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**THE SUPERCRITICAL FLUIDS
FOR REACTION AND EXTRACTION
OF COAL AND HEAVY OILS**

**Second Quarterly Progress Report
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by

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Background

A program for the study of supercritical extraction of coal and coal liquids is being carried out. The purpose of this study is aimed at developing a fundamental understanding of supercritical extraction with emphasis on extraction of coal liquids with supercritical water and deashing of coal liquids, SRC-bottoms and possibly shale oils. The study will focus on the use of supercritical extraction techniques for extraction and fractionation of heavy residues which are often mixed with mineral matter and other non-volatile matter. The study will also include the supercritical extraction of model compounds and their mixtures. An outline of the proposed investigation is available in the proposal. During the period September 1, 1981 to November 30, 1981, an experimental procedure was formulated to study the supercritical extraction process. The details of the experimental set-up, procedure and apparatus have been given in the first quarterly progress report (1) submitted in December 1981. The required equipment and accessories requisitioned during the above period are also listed in the above mentioned report (1). This report briefly describes the progress made during the period December 1, 1981 to February 28, 1982.

Progress

1. An experimental apparatus and procedure have been designed and ordered. A schematic diagram of the experimental set-up is shown in Figure 1. A special custom-made Autoclave reactor has been designed. The reactor is a 1 liter Magnedrive II agitated autoclave rated at 35 MPa and 720 K and provided with ports for inlet and outlet for the process

components, temperature and pressure measurement and cooling water connections. The reactor will be provided with a multiple zone electric furnace for heating the reactor to operating conditions. The top of the reactor (flange), and sampling tubes will be provided with heating elements so as to maintain a constant temperature throughout the reactor and sampling line assembly. This is important as the supercritical extraction process is sensitive to changes in the operating conditions and a drop in the temperature could cause precipitation of the extracted products.

The major equipment such as, the autoclave reactor, solvent pump, data logger, furnace, pressure transducer, temperature measuring and controlling units and accessories such as valves and fittings, heating tapes, etc., have been received. Installation of the reactor, solvent pump and assembly (as described in the experimental set-up in Figure 1) is now underway.

2. It has also been planned to install another experimental unit, for which, the equipment is available at no cost, in order to study the extraction process with model compounds and their mixtures. Some of the model compounds which will be used in this study are listed in the proposal submitted for this program.

The experiments will be carried out in a 300 ml stirred autoclave reactor rated at pressures up to 37 MPa and temperatures up to 617 K. The experimental procedure consists of treating the model compound or a mixture of model compounds with the supercritical solvent. The extracted solvent containing the solute will be analyzed by gas chromatographic techniques. The equipment for this phase of study is expected to be available by May 1982.

The results obtained in this study will be used in developing models to predict the solubility of the solutes and their mixtures in various solvents under supercritical conditions of operation.

3. Attempts are being made at developing a model to predict the solubility of various solutes in solvents under supercritical conditions.

Considering the supercritical fluid as an expanded liquid, Mackay and Paulaitis (2) have developed an expression for the solubility of a solid solute in a supercritical solvent as:

$$y_2 = \frac{f_2^S(P_c) \exp(v_2^C(P - P_c)/RT)}{r_2^\infty(P_c) f_2^L(P_c) \exp \int_{P_c}^P (v_2^\infty/RT) dP} \quad (1)$$

where, y_2 is the mole fraction of solute in the fluid phase,

v_2^C is the molar volume of solid solute,

P_c is the critical pressure of the solvent, serving as the reference state,

P and T are the operating pressure and temperature, respectively,

$f_2^{S,L}(P_c)$ are the fugacity values of the pure solute in the solid and fluid phases, respectively, at reference pressure P_c and their ratio is given by

$$\ln f_2^S(P_c)/f_2^L(P_c) = \frac{\Delta h_2^{\text{fus}}}{R} \left(\frac{1}{T_{m2}} - \frac{1}{T} \right) \quad (2)$$

where, T_{m2} is the normal melting temperature of the solute, and Δh_2^{fus} is the heat of fusion at this temperature.

The value of the partial molar volume at infinite dilution, v_2^∞ , was calculated by using the Redlich-Kwong (RK) equation of state. The values of the activity coefficient at infinite dilution, r_2^∞ , and the binary interaction parameter were obtained by fitting experimental data to the above expression.

In this study, the concept of the supercritical fluid phase considered as an expanded liquid is being used to estimate the solubility of a solid solute, using the Peng-Robinson (PR) equation of state (3), to calculate the partial molar volume at infinite dilution. Figures 2 and 3 show the solubility of Naphthalene in supercritical carbon dioxide as a function of pressure at 308 and 328 K, respectively. The values of r_2^∞ used in this study are the same as those given by Mackay and Paulaitis (2). The solubility calculations were carried out for four values of the binary interaction parameter as shown in Figures 2 and 3.

The predicted results are compared with experimental data of McHugh and Paulaitis (4), at the same temperature levels. Mackay and Paulaitis (2) have reported a value of 0.08 for $k_{1,2}$ using the RK equation, while Modell et al. (5) have suggested a value equal to 0.11 using the PR equation (supercritical phase considered as a compressed gas). In this study, the values of r_2^∞ and the binary interaction parameters will be determined by fitting the experimental data to Equation (1) to obtain the best fit values.

Plan for the Period March 1, 1982 to May 31, 1982:

The installation of the experimental apparatus for the coal-water system is expected to be completed by the third quarter of this program and some exploratory experiments will be conducted to determine the important variables, whose effects will be studied in detail. Plans will also be made in the third quarter to install an experimental unit to study the supercritical extraction of model systems, as described in section 2 of this report.

Work is continuing in developing models to predict the solubility of solutes in supercritical solvents. Attempts will be made to apply these models to multicomponent systems consisting of model compounds representative of coal and heavy oils.

References:

1. First Quarterly Report No. DOE/PC/4080-1, "The Supercritical Fluids for Reaction and Extraction of Coal and Heavy Oils", December 1981.
2. Mackay, M. E. and Paulaitis, M. E., "Solid Solubilities of Heavy Hydrocarbons in Supercritical Solvents", I&EC, Fundamentals, 18, 1979, 149.
3. Peng, D. Y. and Robinson, D. B., "A New Two-Constant Equation of State", I&EC, Fundamentals, 15, 1976, 59.
4. McHugh, M. and Paulaitis, M. E., "Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide", J. Chem. & Eng. Data, 25, 1980, 326.
5. Modell, M., Hong, G. and Haiba, A., "The Use of the Peng-Robinson Equation in Determining Supercritical Behaviour", paper presented at the Industrial Liaison Program Seminar on "Supercritical Fluids - Recent Applications", Mass. Inst. of Tech., December, 1980.

List of Figures:

1. Schematic Diagram of Experimental Set-Up.
2. Effect of Pressure on Mole Fraction of Naphthalene in CO₂
(T = 308 K).
3. Effect of Pressure on Mole Fraction of Naphthalene in CO₂
(T = 328 K).

EXPERIMENTAL APPARATUS

Figure 1:

Figure 2: Effect of Pressure on Mole Fraction of Naphthalene in Supercritical Carbon Dioxide (T=308 K).

Figure 3: Effect of Pressure on Mole Fraction of Naphthalene in Supercritical Carbon Dioxide (T=328 K).