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

First Quarterly Progress Report
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by

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DISCLAIMER

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. This report briefly describes the progress made during the period September 1, 1981 to December 1, 1981.

Progress

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 500 psi and 450^{o}C 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 construction of the reactor is expected to be completed by the beginning of March 1982. The following equipment and accessories have been requisitioned:

1. Pressure transducers
2. Digistrip data logger (temperatures & pressures) and accessories
3. Furnace
4. Pump to handle supercritical solvents
5. Heating tapes
6. Valves and fittings
7. Temperature measuring and controlling units

Equipment and accessories not already received are expected to be delivered by February, 1982.

Process Flow System

The process flow system can be visualized by various subsystems as are described briefly below:

1. Solvent pumping section:

The solvent will be pumped into the reactor through a pump rated at a maximum discharge pressure of 7500 psig and maximum capacity of 1.1 gph. The pump will be capable of handling gases such as CO_2, SO_2, C_2H_4, etc. in a liquified state and liquids such as H_2O, C_7H_8, THF, etc.

2. Solids charging unit:

The powdered solids will be charged into the reactor by flushing the solids in the unit with the high pressure solvent when the reactor attains the desired operating conditions.

3. Reactor unit:

The reactor is a 1 liter autoclave as described above, provided with an electric furnace and heating elements on the top flange to maintain a constant temperature throughout the system. The reactor is also provided with a drain valve at the bottom for convenient draining of reacted contents and cleaning purposes.

4. Measuring and controlling unit:

The transient temperature and pressure during the course of an experiment will be recorded on a multi-channel digistrip data logger. The temperature of the reactor and sampling line assembly wil be controlled individually to provide uniform temperature throughout the system.

5. Sampling and analysis:

This section consists of the sampling tube followed by an ice bath and a reservoir for collecting the noncondensible gases. The products will be analyzed using suitable gas chromatographic techniques.

Basically, two types of systems will be investigated:

(1) Coal-water (reaction) sytstem: This system consists of treating coal, bottoms and heavy residues with supercritical water. It is known that supercritical water can convert substances containing

cellulose and lignin to liquids and synthesis gas at supercritical conditions. This concept will be extended to treating coal and heavy residues to investigate the possibilities of coal conversion and coal deashing processes. These will be the experiments carried out first.

(2) Non reaction system: This system consists of treating model compounds such as naphthalene, anthracene, etc. and their mixtures with various supercritical solvents.

Models are to be developed based on the experimental studies, to describe both the systems mentioned above. This phase work will commence in January.

Planned Experimental Procedure for the Coal-Water (Reaction) System

The apparatus in a schematic way is given in Figure 1. A standard 1-liter, 316 Stainless Steel Autoclave Engineers magnetically stirred autoclave will be used as the reactor. A thermocoupole type K, located in the thermowell fitted on the head of the autoclave will be used to monitor the reactor temperature. A pressure transducer will monitor the reactor pressure. The transient temperatures and pressures during an experimental run will be recorded in a Digistrip-II Data Logger. The reactor and the sampling loop will be independently controlled at the desired temperature. A typical run will consist of half an hour duration.

The autoclave will be charged with 300 cm^3 distilled water and the reactor will be leak-tested with helium at 60 atm. The reactor will then be heated to 150°C and vented to remove residual helium and air. Less than 1 cm^3 of water will be purged during the venting. The reactor will

then be heated to about 10°C above the desired operating temperature. The organic feed, maintained in a reservoir between valves (1) and (2) will be then flushed into the reactor with water.

The autoclave will be operated above the critical conditions of water and enough water will be added so that the total water in the reactor is 310 cm^3. Thus the contents will be brought to the critical density of water (0.31 g/cm^3). As the addition of cold feed tends to cool the reactor contents, the reactor is heated above the desired operating temperature, prior to feed addition so as to ensure that the temperature did not drop significantly below the critical during the feed addition.

At the conclusion of a run, a sample of the reactor contents was obtained by cracking valves (3) and (4). The sample passes through the sample loop to a liquid trap immersed in an ice-bath. Non-condensable gases will be collected in a gas reservoir downstream of the liquid trap. The reactor will be quenched by passing water through the internal cooling coils. The reactor will be inspected for the formation of char or tar.

The gas sample wil be immediately analyzed for H_2, CO, CH_4, CO_2, and C_2 + (i.e. C_2H_4 and C_2H_6) using Hewlett-Packard Gas Chromatograph fitted with a 3.6 m, 0.23 cm ID Porapak Q (80/100 mesh) column. The sample size will be about 0.10 to 0.25 cm^3. A known calibration gas mixture will be used to determine reponse factors for the thermal conductivity detector.

The liquid samples will be extracted with methylene chloride, concentrated by mild evaporation of the solvent, and analyzed on a Hewlett-Packard Gas Chromatograph fitted with a 1-m, 0.23 cm ID OV-17 column with a flame ionization detector. The temperature will be programmed from 70°C to 250°C at 8°C/min. Attempts to analyze selected liquid samples by

GC/MS in an attempt to identify some of the liquid components will be made.

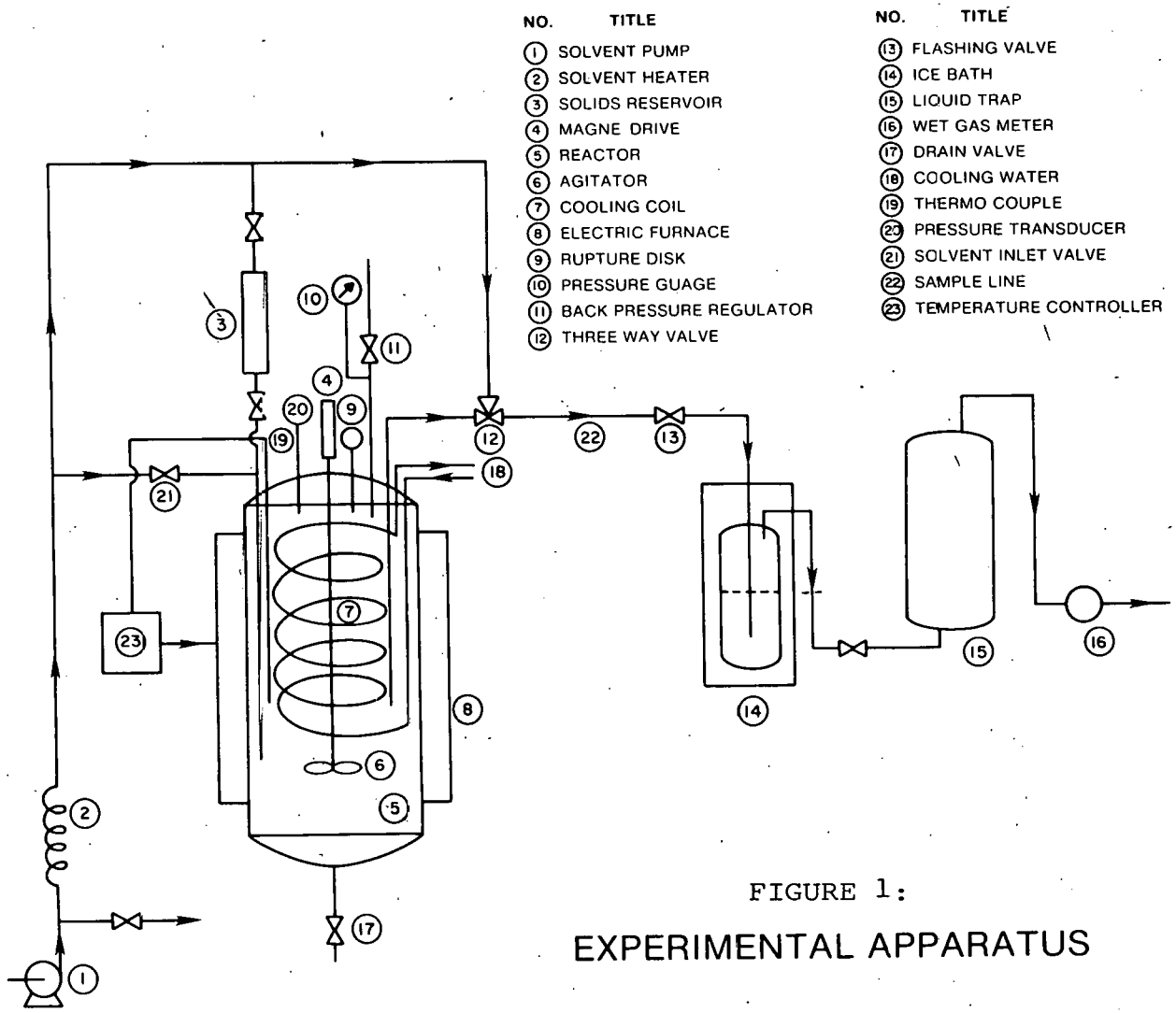

FIGURE 1:

EXPERIMENTAL APPARATUS