Separation of Fischer-Tropsch Wax from Catalyst

Using Supercritical Fluid Extraction

Quarterly Technical Progress Report
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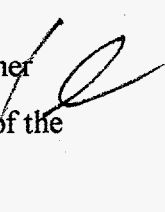
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Executive Summary

During the reporting period, work on the small-scale, continuous-flow apparatus (SCF II) continued. All system leaks have been located and eliminated. The differential thermocouple circuits that existed in the nitrogen bath were found to be faulty, possibly due to oxidation of the copper wires, and have been rebuilt. Initial experiments have been performed on a binary mixture of n-hexane (solvent) and squalane (model compound) at 200 °C, the lower temperature limit of a SBC reactor. A total of fifteen samples were collected at 135, 160, and 208 psig, with pressures being controlled to within ± 2 psi. Results indicate that the equilibrium phase compositions can in principle be measured to a reproducibility of ± 0.5% in the squalane-rich bottom phase and ± 2% in the hexane-rich top phase, with respect to the minor component. For example, a bottom-phase composition of 57.0±0.1 wt % squalane was measured at 160±2 psig and 200.50±0.10 °C for 3 consecutive samples. Similarly, the top phase was found to contain 0.0475±0.0005 wt % squalane in 3 samples collected at the same conditions. However, other data measured at these same conditions at another time exhibited scatter that was as much as 5 times greater. We believe that improvements in (1) the method of preheating the feed to the view cell/phase separator and to (2) the sample collection technique are required before data of high accuracy can consistently be generated. The apparatus modifications required to effect these improvements are currently underway and should be completed by the middle of February.

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., 200-300 °C. Initial work is being performed using n-hexane as the solvent. The success of the project depends on two major factors. First, the supercritical solvent must be able to dissolve the F-T wax; 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. integration of SAFT program into process simulation package
      b. process configuration studies

Detailed Description of Technical Progress

Task 1a. Apparatus Modification and Construction.

Work on the small-scale, continuous-flow apparatus (designated SCF II) continues. The system is now free of any leaks that may have existed. The differential thermocouple (DT) circuits that existed in the nitrogen bath were found to be faulty, possibly due to oxidation of the copper wires, and were rebuilt. Phase equilibrium experiments have been performed using the apparatus, but additional modifications will be required before highly accurate measurements can be obtained.

To improve accuracy, DT circuits are being used to measure the temperature in the cell. Conventional thermocouple measurement devices use electronic compensation, and errors of ± 2 °C are not uncommon. Previous work at Clemson indicates that by combining a DT circuit with a secondary RTD, accuracies of better than ± 0.1 °C can be obtained.

The DT circuit is arranged in the following manner. A measuring junction is inserted at the point where the temperature measurement is desired (either in the feed stream or in the cell), and the reference junction is inserted into an aluminum block, which serves as a constant-temperature environment. The temperature of the aluminum block is accurately measured to ± 0.05 °C with a secondary standard RTD. Because the DT circuit is only measuring a temperature difference of a few degrees at most, essentially no correction to the thermocouple reading is required. Thus, the temperature difference read by the DT circuit is simply added to the temperature of the block to obtain the actual feed or cell temperature. Three separate DT circuits have been set up in the nitrogen bath. One is connected to the feed line, and two are connected to the equilibrium cell (one in the top phase and one in the bottom phase).

Task 1b. Experimental Measurement of Selected Model System.

Experimental Runs. After completing the previously described work on the SCF II apparatus, experiments commenced on the first model system, a binary mixture of n-

hexane (solvent) and squalane (model compound). Initial experiments were performed at 200 °C, the lower temperature limit of a SBC reactor. A total of three runs were made, corresponding to the three different pressures that were investigated; during these runs, 15 samples were collected. The operating temperatures, pressures, and equilibrium phase compositions measured for each sample are shown in Table I. The reported temperatures are the average of those measured by the top- and bottom-phase thermocouples and were always within ± 0.2 °C of each other. However, problems still exist in the temperature-measurement scheme being used. On occasion, the temperature in the feed line was more than 2 °C higher then the temperatures in the cell. Previous work at Clemson has shown that the feed temperature should be within 1 °C of the cell temperature at worst. Pressure control was good; normally it was controlled to within ± 1 psi of the desired setpoint and was always within ± 2 psi.

Table I. Experimental Data for n-Hexane/Squalane Binary

Sample No.	Temperature (°C)	Pressure (psig)	x (mass % squalane)	y (mass % squalane)	Total Flow Rate (mL/h)
1	200.83 ± .08	208 ± 2	34.27	0.0416	151.0
2	200.83 ± .18	208 ± 2	35.33	0.0571	151.0
3	200.83 ± .23	208 ± 2	32.66	0.0295	151.0
4	200.81 ± .08	208 ± 2	32.79	0.0335	151.0
5	200.44 ± .08	135 ± 2	66.04	0.0513	121.5
6	200.41 ± .08	135 ± 2	66.21	0.0540	121.5
7	200.43 ± .13	135 ± 2	65.95	0.0555	121.5
8	200.44 ± .08	135 ± 2	66.88	0.0575	121.5
9	200.44 ± .08	135 ± 2	66.71	0.0594	121.5
10	200.49 ± .10	160 ± 2	57.25	0.0448	135.3
11	200.53 ± .05	160 ± 2	56.97	0.0503	135.3
12	200.50 ± .05	160 ± 2	57.09	0.0491	135.3
13	200.50 ± 0.0	160 ± 2	57.06	0.0478	135.3
14	200.51 ± .15	160 ± 2	56.85	0.0474	135.3
15	200.49 ± .08	160 ± 2	58.29	0.0471	135.3

As is evident from Table I, some variability in the reported phase compositions exists that cannot be explained solely on the basis of the observed temperature deviations. Problems during the early samples were probably at least partly due to not allowing

sufficient time to reach equilibrium. For example, in samples 1 and 2 only 15 minutes were allowed before beginning sample collection. In samples 3 and 4, results look better after more time had elapsed. Subsequent calculations of the system residence time indicate that approximately half an hour should be allowed for the system to reach equilibrium. Thus, for the run at 160 psig, this extra time was allotted. As seen in the Table, the data for samples 10 through 14 are more reproducible, especially in the bottom (liquid) phase. What happened in the liquid phase of sample 15 is unclear. For future runs, approximately one-half hour will be allowed for equilibration before sampling begins.

Sample Analysis. Analytical techniques for measuring top- and bottom-phase compositions have been developed. For the bottom phase, the method is as follows. First, approximately 0.1 g of the internal standard tetracosane is added to a tared vial. Next, the bottom phase sample is added. It is important to try and get a mass ratio between the squalane in the sample and the internal standard of between 0.5 - 2.0. In this range, the method is most accurate. The above mixture is then diluted with about 25 g of stabilized tetrahydrofuran (THF). Two samples are drawn off from this mixture, put into GC sampling vials, and analyzed. The analysis is performed using an HP 5890 GC equipped with a flame ionization detector. A .53 mm i.d. x 10 m long polydimethylsiloxane (1.2 μm film thickness) capillary column is used. Error analysis indicates that a given bottom-phase sample can be measured to an accuracy of ± 1% with this technique.

For the top phase, the method of analysis is slightly different. An internal standard solution of tetracosane and THF is made before analysis begins. The solution consists of approximately 0.02 g of tetracosane per 100 g of THF. A mass (~1 g) of the top-phase sample is added to a tared vial. Then the solution is added to the sample. Due to the low concentrations of squalane found in the vapor phase (see Table I), it is necessary to use this method. Although some of the highly volatile THF in the internal standard solution volatilizes, the amount of added solution (~1 g) is large enough to minimize its impact on sample accuracy. Error analysis indicates that a given top-phase sample can be measured to an accuracy of ± 3% with this technique.

Task 1c. Catalyst/Wax Separation Studies.

No effort planned for this quarter.

Task 2a and 2b. Programming and Testing SAFT for Nonassociating and Associating Systems.

No effort planned for this quarter.

Task 2c and 2d. Modeling VLE Data and Determining Pure Component/Mixture SAFT Parameters.

No effort planned for this quarter.

Task 3. Process Design Studies.

No effort planned for this quarter.

Plans for Next Quarter

Additional changes to the apparatus will be required before data of the desired accuracy can be obtained. Based on our previous work, temperature and pressure deviations of no more than ± 0.3 °C and ± 2 psi, respectively, can be achieved. More importantly, vapor- and liquid-phase compositions accurate to $\pm 3\%$ and $\pm 1 \%$ error, respectively, are possible. Areas for improvement include the preheating section and the method of sample collection for the top phase.

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