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**Separation of Fischer-Tropsch Wax from Catalyst
Using Supercritical Fluid Extraction**

Quarterly Technical Progress Report
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Executive Summary

Programming and testing of the highly complex Statistical Associating Fluid Theory (or SAFT) equation of state (Tasks 2a and 2b) is essentially complete. As an accuracy check, results from our program were compared and found to be in excellent agreement with those of two other research groups (one in the US and two in Europe) for both a nonassociating (methane-hexadecane) and an associating (carbon dioxide-methanol) system. This equation is being used to model the solubility of Fischer-Tropsch compounds in supercritical solvents such as hexane. SAFT has been chosen for this work because of its fundamental rigor. Therefore, extension of our model compound results to the poorly defined Fischer-Tropsch waxes should be more successful compared to more empirical equations such as Peng-Robinson.

Computer-controlled automation of one of our dynamic supercritical fluid (SCF) extraction apparatus (Task 1a) is complete. The apparatus collects samples automatically, dramatically reducing operator manpower and fatigue, and is also capable of controlling the operating pressure more precisely (i.e., within ± 2 psi). This apparatus (SFE I) will be used for future experiments with actual Fischer-Tropsch waxes.

Modification/construction of another apparatus (SCF II) that will be used for our model component-SCF phase equilibria/solubility studies (Task 1b) is nearly complete; it is currently being leak-tested. This apparatus was built to handle the low mass flow rates that will be required when measuring solubility data for the more expensive model compounds, such as n-C₄₀. Anticipated results for the next quarter include VLE measurements for hexane-squalane at temperatures to 573 K.

Technical Objectives

The objective of this research project is to evaluate the potential of SCF extraction for separating the catalyst slurry of a Fischer-Tropsch (F-T) slurry bubble column (SBC) reactor into two fractions: (1) a catalyst-free wax containing less than 10 ppm particulate matter and (2) a concentrated catalyst slurry that is ready for recycle or regeneration. The wax will be extracted with a hydrocarbon solvent that has a critical temperature near the operating temperature of the SBC reactor, i.e., 473-573 K. The success of the project depends on two major factors. First, the supercritical solvent must be able to dissolve the F-T wax product; furthermore, this must be accomplished without entraining the solid catalyst. Second, the extraction must be controlled so as not to favor the removal of the low molecular weight wax compounds, i.e., a constant carbon-number distribution of the alkanes in the wax slurry must be maintained at steady-state column operation.

To implement our objectives, the following task structure is being implemented:

Task 1: Equilibrium Solubility Measurements

- a. apparatus modification and construction
- b. experimental measurement of selected model systems
- c. catalyst/wax separation studies

Task 2: Thermodynamic Modeling

- a. programming and testing of SAFT equation for nonassociating systems
- b. programming and testing of SAFT equation for associating systems
- c. modeling measured results with the SAFT equation
- d. pure component and mixture SAFT parameter determination for selected model systems

Task 3: Process Design Studies

- a. installation of our SAFT program into process simulation package
- b. process configuration studies using above simulation package

Detailed Description of Technical Progress

Task1a. Apparatus Modification and Construction. For the Jan-Mar 95 reporting period, we described our initial efforts towards automating one of our two SCF extraction apparatus (SCF I). This apparatus will be used for future catalyst/wax studies. Subsequent additional work was directed towards providing simultaneous control of both the system pressure (through top-phase valve adjustment) and the interface level in the equilibrium cell (through bottom-phase valve adjustment). Both hardware (i.e., improved stepping motors for controlling the valves) and software (rewriting the process control programs) modifications were made. As shown in Figure 1, both pressure and interface control (the voltage level is proportional to the interface level) for the test system of petroleum pitch and toluene are excellent compared to what can be done manually for a

system in the region of liquid-liquid equilibria (LLE). For the VLE measurements that will be required for our Fischer-Tropsch wax/SCF solvent systems, pressure control with SCF I is predicted to be better than ± 2 psi.

Because SCF I is designed for systems in which relatively large quantities of the feed material are inexpensive and readily available, one of our other SCF apparatus (designated SCF II) is being modified to handle the low mass flow rates required when working with expensive model compounds. For example, many of the C₂₀+ compounds cost over \$1000/kg.

SCF II has been modified so that both liquid and solid F-T model components can be handled without any difficulty. A simplified schematic of the apparatus is shown in Figure 2. For solid F-T compounds (such as eicosane or triacontane), an indirect pumping method is necessary. The feed reservoir now consists of a high-pressure cylinder that contains a piston with an O-ring seal. For a typical experiment, the cylinder is first filled with the solid solute of interest and is then heated (under nitrogen blanket) such that the contents are melted into a liquid at constant temperature. A working fluid (typically the same fluid as the solvent to prevent possible system contamination) is pumped to the bottom of the piston using a Milton Roy LDC pump or an Isco Electronic Syringe pump, causing the liquefied F-T solute to flow into the equilibrium cell at a constant flow rate. Previous work has shown that this setup yields excellent results. If the solute is a liquid (e.g., squalane), it can be pumped directly with one of the previously mentioned pumps. The solvent that is to be heated to supercritical conditions, e.g., hexane, is pumped as a liquid at ambient temperature using a separate Milton Roy pump.

Following the feed section, the solvent and F-T solute are brought into the isothermal nitrogen bath, heated to the desired supercritical operating temperature, and then mixed together in a specially designed mixing tee following by a long mixing coil. An in-line thermocouple has been installed to ensure that this two-phase mixture is within 1 K of the cell temperature. After separating in the view cell, the phases are reduced in pressure through micrometering valves and collected. By adjusting the top- and bottom-phase micrometering valves, the system pressure and interface level are controlled. Because the solvent is of low volatility, samples must be cooled to prevent losses.

Safety was a major emphasis in the design of the apparatus. In order to prevent the possibility of explosion (in case of leaks, for example), the isothermal bath is kept under a constant nitrogen purge. The oxygen content in the oven is kept under 2 mol % (well below the lower explosion limit for the compounds we are investigating) and is monitored by gas chromatography (GC).

Task 1b. Experimental Measurement of Related Model Systems.

Sample Analysis. Our first VLE measurements, which will begin next quarter, will be for the model system hexane-squalane; temperatures to 573 K and pressures up to the mixture critical pressure will be investigated. Gas chromatography (GC) with FID detector has been selected for analysis of the samples to be collected. Preliminary

experiments indicate that tetracosane is a good choice as the internal standard for the squalane; for experiments in which a known sample was analyzed for composition by our method, the deviation between the actual and calculated compositions was less than 1%. Because we know from previous work that the apparatus itself typically produces samples that are more reproducible than the GC, we are confident that excellent results will be obtained.

Task 1c. No effort planned for this quarter.

Tasks 2a and 2b. Programming and Testing of SAFT Equation for Nonassociating and Associating Systems. Although we thought that we had finished this task during the past reporting period, discrepancies among SAFT results from research groups at Karlsruhe, Hamburg-Harburg (both in Germany), Rice (Texas) and our results reappeared this past summer. Although the error was not found in our version of SAFT, several weeks passed by until we were definitely able to determine wherein the problem lay. We have now reconfirmed that both our nonassociating and associating versions are correct. Future work will be concerned with the determination of the pure component SAFT parameters for F-T solutes (Task 2d).

Tasks 2c and 2d. No effort planned for this quarter.

Task 3. No effort planned for this quarter.

Plans for Next Quarter

Work next quarter will first involve getting the new apparatus into fully functioning condition. Some leaks still exist and need to be eliminated before continuing. As soon as the system is operational, phase equilibrium experiments with the binary mixture of squalane and hexane will begin.

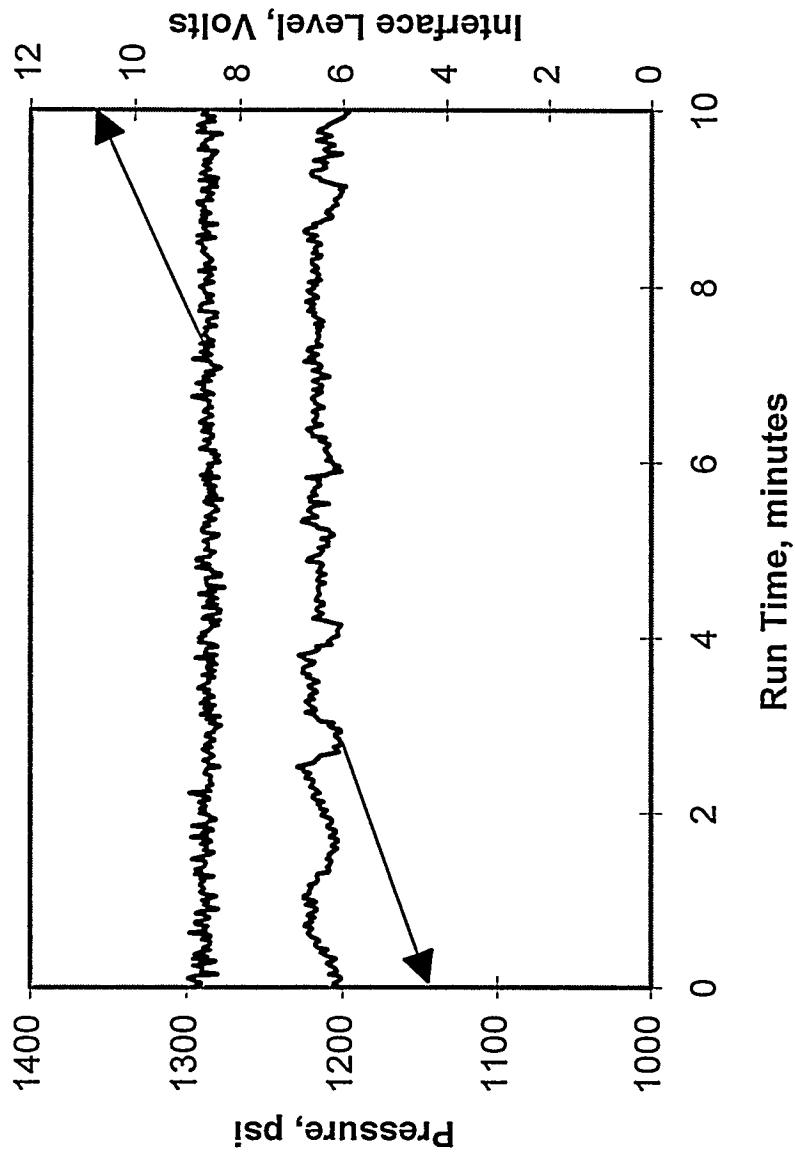


Figure 1. Typical operation of the SCF I apparatus during LLE sample collection. The automated pressure and interface level control is shown.

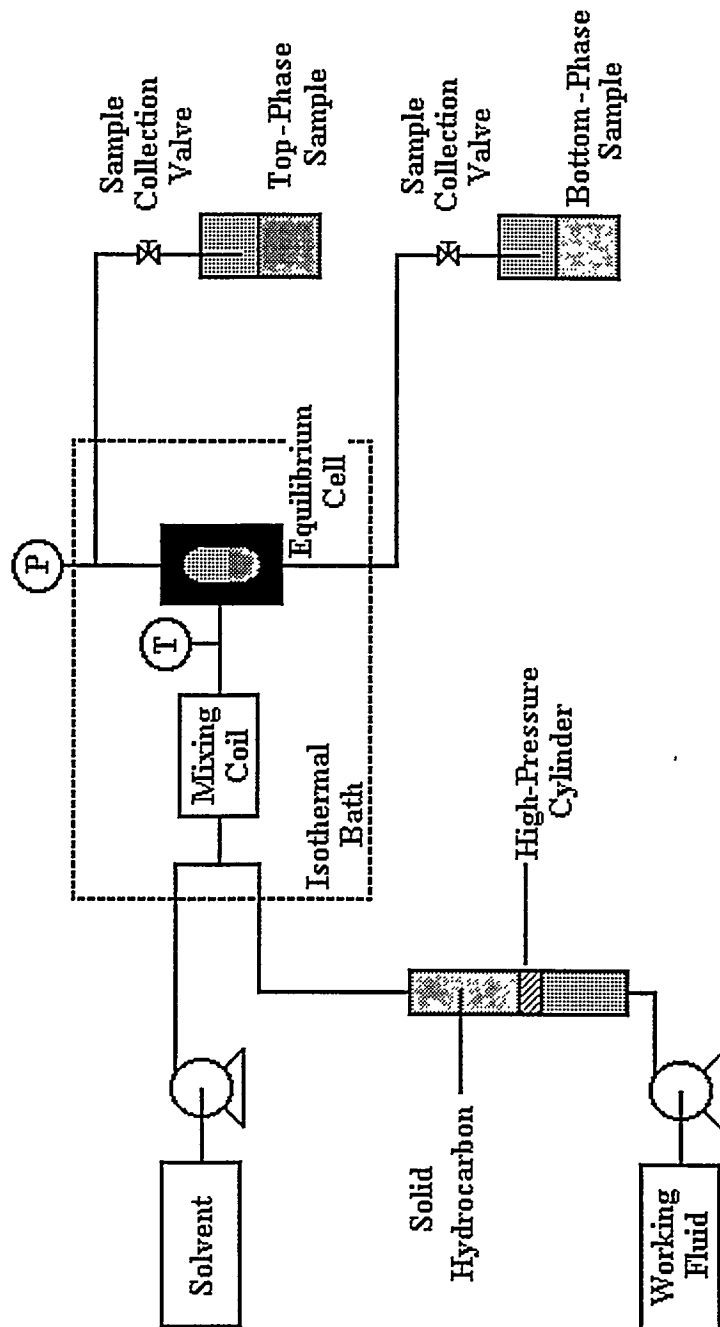


Figure 2. Simplified schematic of the SCF II apparatus.