circ C$  and 63.5 bar using 4.5 grams of  $CH_3OK$  and 6 grams of copper-chromite in 150 cc methanol. The feed  $H_2/CO$  ratios were kept constant in each run. Results are shown in Figure 3. A decrease in the methanol production rates with time was found in all three runs. Since the liquid methyl formate concentrations were close to equilibrium values, the decrease in the methanol production rates was attributed to decreased hydrogenolysis rates. The rate of decrease in methanol production seems related to the  $H_2/CO$  ratio. A higher feed  $H_2/CO$  ratio (lower CO pressure) gives a slower rate of decrease in methanol production. Since  $H_2$  does not affect the hydrogenolysis catalyst, this indicates that the decrease in the methanol production rates is probably related to CO partial pressure in the reactor, as observed in previous reports. The higher the CO partial pressure, the higher the rate of decrease in methanol production. However, it is difficult to correlate the slope of the lines with the partial pressure of CO in the reactor because the  $H_2/CO$  ratio inside the reactor depends on the methanol production rate and, therefore, changes with reaction time.

#### 1.6 Thermodynamics of the Concurrent Two-Step Reaction in a Single Slurry Reactor using Methanol as the Carrier Alcohol

The sum of the two-step methanol synthesis reactions gives the same overall reaction as the current industrial direct methanol synthesis. Hence, thermodynamics of the concurrent two-step methanol synthesis in one reactor is the same as that for the direct synthesis. But the reaction driving force for the two synthesis methods is different at the same temperature and pressure because different reaction media are used. For the direct methanol synthesis, the reaction is carried out in the gas phase or in a high boiling paraffin solvent.

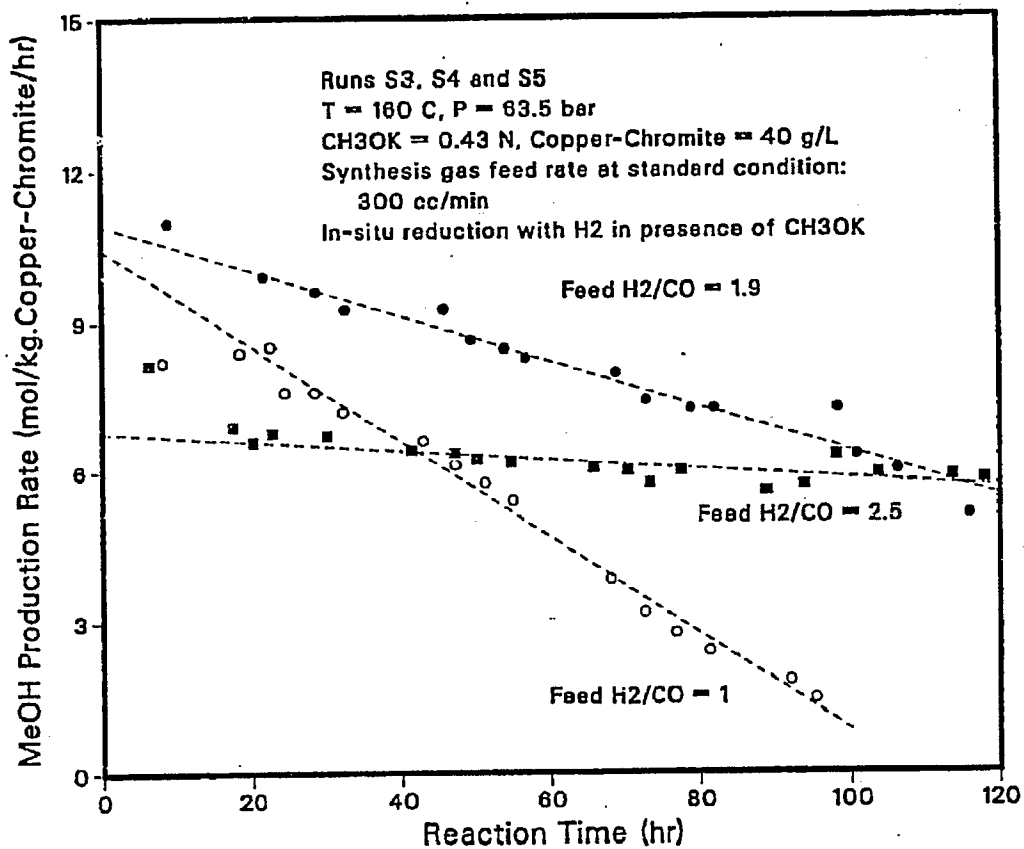


Figure 3: Effect of H<sub>2</sub>/CO ratio on concurrent MEOH synthesis using in-situ reduction.

The reaction temperature is high (240-260°C). The methanol produced is in the gas phase and is withdrawn from the reactor with the gas effluent. The partial pressure of methanol in the reactor is small (much less than its vapor pressure). The driving force can be written as  $P_{\text{MeOH},e} - P_{\text{MeOH}}$ , where  $P_{\text{MeOH},e}$  is the equilibrium partial pressure of MeOH. For the concurrent methanol synthesis using methanol as the carrier alcohol, however, the reaction is carried out in a methanol-rich environment. The partial pressure of methanol equals its vapor pressure and the driving force for the reactions can be written as  $P_{\text{MeOH},e} - P_{\text{MeOH},v}$ , where  $P_{\text{MeOH},v}$  is the vapor pressure of methanol. If the equilibrium methanol partial pressure equals the vapor pressure of methanol, the concurrent reaction will not occur. Using this as a criterion, an equilibrium relation between temperature and total pressure for the concurrent synthesis was calculated and is shown as a line in Figure 4. The equilibrium constants were calculated using the method recommended by Wade et al. [6]. Fugacity coefficients used were calculated using the method recommended by Tsonopoulos [7]. The vapor pressure of methanol equals the equilibrium methanol pressure at conditions represented by the line. Since the equilibrium methanol partial pressure must be higher than the vapor pressure of methanol for the reaction to occur, the shaded area in Figure 4 above the equilibrium line represents possible reaction conditions (temperature and pressure) at which methanol can be produced. The area below the line represents conditions at which concurrent methanol synthesis is thermodynamically impossible. Figure 4 provides a simple but useful way for determination of feasible reaction conditions for the concurrent methanol synthesis when methanol is used as the carrier alcohol.



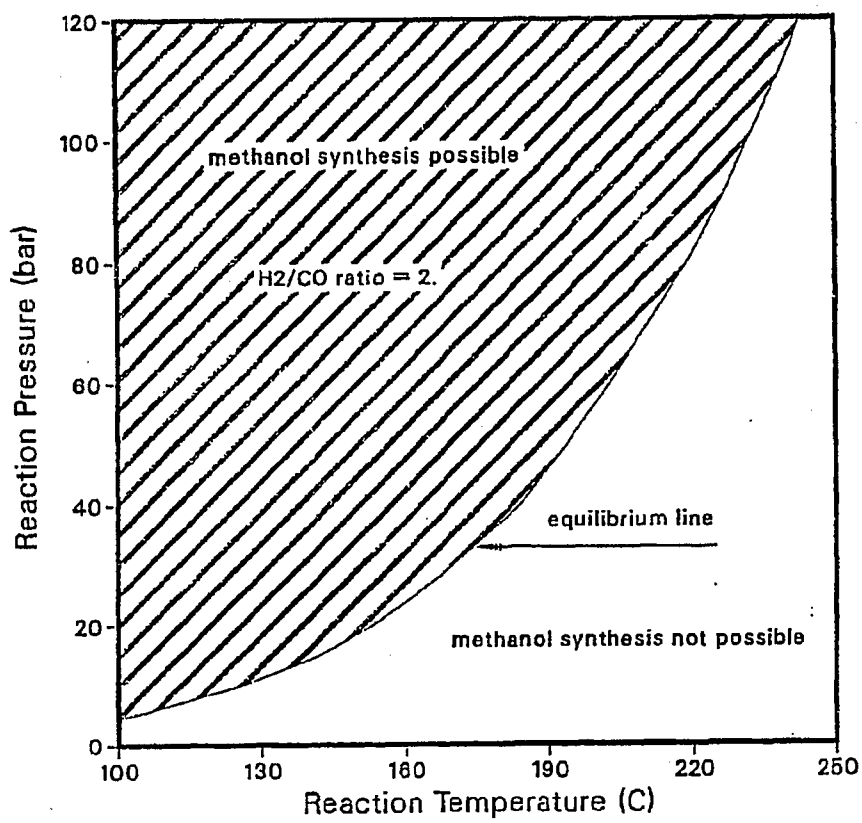


Figure 4: Thermodynamic analysis of reaction conditions for concurrent MEOH synthesis using MEOH as the carrier alcohol.

### 1.7 Modeling of Non-Isothermal Fischer-Tropsch Slurry Reactors

Modeling studies for the Fischer-Tropsch reaction when carried out adiabatically in a slurry reactor were continued by Dr. Y. T. Shah at the University of Tulsa. Of particular interest is the determination of multiple steady states for the reaction. In the range of operating conditions which have been tested, either one or three steady states have been found. This work will be finished during the next quarter, and a paper is being prepared for submission for publication.

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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 change dramatically with pressure at near critical conditions. 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 rate and liquid/solvent ratios that would be appropriate for a supercritical system.

## 2.1 Results and Highlights

During the quarter, we prepared a paper on Supercritical Fluid-Solid Mass Transfer. The first draft of this paper is attached for approval and constitutes the report for this period.

## 2.2 Future Work

Next quarter, we will continue experimental studies for mass transfer in multiple layers of solid pellets. We will also review the implications of these results for coal liquefaction.

## **APPENDIX A**

### **Supercritical Fluid-Solid Mass Transfer Coefficients in the CO<sub>2</sub> - Naphthalens System**

## **SUPERCRITICAL FLUID-SOLID MASS TRANSFER COEFFICIENT IN THE CO<sub>2</sub>-NAPHTHALENE SYSTEM**

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**ABSTRACT:** It is generally known that a supercritical fluid enhances the dissolution of solid particles. This is largely attributed to the enhanced solubility of the solid in the supercritical fluid. Little information, however, is available in the literature for the mass transfer coefficient between supercritical fluids and solids. In this paper, we present mass transfer coefficient data for the naphthalene-supercritical carbon dioxide system. The experimental data are obtained in the temperature of 35°C, pressures of 100 atm to 200 atm and for a single layer of naphthalene in a packed bed of inert particles. For experimental conditions, the ranges of dimensionless parameters are  $2 < Re < 55$ ,  $8 < Sc < 11$  and  $0.8 \times 10^6 < Gr < 5.0 \times 10^6$ . Both forced and natural convection are considered to be important under experimental conditions. The experimental mass transfer coefficients are correlated and discussed.

### **KEY WORDS**

Supercritical, Mass Transfer Coefficient, CO<sub>2</sub>-Naphthalene

### **INTRODUCTION**

The use of supercritical fluids in separation processes has received considerable attention in the past several years and the fundamentals of supercritical fluid (SCF) extraction and potential application have been described in a number of review articles (most recent of which is by Paulaitis et al., 1983). Supercritical fluid extraction utilizes the solvent power of supercritical fluids at temperatures and pressures near the critical point. In comparison with liquid solvents, the supercritical fluids have a high diffusivity and low density and viscosity, thus allowing rapid extraction and phase separation.

While numerous studies have been carried out on solubility of solutes in SCFs, very little information is available on the mass transfer coefficient in SCF-solid systems. In the present study, we present experimental data for the mass transfer coefficient for a well defined naphthalene-supercritical CO<sub>2</sub> system and compare these data with solid-gas and solid-liquid systems.

### **BACKGROUND**

Historically, interest in supercritical fluids was related to the observation that such fluids were often excellent solvents. This fact was discovered over 100 years ago by Hannay (1880) and by Hannay and Hogarth (1879, 1880). Prior to that

time, it was generally thought that fluids above their critical temperatures would be gaseous in nature and thus, poor solvents.

Studies of solubilities in supercritical fluids have been continued (Buchner, 1906; Centnerszwer, 1903) 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 pressures became available in the 1930's (Sage et al., 1936; Kay, 1938) and the first patent for the practical application of supercritical extraction was made in 1943 (Messmore, 1943). Later, Maddocks (1977), Tugrul (1978) and Bartle et al. (1975) described the extraction of components of low volatility from coal liquids using supercritical toluene. Barton and Fenske (1970) suggested the use of C<sub>11</sub> and C<sub>12</sub> paraffinic fractions to desalinate sea water. Hubert and Vitzhum (1978) studied the removal of nicotine from tobacco leaves, the extraction of caffeine from green coffee beans, and the separation of a hop extract from commercial hops by using supercritical carbon dioxide. Modell et al. (1978, 1979) discussed the regeneration of activated carbon by the use of supercritical carbon dioxide.

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°K (31°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 the extraction of caffeine from green coffee beans.

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 for CO<sub>2</sub> in Figure 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 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.

In addition, SCFs have better physicochemical properties than do gases and liquids. The order-of-magnitude comparison shown in Table 1 indicates that while SCFs have liquid-like densities, their viscosities and diffusivities are intermediate to those properties for liquids and gases. Thus SCFs have the solvent power of liquids with better mass-transfer properties.

TABLE I  
ORDER OF MAGNITUDE COMPARISON OF GAS, SCF AND  
LIQUID PHASES(Paulaitis et al., 1983)

<u>Property</u>	<u>Gas</u>	<u>Phase SCF*</u>	<u>Liquid</u>
Density (gr/cm <sup>3</sup> )	10 <sup>-3</sup>	0.7	1
Viscosity (poise: gr/cm sec)	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>
Diffusion coefficient (cm <sup>2</sup> /s)	10 <sup>-1</sup>	10 <sup>-4</sup>	10 <sup>-5</sup>

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

#### DIFFUSION COEFFICIENT AND VISCOSITY

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

Experimental data on diffusion coefficients in supercritical condition are scarce. Most studies on diffusion coefficients at high pressure had been limited to the measurement of self diffusion coefficients, and binary diffusion coefficients in some systems such as H<sub>2</sub>-N<sub>2</sub>, He-N<sub>2</sub> and H<sub>2</sub>-Ar (Balenovic et al., 1979). 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 ratios of  $(D_{V\rho})/(D_{V\rho})^0$  were found to be 0.8 to 1.2 where  $(D_{V\rho})^0$  is the value calculated on the basis of the low density theory for a gas at the given temperature. At present, for the CO<sub>2</sub>-naphthalene system, a linear relationship between  $\log D_V$  and  $\rho$  at constant temperature has been presented by several researchers who determined the diffusivities in supercritical fluids (Feist and Schneider, 1982; Debenedetti, 1984).

We determined a relationship by using the diffusivity data for CO<sub>2</sub>-naphthalene (Iomtev and Tsekhanskaya, 1964) as shown in Figure 2. At 35°C the relationship is

$$D_V = 2.664 \times 10^{-0.568 \times \rho} \quad T = 35^\circ\text{C} \quad (1)$$

The above equation was used for calculating diffusivities in the present studies.



The viscosity of compressed fluids has been studied quite extensively. In Figure 3, the typical data of the viscosities of supercritical carbon dioxide is given as a function of pressure (Stephen and Lucas, 1979).

## EXPERIMENTAL APPARATUS AND PROCEDURE

The schematic diagram of the experimental apparatus used in this study is shown in Figure 4. 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 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 which is 104 cm<sup>3</sup> in volume, 14.8 cm in length and 3.45 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 active packing in the bed can be changed by using inert packing at the bottom and the top of the bed. Because the surface area of the pellets decreases (by 5 to 20%) during an extraction, the average area and particle diameter is used assuming that uniform extraction of the particles takes place. For a single layer this should be valid. The inert packing material consisted of glass beads with diameter similar to that of the pellets. An advantage in using the inert pellets is to reduce end effects in the packed bed being used as the extractor. Pressure at the inlet of the extractor is measured using a pressure transducer. The temperature of the extractor is measured at the inlet using a thermocouple (type K).

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 the total amount of gas flow through the wet-test meter, the mole fraction of solids in the supercritical fluid can be readily determined. The temperature and pressure in the 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 which will help dissolve the extract (naphthalene) from the carbon dioxide. These vessels are operated at 30 to 35 atm where the solubility of the solid in the carbon dioxide is near 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 this second vessel 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 before samples are collected.

The whole apparatus is rated for a pressure of 330 atm. All measured temperatures and pressures are recorded on a data logger at regular time intervals. The SCF-solid mass transfer coefficient was measured as a function of flowrate and pressure (or density). The range of the system parameters examined in this study is shown in Table II.

**TABLE II**  
**RANGES OF SYSTEM PARAMETERS IN EXPERIMENTAL STUDY**

System:	Naphthalene - Supercritical CO <sub>2</sub>
Pellet Characteristics:	
Material:	Naphthalene
Shape:	Cylindrical
Size:	Length (cm) = 0.476 Diameter (cm) = 0.476
Height of Bed (cm):	0.476
Temperature of Bed (°C)	35
Pressure (atm):	100, 200
Flow Rates (STD. liter/min at 0°C and 1 atm):	0.8 ~ 31
Reynolds Number:	2 < Re < 55
Schmidt Number:	8 < Sc < 11
Grashof Number:	0.8x10 <sup>6</sup> < Gr < 5.0x10 <sup>6</sup>

Additionally, one run was conducted at 45°C and 100 atm and resulted in complete dissolution of the naphthalene.

#### CELL MODEL

Since the present experimental study was carried out with a single layer of particles and for small Reynolds numbers, the effects of axial dispersion and natural convection on the experimental results would be important.

In the present study, a cell model is used to analyze the data. Kramers and Alberda (1953) first discussed an analogy between a packed bed and a series of mixing vessels. For a small number of mixers, Kramers and Alberda (1953) derived a relationship

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

Although approximate, equation 2 is used in this study for determining the number of perfect mixers to be used in the cell model below.

#### MASS-TRANSFER COEFFICIENTS 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 (Cholette and Cloulier, 1959; Danckwerts, 1953; Adler and Hovorka, 1961; Deans and Lapidus, 1960; Levenspiel, 1962).

A general correlation of existing data of the axial dispersion coefficient for liquids and gases respectively (Sherwood et al., 1975) is shown in Figure 5. The dashed lines represent the molecular-diffusion asymptotes, for  $P_{e,a} = (Re)(Sc)T_e/\epsilon$ . The lines shown are for  $T_e = \sqrt{2}$  and  $\epsilon = 0.4$ . In the case of gases,  $P_{e,a}$  remains approximately constant, 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 correlation 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 ( $Sc = 1.0$ ) and liquids ( $Sc = 1000$ ). By comparing the order of magnitude of Schmidt number of gases, supercritical fluids and liquids, we assume that the value of  $P_{e,a}$  for SCF is so close to the value of  $P_{e,a}$  for gas and is approximately equal to 2.0 when Re is greater than 1.0.

Since complete mixing is assumed in a cell, the mole-fraction of a solute in out-going stream from the nth cell is  $y_n$ . 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 gives

$$k_y = \left(\frac{V_T}{A_T/n}\right) \left[\left(\frac{y^*}{y^* - y_n}\right)^{1/n} - 1\right] \quad (3)$$

In the present study, all the experiments were carried out with a single layer of particles. 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). With one layer of particles, the number of cells is two; that is,  $n = 2$  in equation (3).

#### EFFECT OF NATURAL AND FORCED CONVECTION

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. The mass-transfer between a fluid and a packed bed of solid can be described by correlations of the following form.

$$Sh = f(Re, Sc, Gr) \quad (4)$$

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 (1950) from a consideration of the boundary value theory.

Recently, Debenedetti and Reid (1986) 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 densities and low viscosities. The effect of buoyant forces is more than two orders of magnitude higher in supercritical fluid than in normal liquids at the same Reynolds number.

When natural convection is controlling the effect of Reynolds number is unimportant, and the general expression reduces to

$$Sh = g(Sc, Gr) \quad (5)$$

For large Schmidt number (usually liquid-solid system) Karabelas et al. (1971) proposed the following relationship for laminar, natural convection,

$$Sh = a(Sc Gr)^{1/4} \quad (6)$$

For liquid-solid systems, Mandelbaum and Böhm (1973) indicated that natural convection should be considered for the range of Reynolds numbers studied in this system.

If forced convection is controlling equation (6) will not correlate the data. In the forced convection regime, the Grashof number is unimportant and the general expression is reduced to,

$$Sh = h(Re, Sc) \quad (7)$$

For a wide range of Reynolds numbers, the following relationship was found to be effective,

$$Sh = cRe^d Sc^{1/3} \quad (8)$$

## RESULTS AND DISCUSSION

Table III and IV show a summary of the experimentally measured results for the present study. At 100 atm the Sh is almost independent of Re and Sh is best correlated as a function of Gr and Sc numbers as follows:

$$Sh = a(Sc Gr)^b \quad (9)$$

The "optimal" exponent was 0.253, but 'b' was set at 1/4 without significantly altering the accuracy of the correlation. With this restriction  $a = 0.665$  and  $b = 0.25$ . According to Karabelas et al. (1971), this indicates that pure natural convection is dominating. The results are compared with those reported by Karabelas et al. (1971) and Mandelbaum and Böhm (1973) in Figure 6. Both of these earlier studies were carried out using the electrochemical technique.

At 200 atm, the Sh number was strongly dependent upon Re and not correlated with the product ScGr. The following correlation described the data well,

$$\text{Sh} = 5.081 \text{Re}^{0.439} \text{Sc}^{1/3}$$

(10)

The data and correlations at 100 atm and 200 atm are compared with each other and with literature values in Figures 7, 8 and 9. Figure 7 shows that the 100 atm data is independent of Re and is therefore in the natural convection regime. At 200 atm, the supercritical carbon dioxide is more dense and the effect of dissolved naphthalene has a less significant effect on the gas density. The density gradients across the boundary layer are smaller and forced convection is the controlling mechanism. This conclusion is supported by Figures 8 and 9 which show that the mass transfer j factor and the mass transfer coefficients are much higher at 100 atm where the large density gradients across the boundary layer produce very large buoyant forces. Considering the size of the naphthalene pellets (3/16 inch), the mass transfer rates in supercritical fluids is much higher than those obtained at low pressure.

Several factors can affect this enhanced mass transfer. First as Debenedetti and Reid (1986) pointed out, the very low kinematic viscosities give rise to very high buoyant forces which serve to enhance natural convection at the same Reynolds number. This is accentuated by large density differences that can occur as naphthalene dissolves in the CO<sub>2</sub>. It is possible to have very large, negative partial molar volumes for a solute at conditions near the critical point (Ziger, 1983) which causes the fluid density to depend strongly on composition. At 35°C and 100 atm, naphthalene's partial molar volume at infinite dilution is approximately -500 cc/mol. This can cause a significantly higher fluid density at the solid surface as compared to the bulk. Additionally, near critical conditions, the compressibility of the fluid begins to diverge and molecular level density fluctuations can occur and lead to additional convective contributions. The partial molar volume effects decrease rapidly as the pressure increases beyond the critical point and at 200 atm this effect is relatively minor. A decreased density gradient explains why the natural convection is no longer controlling. The effects of buoyant forces should be much larger as the critical point of the mixture is approached and mass transfer coefficients should increase. For example, at 45°C and 100 atm, the infinite dilution partial molar volume of naphthalene in carbon dioxide is near -2500 cc/mol. The one experiment done at these conditions resulted in complete dissolution of the naphthalene particles (possibly due to very large natural convection contributions) and required discontinuation of runs at these conditions. These effects require further theoretical and experimental studies.

## CONCLUSIONS

Mass transfer at supercritical conditions is dramatically enhanced by strong natural convection effects. The effect of natural convection is strongest at pressures near the critical point and diminishes as pressure is increased. In the near future, we will present results for multiple layers of naphthalene particles and for different temperatures.

## NOMENCLATURE

$A_T$	Total surface area of pellets in extractor [cm <sup>2</sup> ]
$d_p$	Average diameter of sphere possessing the same surface area as a piece of packing [cm]
$D_v$	Molecular diffusivity [cm <sup>2</sup> /sec]
$E_a$	Axial dispersion coefficient [cm <sup>2</sup> /sec]
$g$	Gravitational acceleration [cm/sec <sup>2</sup> ]
$G$	Superficial mass velocity [g/cm <sup>2</sup> sec]
$Gr$	Grashof number = $d_p^3 g \rho \Delta \rho / \mu^2$
$j_d$	Mass transfer factor = $Sh Re^{-1} Sc^{-1/3}$
$k_y$	Mass transfer coefficient [gmole/cm <sup>2</sup> sec mole-fraction]
$L$	Total height of bed [cm]
$M_{av}$	Average molecular weight [g/gmole]
$n$	Number of perfect mixers
$P$	Total pressure [atm]
$P_c$	Critical pressure [atm]
$Pe$	Peclet number = $u_s d_p / D_v$
$Pe_a$	Axial Peclet number = $u d_p / E_a$
$P_r$	Reduced pressure = $P / P_c$
$R$	Gas constant = 0.08205 [atm liter/gmole °K]
$Re$	Reynolds number = $\rho d_p u_s / \mu$
$Sc$	Schmidt number = $\mu / \rho D_v$
$Sh$	Sherwood number = $k_y M_{av} d_p / \rho D_v$
$T$	Temperature [C]
$T_c$	Critical temperature [K]
$T_r$	Reduced temperature (absolute)
$T_c$	Tortuosity of bed
$u$	Interstitial velocity [cm/sec]
$u_s$	Superficial velocity [cm/sec]
$V_T$	Total molal flow rate [gmole/sec]
$y^*$	Equilibrium mole fraction of component of A
$y_n$	Mole fraction of component A in stream outgoing from nth cell

## GREEK LETTERS

$\epsilon$	Void fraction
$\mu$	Viscosity [g/cm sec]
$\rho$	Average density over the bed length [g/cm <sup>3</sup> ]
$\rho_c$	Critical density [g/cm <sup>3</sup> ]
$\rho_i$	Density at solid-solvent interface [g/cm <sup>3</sup> ]
$\rho_r$	Reduced density = $\rho / \rho_c$
$\Delta \rho$	Average density difference = $\rho_i - \rho$ [g/cm <sup>3</sup> ]

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TABLE III

MASS TRANSFER COEFFICIENTS AND DIMENSIONLESS GROUPS  
WITH ONE LAYER OF NAPHTHALENE PELLETS AT 35°C AND 100 ATM

Run No.	Velocity (l/min) at 0°C, 1 atm	$y \times 10^3$ (mole-fraction)	$G \times 10^2$ * (gr/cm sec)	$k_y \times 10^4$ (gmole/cm <sup>2</sup> -sec)
1-10	31.30	1.24	11.04	2.53
1- 9	20.98	2.47	7.41	2.59
1- 8	13.45	3.73	4.76	2.56
1- 7	9.22	4.73	3.27	2.48
1- 5	7.16	5.08	2.54	2.01
1- 6	4.87	6.26	1.73	2.14
1- 1	2.56	8.01	0.91	2.10
1- 3	0.83	9.82	0.30	1.86

Run No.	Re*	$J_d$ *	$G_r \times 10^{-6}$ *	Sh*	Sh Sc <sup>-1/3</sup> *	ScGrx10 <sup>-7</sup> *
1-10	54.45	0.41	2.675	45.40	22.47	2.205
1- 9	44.15	0.63	4.401	55.86	27.70	3.610
1- 8	29.94	0.96	4.811	58.14	28.87	3.927
1- 7	20.65	1.36	4.604	56.47	28.08	3.744
1- 5	16.70	1.41	5.069	47.43	23.60	4.177
1- 6	11.02	2.21	4.290	48.91	24.37	3.470
1- 1	5.84	4.10	3.875	48.01	23.97	3.115
1- 3	2.13	11.13	4.715	47.75	23.73	3.768

\* Densities are averaged over the bed length. The change in density due to dissolved naphthalene is estimated using the Peng-Robinson (1976) equation of state with a binary interaction parameter of 0.095.

TABLE IV  
 MASS TRANSFER COEFFICIENTS AND DIMENSIONLESS GROUPS  
 WITH ONE LAYER OF NAPHTHALENE PELLETS AT 35°C AND 200 ATM

Run No.	Velocity (l/min) at 0°C, 1 atm	$y \times 10^3$ (mole-fraction)	$G \times 10^2$ * (gr/cm <sup>2</sup> sec)	$k_y \times 10^4$ (gmole/cm <sup>2</sup> -sec)
2-11	18.26	3.66	6.46	2.49
2- 9	13.89	3.71	4.92	1.94
2- 8	10.65	3.26	3.77	1.62
2-10	6.21	5.53	2.20	1.26
2- 5	3.89	7.75	1.38	1.44
2- 4	3.84	7.48	1.37	1.30
2- 7	2.89	7.45	1.03	0.88
2-12	2.14	9.57	0.76	1.13
2- 6	1.56	8.81	0.56	0.61
2- 3	1.12	9.21	0.40	0.44

Run No.	Re*	$J_d$ *	Sh*	$Gr \times 10^{-6}$ *	Sh Sc <sup>-1/3</sup> *	ScGr $\times 10^{-7}$ *
2-11	28.24	0.84	52.91	1.195	23.78	1.315
2- 9	21.42	0.86	41.04	1.182	18.45	1.301
2- 8	14.51	0.94	30.40	0.831	13.66	0.916
2-10	10.40	1.25	28.18	1.393	12.96	1.531
2- 5	6.32	2.88	31.94	1.142	14.38	1.252
2- 4	6.33	2.08	29.18	1.210	13.14	1.327
2- 7	5.02	1.86	20.79	1.411	9.36	1.548
2-12	3.60	3.24	25.92	1.162	11.67	1.272
2- 6	2.79	2.40	14.88	1.446	6.70	1.585
2- 3	2.11	2.38	11.18	1.652	5.03	1.810

\* See footnote for Table III.

## LIST OF FIGURES

- Figure 1 Reduced density-reduced pressure diagram for carbon dioxide at various reduced temperatures ( $T_r$ ) in the vicinity of the critical point (Paulaitis et al., 1983).
- Figure 2 Binary diffusivity of  $\text{CO}_2$ -Naphthalene system (Iomtev and Tsekhanskaya, 1964).
- Figure 3 Viscosity of carbon dioxide (Stephen and Lucas, 1979).
- Figure 4 Schematic diagram of the experimental apparatus.
- Figure 5 Relationship between axial Peclet number ( $P_{e,a}$ ) and Reynolds number ( $Re$ ) (Sherwood et al., 1975).
- Figure 6 Correlation between  $Sh$  and  $ScGr$  at  $35^\circ\text{C}$ .
- Figure 7 Correlation for natural and forced convection.
- Figure 8 Comparison of mass transfer correlations under supercritical (100-200 atm,  $35^\circ\text{C}$ ) and subcritical (1 atm,  $25^\circ\text{C}$ ) conditions.
- Figure 9 Comparison between supercritical mass transfer coefficients (100-200 atm,  $35^\circ\text{C}$ ) and subcritical mass transfer coefficients (1 atm,  $25^\circ\text{C}$ ).

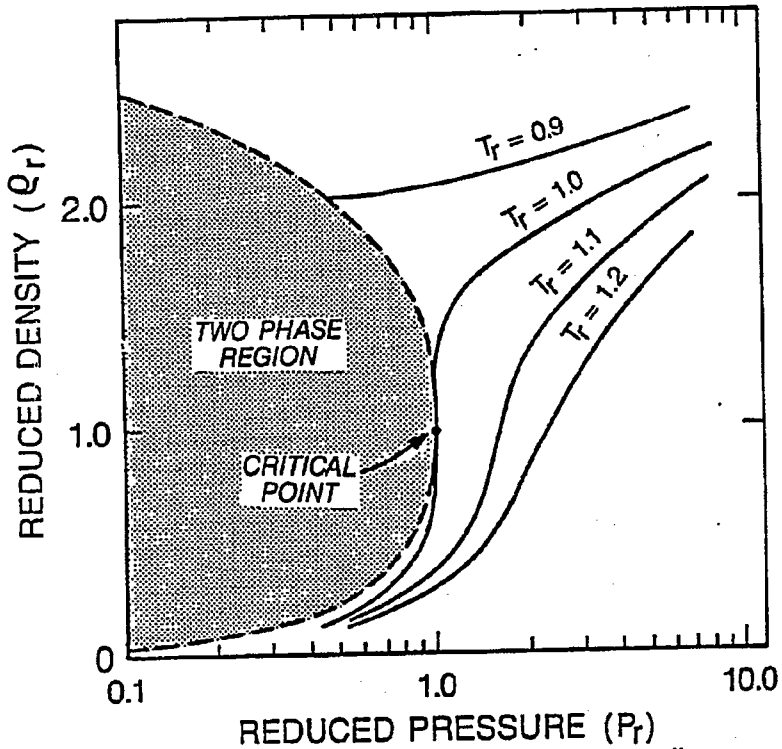


Figure 1. Reduced density-reduced pressure diagram for carbon-dioxide at various reduced temperatures ( $T_r$ ) in the vicinity of the critical point (Paulaitis et al., 1983).

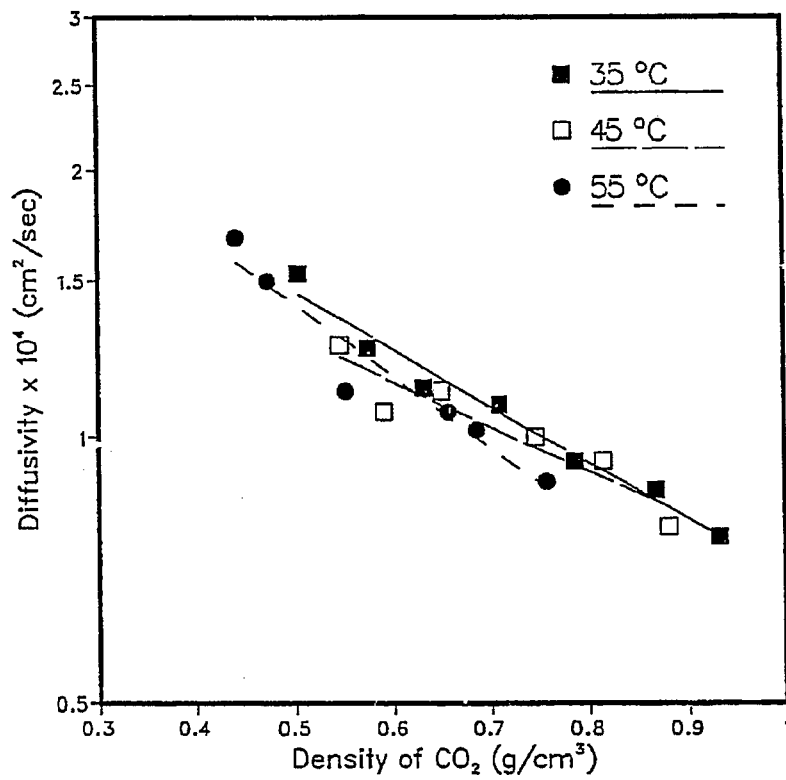


Figure 2. Binary diffusivity in CO<sub>2</sub> - Naphthalene system (Iomtev and Tsekhanskaya, 1964).

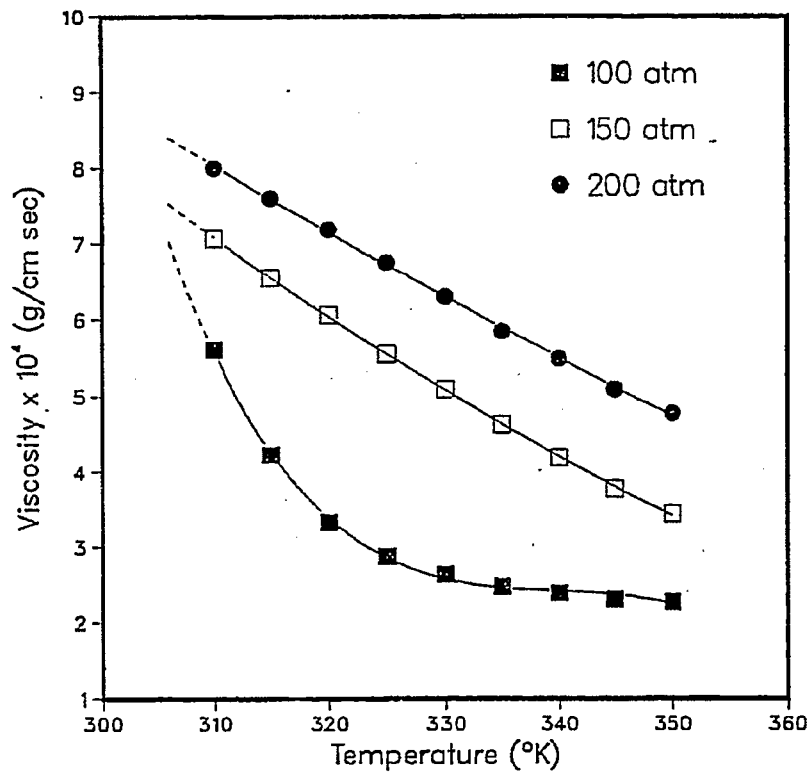
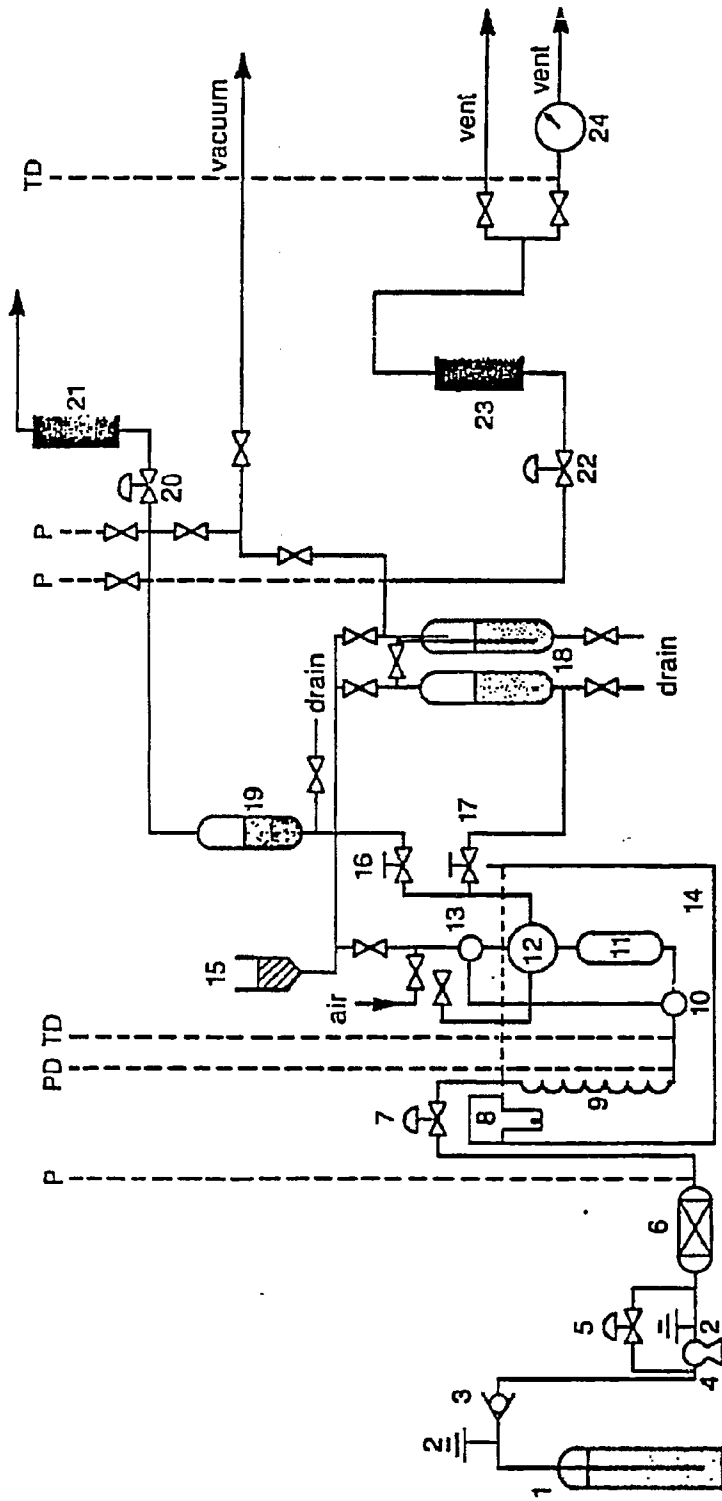


Figure 3. Viscosity of carbon dioxide (Stephan and Lucas, 1979).



- |                                    |                     |                             |
|------------------------------------|---------------------|-----------------------------|
| 1. Liquid CO <sub>2</sub> cylinder | 9. Preheater        | 17. Metering valve          |
| 2. Relief valve                    | 10. Three-way valve | 18. Sample tanks            |
| 3. Check valve                     | 11. Extractor       | 19. Solid trap              |
| 4. Liquid pump                     | 12. Four-way valve  | 20. Back pressure regulator |
| 5. Back pressure regulator         | 13. Three-way valve | 21. Rotameter               |
| 6. Surge Tank                      | 14. Water bath      | 22. Back pressure regulator |
| 7. Pressure gauge                  | 15. Solvent tank    | 23. Rotameter               |
| 8. Temperature controller          | 16. Metering valve  | 24. Wet test meter          |

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

Figure 4. Schematic diagram of the experimental apparatus.



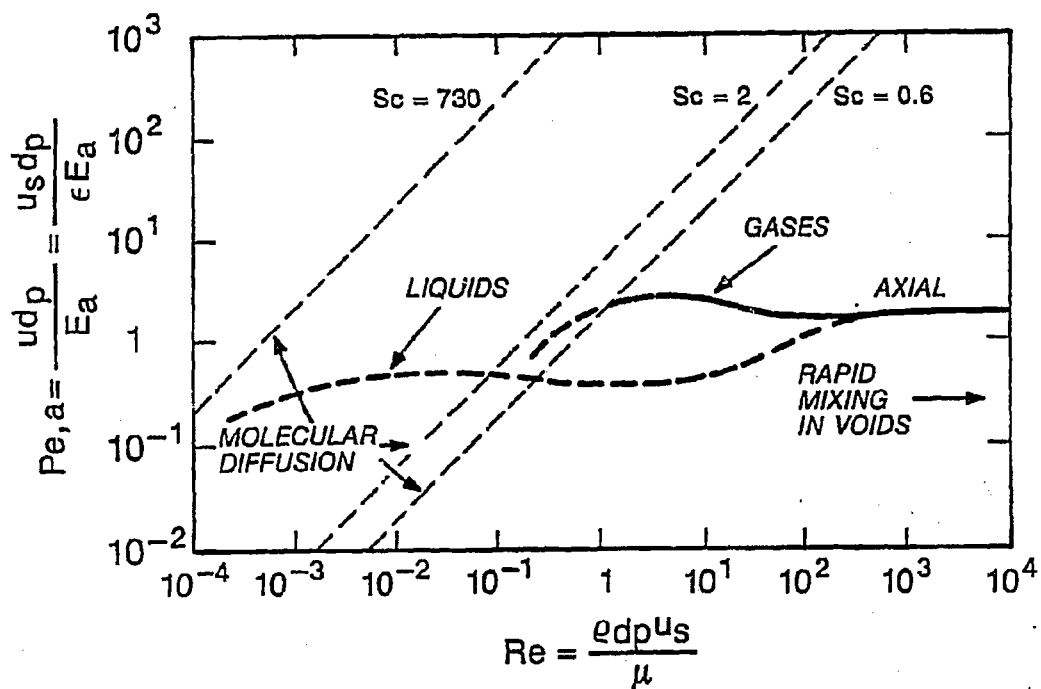


Figure 5. Relationship between axial Peclet number ( $Pe,a$ ) and Reynolds number ( $Re$ ) (Sherwood et al., 1975).

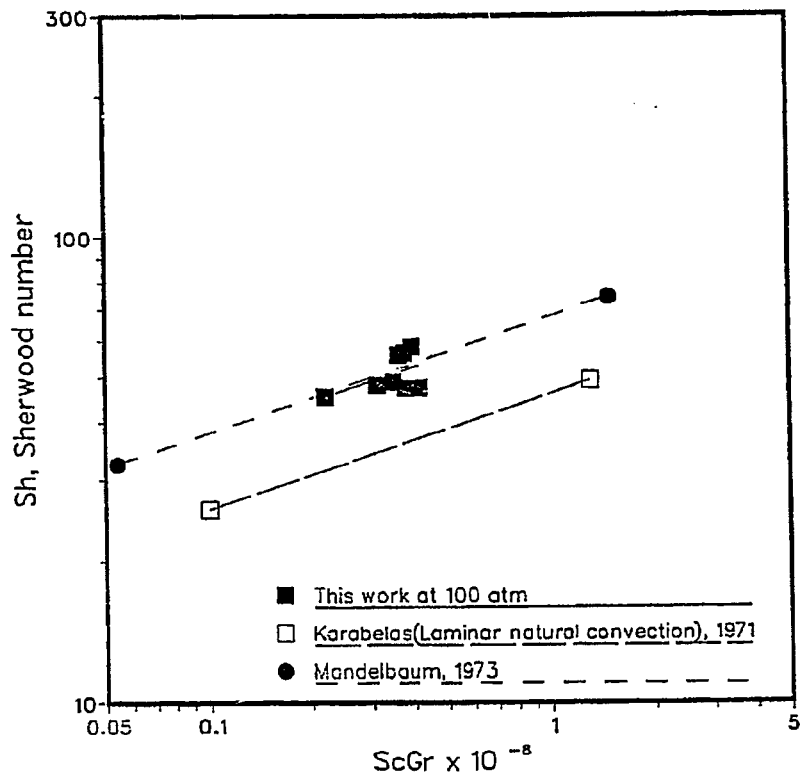


Figure 6. Correlation between Sh and ScGr at 35 °C.

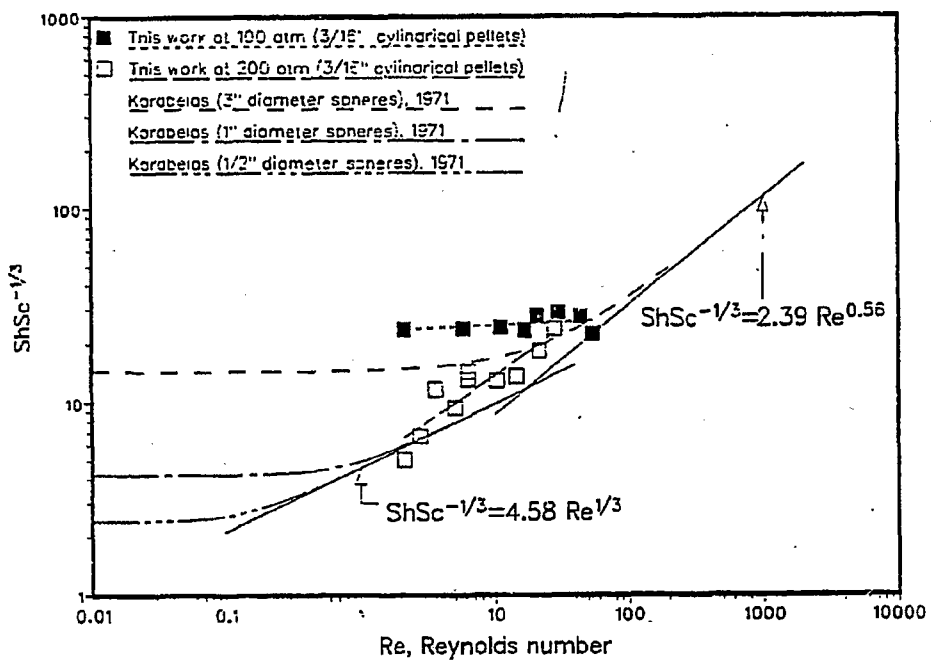


Figure 7. Correlation for natural and forced convection.

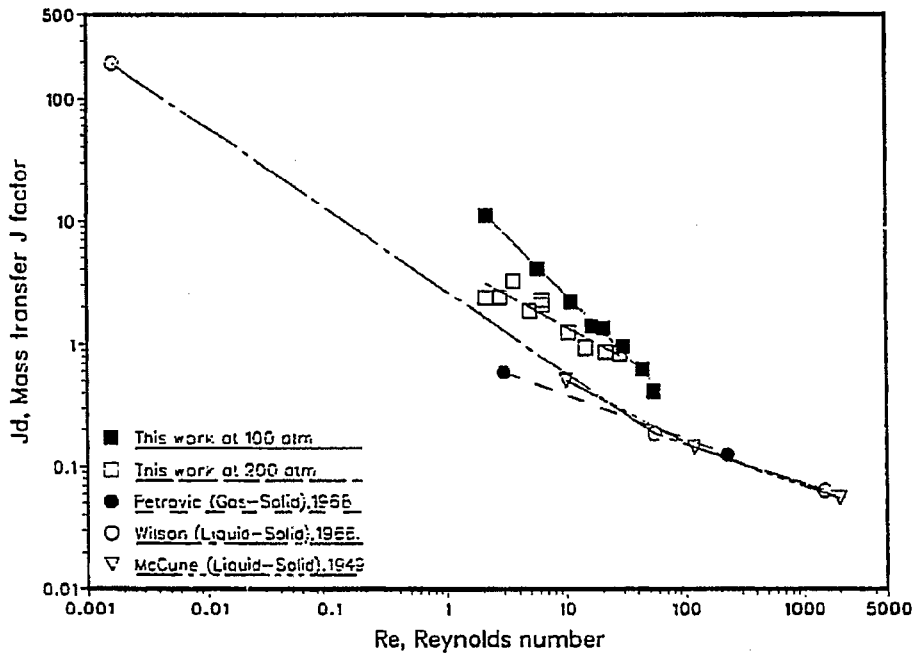


Figure 8. Comparison of mass transfer correlations under supercritical (100 - 200 atm, 35 °C) and subcritical (1 atm, 25 °C) conditions.

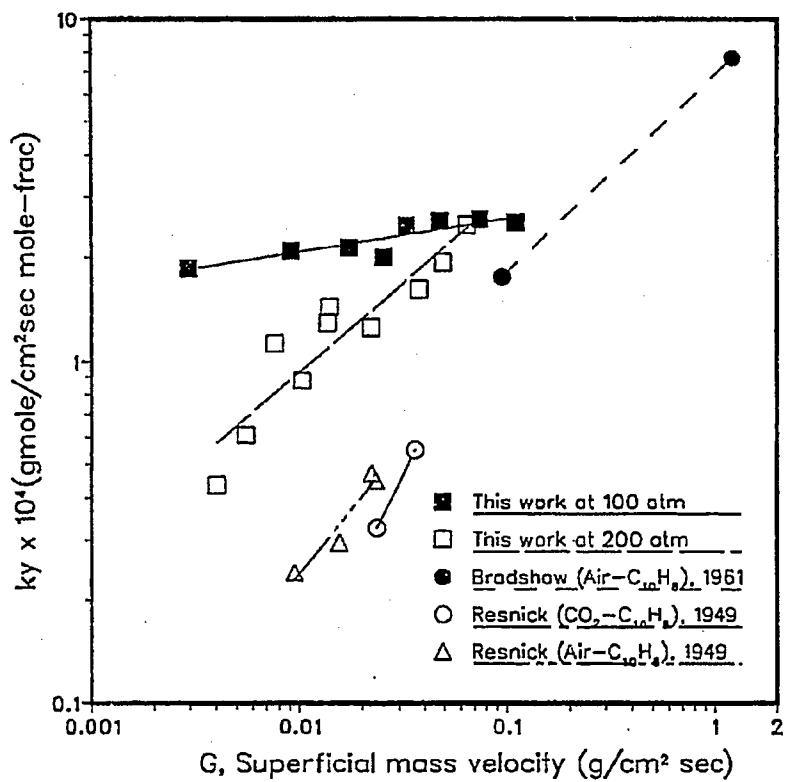


Figure 9. Comparison between supercritical mass transfer coefficients (100 - 200 atm, 35 °C) and subcritical mass transfer coefficients (1 atm, 25 °C).

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