

SEPARATION OF FISCHER-TROPSCH WAX FROM CATALYST
BY SUPERCRITICAL FLUID EXTRACTION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Mark C. Thies, Principal Investigator
Clemson University
Dept. of Chemical Engineering
Clemson, SC 29634-0909

Technical Progress Report
Jan-Mar 1995 Reporting Period

US DOE PATENT CLEARANCE NOT REQUIRED
PRIOR TO PUBLICATION OF THIS REPORT.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *DLc*

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SEPARATION OF FISCHER-TROPSCH WAX FROM CATALYST BY SUPERCRITICAL FLUID EXTRACTION

The objective of this research project is to evaluate the potential of supercritical fluid (SCF) extraction for separating the catalyst slurry of a Fischer-Tropsch (F-T) slurry bubble column reactor into two fractions: (1) a catalyst-free wax containing <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 F-T reactor, i.e., 473-573 K. The success of the proposed separation technique depends on the ability of the supercritical solvent to (1) dissolve the F-T wax product without entrainment of the solid catalyst and (2) maintain a constant carbon-number distribution of the alkanes in the wax slurry at steady state.

During the previous reporting period, our efforts focused on two different tasks: modification of the experimental apparatus, and programming and testing of the SAFT equation.

Modification of Experimental Apparatus. The basic scientific measurements that will dictate whether or not our proposed process is feasible are the equilibrium solubilities of wax solutes in candidate supercritical solvents, both as binary and multicomponent mixtures. Although the actual separation process may not operate at equilibrium, it is the equilibrium state that will dictate the potential process performance.

A continuous-flow apparatus especially designed for elevated temperature and pressure operation and with visual capability will be used for equilibrium-solubility measurements. Although the apparatus in its current state can be used to obtain accurate phase-equilibrium data, measurements are tedious and labor-intensive. A process control scheme that automates many of the experimental tasks, including the collection of the top and bottom phases, is being designed and constructed. Although the control system has not yet been completed, it has been developed to the point where preliminary tests can be made.

The automated apparatus was recently evaluated by measuring the liquid-liquid phase equilibrium for the system supercritical toluene-petroleum pitch at 613K and 70 bar. Top- and bottom-phase micrometering valves were automatically opened and closed during sample collection over a three-hour period, as both the operating pressure and interface level were maintained at their desired setpoints. Stepping motors were used to control the micrometering valves, and an AC impedance bridge located within the view cell provided a voltage output to the control system that was proportional to the interface level in the cell. All input and output functions were controlled through an appropriately modified 486 PC. Samples of excellent reproducibility were obtained, and the system pressure never deviated by more than 15 psi. During earlier experiments in which only manual operation was used, pressure control had never been better than 50 psi! It should also be noted that accurate pressure control of a system containing two relatively incompressible fluids is a worst-case scenario. Many of our experiments will involve vapor-liquid equilibrium; thus, pressure control to within 1-2 psi of the setpoint is expected. Although further work is needed to complete the control system, this early test provides strong evidence that our ability to produce experimental phase-equilibrium data will be significantly enhanced.

Finally, a comment is in order regarding the test system that was used, petroleum pitch and toluene. Petroleum pitch was used instead of a F-T wax or model component for practical reasons: that was the system whose phase equilibria was being measured at the time the control equipment

was ready for testing. We typically use our apparatus to measure VLE or LLE for several different systems during a year. Switching from system to system is nontrivial, with thorough flushing of lines (and sometimes even their replacement) required. Thus, we typically will operate with a given system for one to two months at a time before switching. Again, it should be emphasized that petroleum pitch is much harder to work with than F-T waxes, so that our test was in many ways a valuable worst-case study.

SAFT equation. The Statistical Associating Fluid Theory, or SAFT equation will be used to fit both the VLE and LLE data that we measure for F-T wax-solvent systems. Recent evidence suggests that SAFT, as opposed to conventional cubic equations of state, is a more appropriate choice for our thermodynamic modeling work because it was developed specifically for poorly defined mixtures such as F-T waxes. Attempts to use the Peng-Robinson equation to correlate the liquid-liquid phase equilibrium for a multicomponent system consisting of supercritical toluene and a complex, poorly defined mixture of heavy hydrocarbons were spectacularly unsuccessful, as the presence of two liquid phases was not even predicted. In contrast, reasonable results have been obtained with the SAFT equation in terms of predicting both phase compositions and average molecular weight distributions.

These results bode well for our ability to model actual F-T wax-solvent systems after we have developed an appropriate database by measuring fluid phase equilibria for a limited number of binary and ternary model-wax/solvent mixtures.