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Separation of Fischer-Tropsch Wax from Catalyst by Supercritical Extraction

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Executive Summary

One of the major objectives of this research project is to predict the phase behavior of model wax compounds in dense supercritical fluids such as hexane. Because initial results with the SAFT equation have been less promising than expected, the group at North Carolina State University has focused their recent attention on cubic equations of state, in particular the Peng-Robinson and Soave-Redlich-Kwong versions. The focus of this work has been on developing correlations that can be used to predict binary interaction parameters (i.e., k_{ij}s) for a given binary wax-solvent system. As a first step, k_{ij}s were first calculated from experimental data on systems containing alkanes between nC_4 and nC_{23} at temperatures between 25 and 357 °C. Attempts were then made to correlate these parameters with specific pure component properties of the alkanes of interest. Reasonably good agreement between experimental and predicted k_{ij}s was found using a correlation that incorporates both temperature and the molecular size of the alkanes. As phase equilibrium data becomes available for higher molecular weight model wax compounds, the ability of the correlation to handle such systems will need to be tested.

The phase equilibrium apparatus is currently undergoing modifications that will allow the system to run components that are solids at ambient temperatures. Some problems are still being resolved, as the heavy component tends to precipitate in the sample lines. Modifications have been made that should allow the system to operate reliably.

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

Detailed Description of Technical Progress

Task 1a. Apparatus Modification and Construction

Modification of the apparatus to allow the measurement of model wax compounds that are solids at ambient conditions has begun. Unfortunately, the model wax compound (in this case hexadecanol) being used has been precipitating in the sample lines. In order to deal with this problem, two changes have been made. The sample lines have been simplified. All of the valves and tees have been removed, leaving only straight lengths of stainless steel tubing that can be easily heated with heating tape. It is possible to wrap almost all of the tubing with heating tape, except for a short length of tubing that is inserted in the sample vial. This has been a major problem, because stainless steel is a poor conductor of heat. The poor conduction has caused the temperature at the end of the sample line to be too low to allow operation of the system. It is not safe to run the heating tape into the vial because it would put the heating elements in direct contact with a flammable liquid. Therefore, the sample line that runs into the vial has been changed to a soft copper tubing. Copper is an excellent conductor of heat, and the temperature at the end of the sample line can be kept above the melting point of the model wax compound. It is believed these changes will allow for operation of the phase equilibrium apparatus.

Task 1b. Experimental Measurements for n-Hexane/Hexadecanol System

Experiments on the n-hexane/hexadecanol binary have been delayed by the apparatus modifications. As soon as the problems involving precipitation have been corrected, experiments will begin.

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.

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

In order to model the separation and extraction of Fischer-Tropsch waxes with supercritical fluids, the phase behavior of solvent-wax systems must be accurately described. To accomplish this, the group at North Carolina State University has been focusing on two cubic equations of state, Peng-Robinson and Soave-Redlich-Kwong. (The SAFT equation is not being considered at the moment because initial results were less promising than expected.) During the last reporting period, vapor-liquid equilibrium calculations were performed for 8 binary hydrocarbon systems using each cubic equation, and the binary interaction parameters (i.e., k_{ij}s) that minimized the deviation between experimental and calculated phase equilibrium data were calculated. Binary interaction parameters have been determined for alkanes between nC_4 and nC_{23} at temperatures between 25 and 357 °C.

During this reporting period, efforts focused on developing a method for predicting these k_{ij}s for solvent-wax systems. Such a predictive tool is essential if one is to simulate processes that contain large numbers of components, such as the Fischer-Tropsch process. To correlate the dependence of k_{ij} on temperature, an inversely linear form was chosen:

$$k_{ij} = \alpha \left(\frac{1}{T} - \frac{1}{T_o} \right)$$
(1)

where α is the slope, T is the temperature of the mixture, and T_o is the temperature at which the value of k_{ij} is zero. Similar equation forms have been used previously to correlate binary interaction parameters in various equations of state (Gregg et al., 1993; Mohamed, et al., 1987; Pongsini and Viswanath, 1989). It was assumed that the variable

T_o incorporates all of the carbon number dependence and that α is independent of both the temperature and the specific n-paraffin system. To incorporate the carbon number dependence into T_o, the literature suggests that either carbon number itself or critical temperature are the best means to account for the effect of carbon number on k_{ij} (Tsonopoulos, 1979; Breman and Beenackers, 1996). Therefore, the following linear relationships were chosen:

$$T_o = a + b\left(n_{ci}\, n_{cj}\right) \qquad (2)$$

$$T_o = a' + b'\left(T_{ci}T_{cj}\right)^{1/2} \qquad (3)$$

To test the validity of these three relationships, plots were constructed using k_{ij}s calculated from binary vapor-liquid equilibrium data, using both the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. Plots of T_o versus $(n_{ci}\, n_{cj})$, T_o versus $(Tc_iTc_j)^{1/2}$, and k_{ij} versus $(1/T - 1/T_o)$ all showed linear trends, validating the assumed equation forms.

A more rigorous test was then performed using nonlinear regression. Substituting Equations 2 and 3 into Equation 1, one obtains:

$$k_{ij} = \alpha\left(\frac{1}{T} - \frac{1}{a + b\left(n_{ci}\, n_{cj}\right)}\right) \qquad (4)$$

$$k_{ij} = \alpha'\left(\frac{1}{T} - \frac{1}{a' + b'\left(T_{ci}T_{cj}\right)^{1/2}}\right) \qquad (5)$$

Using the k_{ij}s previously calculated from phase equilibrium data, the temperature, and $(n_{ci}\, n_{cj})$ or $(T_{ci}T_{cj})^{1/2}$, a nonlinear regression was done using the least squares function from Matlab to obtain values for α, a, and b (α', a', and b'). The initial guesses for the

three parameters were varied to ensure no sensitivity due to starting point in the final results. The resulting parameters for equations 4 and 5 can be seen in Table 1. The sum of squares for these regressions were 0.0022 and 0.0028 for PR and 0.0033 and 0.0034 for SRK, respectively.

Table I. Empirical parameters obtained from nonlinear regression.

	$(T_{ci}T_{cj})^{1/2}$		
	α'	a'	b'
Peng-Robinson	-84.34	-331.65	1.520
Soave-Redlich-Kwong	-107.9	-33.64	0.9335
	$(n_{ci}n_{cj})$		
	α	a	b
Peng-Robinson	-82.19	368.6	2.084
Soave-Redlich-Kwong	-102.9	401.7	1.203

Figure 1 shows a parity plot of the predicted k_{ij} values from equation 4 and the actual k_{ij}s for PR. The predicted values agree fairly well with the actual values, as evidenced by the points being centered around the 45° line. Similar results are also seen for SRK and for both equations of state using equation 5.

In conclusion, the developed correlation that uses either $(n_{ci}\, n_{cj})$ or $(T_{ci}T_{cj})^{1/2}$ shows promise in the prediction of binary interaction parameters for unstudied systems containing heavy paraffins and hydrocarbon systems at various temperatures. However, it should be noted that the carbon number range (i.e. nC_4 to nC_{23}) of n-alkanes used to develop the correlation is not nearly as large as what occurs in a Fischer-Tropsch reactor. (This cannot be helped at the moment; no other data are available.) As higher molecular weight alkanes are experimentally measured by this group, the correlations ability to be extrapolated outside its current range will be tested.

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Task 3. Process Design Studies

No effort planned for this quarter.

Plans for Next Quarter

Phase equilibrium experiments on the hexadecanol/hexane binary will begin. Also, results from process design studies will be presented.

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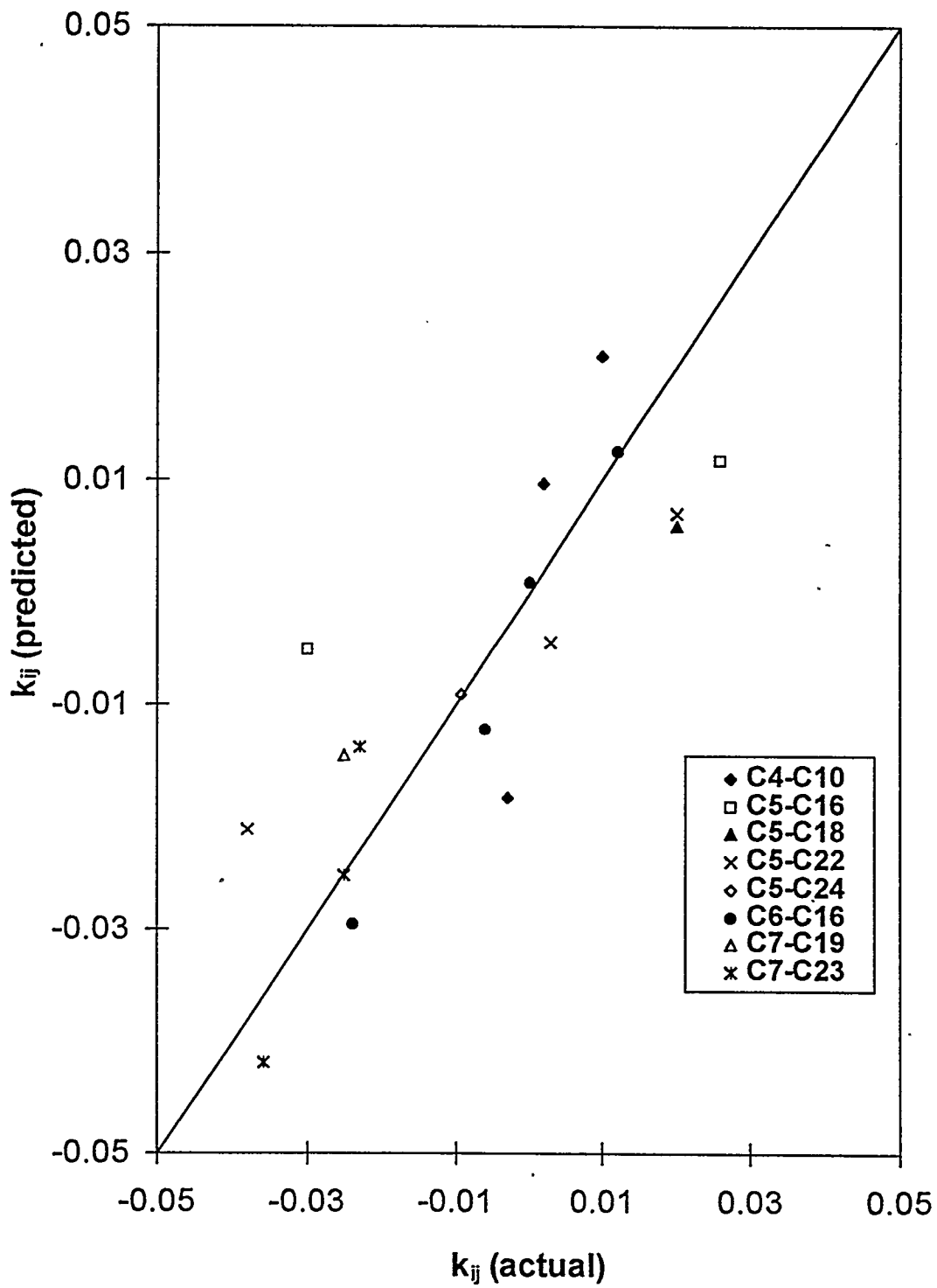
Figure 1. Parity plot of the predicted and experimental k_{ij}'s.