Separation of Fischer-Tropsch Wax from Catalyst by Supercritical Extraction

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Executive Summary

Because our phase equilibrium measurements for Fischer-Tropsch waxes in supercritical fluids encompass both liquid and vapor compositions, they present us with a unique opportunity for evaluating equation-of-state models for short alkane-long alkane systems. Thus, a modification of the Peng-Robinson equation (m-PR) is being investigated for fitting our VLE measurements, with an emphasis on those containing the longer (i.e., C_{24} and up) waxes. The essence of the modification is that pure component liquid densities and vapor pressures are used to determine new pure component parameters. After eliminating the unreliable pure component data in the literature, our experimental results for mixtures of hexane with tetracosane (C_{24}), squalane (2,6,10,15,19,23-hexamethyltetracosane), and hexatriacontane (C_{36}) were fit with m-PR. Good fits were obtained to both vapor and liquid phases, in fact, better fits than are obtained with SAFT. For systems containing waxes smaller than C_{20}, k_{ij} is essentially constant over a wide range of temperatures. For C_{24} and higher solutes, k_{ij}’s decreased with increasing temperature. Whether or not this change in k_{ij} with temperature is well-behaved and independent of solvent will require a larger database, that is, additional VLE measurements for model wax compounds with solvents other than hexane.
Technical Objectives

The objective of this research project is to evaluate the potential of supercritical fluid (SCF) extraction for the recovery and fractionation of the wax product from the slurry bubble column (SBC) reactor of the Fischer-Tropsch (F-T) process. The wax, comprised mostly of branched and linear alkanes with a broad molecular weight distribution up to C\textsubscript{100}, 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 factors. First, the supercritical solvent must be able to dissolve the F-T wax; furthermore, this must be accomplished at conditions that do not entrain the solid catalyst. Second, the extraction must be controlled so as not to favor the removal of the low molecular weight wax compounds. That is, a constant carbon-number distribution in the wax slurry must be maintained at steady-state column operation. Three major tasks are being undertaken to evaluate our proposed SCF extraction process.

Task 1: Equilibrium solubility measurements for model F-T wax components in supercritical fluids at conditions representative of those in a SBC reactor.

Task 2: Thermodynamic modeling of the measured VLE data for extending our results to real wax systems.

Task 3: Process design studies of our proposed process.

Task 1: Equilibrium Solubility Measurements
   a. apparatus modification and construction.
   b. experimental measurements of selected model systems.
   c. design and construction of new apparatus for measuring VLE of C\textsubscript{36}+ alkanes with hexane.

Task 2: Thermodynamic Modeling
   a. modeling VLE data using cubic equations of state.
   b. examination of theoretically based models, including the SAFT equation.

Task 3: Process Design Studies
   a. process configuration studies using the ASPEN PLUS simulation package.
Detailed Description of Technical Progress

Task 1a. Apparatus Modification and Construction

This task has been completed.

Task 1b. Experimental Measurements for Model Wax Components

This task has been completed.

Task 1c. Design and Construction of New Apparatus

Even with cost-sharing by Clemson University being greater than was originally proposed, project funds turned out to be insufficient to build an apparatus of the complexity required for measuring systems containing F-T waxes greater than C_{44}. A future goal of our research is to secure the necessary funds to build such an apparatus.

Task 2a. Modeling VLE Data Using Cubic Equations of State

Investigation of the modification of the Peng-Robinson equation of state (m-PR), in particular a modification that determines pure component parameters by regressing pure component liquid density and vapor pressure data, continued. Before using m-PR, it was necessary to critically evaluate the liquid densities and vapor pressures to be used in the regression. Of particular concern was the accuracy of data for the higher molecular weight wax compounds. For liquid densities, data over a wide range of temperatures and pressures are available from Doolittle up to a carbon chain length of 40 [1]. Other density data are available for even higher molecular weight alkanes (up to C_{94}), but the measurements are limited to small temperature and pressure ranges. Fortunately, we have found that the methods given by Doolittle for extrapolating density data to higher molecular weight alkanes agree with experimental measurements from other sources. For example, extrapolation to calculate the density of C_{94} shows good agreement with experiment (see Table I). Therefore, the method of Doolittle was used to calculate densities for use in parameter regression when experimental values were not available.
Table I. Comparison of experimental and calculated densities for C_{94}.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ρ (exp)</th>
<th>ρ (calc)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>0.7833</td>
<td>0.7848</td>
<td>-0.19</td>
</tr>
<tr>
<td>125</td>
<td>0.7774</td>
<td>0.7796</td>
<td>-0.28</td>
</tr>
<tr>
<td>135</td>
<td>0.7714</td>
<td>0.7742</td>
<td>-0.36</td>
</tr>
</tbody>
</table>

Few experimental vapor pressure data are available in the literature for alkanes larger than C_{36}. Furthermore, it has only been possible to examine vapor pressure data from multiple sources (i.e., to check the consistency data) for alkanes up to C_{28}. Although API-44 lists vapor pressures for components up to C_{100}, they are not actual experimental measurements, but an extrapolation to long-chain alkanes from short-chain alkanes. Another source for vapor pressure “data” is from a handbook by Stephenson and Malanowski [2]. This source also has Antoine constants available up to C_{100}, but it is unclear to us how these constants were determined. It is almost certain, however, that they are only estimations for the higher molecular weight alkanes.

To determine the best data source for high molecular weight alkane vapor pressures, a comparison was made between the vapor pressures from the various sources to those determined from extrapolating our binary VLE data for hexane/hexatriacontane (C_{36}). Using the enhancement factor plot (used previously to check the consistency of experimental vapor-phase compositions), one can use low to moderate pressure vapor phase data from binary VLE to extrapolate to the pure model wax component vapor pressure (i.e., where the ln of the enhancement factor equals zero). As an example, Figure 1 shows how vapor pressure (P_{sat}) data obtained by this method agree closely with measured P_{sat} data for hexadecane. Similar agreement between measured and extrapolated P_{sat}’s was found for tetracosane and squalane. Therefore, to test the various P_{sat} data sources for C_{36}, vapor pressures were obtained by extrapolation of the binary C_{6}/C_{36} VLE data. As can be seen in Figure 2, the vapor pressures from Stephenson agree most closely with our results. Thus, it was assumed for the time being that the Antoine constants from Stephenson best represent the actual vapor pressures of long-chain alkanes.

Regression of parameters for m-PR continued during this reporting period to systems containing C_{30} and higher alkanes. During the previous quarter, it was reported
that the regressed critical properties for hexatriacontane were not well-behaved functions of molecular weight when compared to smaller linear alkanes. This has now been found not to be the case. When densities [1] and vapor pressures [2] over a wide range of temperatures were used, the new regressed parameters are well behaved when compared to smaller alkanes.

Both the hexane/hexatriacontane and hexane/squalane systems were modeled using m-PR. Figures 3 and 4 show the fit of m-PR to the liquid-phase data for C₆/C₃₆ and C₆/squalane, respectively. The vapor-phase fits for C₆/C₃₆ and C₆/squalane are shown in Figures 5 and 6, respectively. As can be seen in the figures, it was possible to obtain good fits to both the liquid- and vapor-phase compositions. However, as was seen previously with hexane/tetracosane, m-PR does not represent the critical region well. This is not unexpected, as the parameters are not fit to the pure component critical points. In addition, the optimized binary interaction parameters are relatively large and vary strongly with temperature (see Tables II and III).

Table II. Optimized binary interaction parameters for m-PR and deviations between experimental and calculated results for the hexane/hexatriacontane system.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Optimized k_ij</th>
<th>x error a (%)</th>
<th>y error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>248.5</td>
<td>-0.04</td>
<td>18.2</td>
<td>16.3</td>
</tr>
<tr>
<td>299.9</td>
<td>-0.08</td>
<td>3.1</td>
<td>13.4</td>
</tr>
<tr>
<td>348.7</td>
<td>-0.10</td>
<td>4.9</td>
<td>13.4</td>
</tr>
</tbody>
</table>

\[ a_{AAPD} = \sum_{i} \left| \frac{x_{\text{calc}} - x_{\text{exp}}}{x_{\text{exp}}} \right| \times 100\% \]

Table III. Optimized binary interaction parameters for m-PR and deviations between experimental and calculated results for the hexane/squalane system.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Optimized k_ij</th>
<th>x error a (%)</th>
<th>y error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>196.6</td>
<td>0.00</td>
<td>16.1</td>
<td>7.7</td>
</tr>
<tr>
<td>251.1</td>
<td>-0.03</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>301.4</td>
<td>-0.05</td>
<td>3.9</td>
<td>8.2</td>
</tr>
<tr>
<td>350.1</td>
<td>-0.08</td>
<td>5.0</td>
<td>8.8</td>
</tr>
</tbody>
</table>

\[ a_{AAPD} = \sum_{i} \left| \frac{x_{\text{calc}} - x_{\text{exp}}}{x_{\text{exp}}} \right| \times 100\% \]

Although only limited experimental data are available, it was nevertheless used to
determine if the interaction parameter \( (k_{ij}) \) varied in a well-behaved manner with system parameters such as reduced temperature and system asymmetry. Initial results indicate that when the solute is smaller than \( C_{20} \) in size, the interaction parameter is small \( (k_{ij} \approx -0.01) \) and constant with respect to temperature and the size of the solvent. For example, the interaction parameters for \( C_6/C_{16} \) and for \( C_2/C_{20} \) are the same at all temperatures (see Figure 7). However, for systems where the solute is larger than \( C_{24} \), the interaction parameter is larger and is also a function of temperature. As can be seen in Figure 8, \( k_{ij} \) decreases with increasing reduced temperature. However, the limited data available suggest that the size of the solvent is not important (see Figure 8). More high quality VLE data are required to determine what effect alkane length has on the optimized \( k_{ij} \).

Task 2b. Examination of Theoretically Based Equations of State

This task has been completed.

Task 3a. Process Configuration Studies Using the ASPEN PLUS Simulation Package

Recent results will be presented in the next quarterly report.

Plans for Next Quarter

Simulation results that demonstrate the feasibility of our proposed process will be completed. The end of the next quarter is the end of this project.

References


Figure 1. Comparison of the vapor pressure extrapolated from binary VLE data with measured $P^{\text{sat}}$ data for hexadecane.
Figure 2. Comparison of literature data sources versus the vapor pressure extrapolated from VLE data for C₆/C₃₆.
Figure 3. Comparison of Peng-Robinson with experimental data for the liquid-phase compositions of the hexane/hexatriacontane system (the solid line is m-PR and the dashed line is P-R with experimental critical properties).
Figure 4. Comparison of m-PR with experimental data for the liquid-phase compositions of the hexane/squalane system.
Figure 5. Comparison of Peng-Robinson with experimental data for the vapor-phase compositions of the hexane/hexatriacontane system (the solid line is m-PR and the dashed line is P-R with experimental critical properties).
Figure 6. Comparison of m-PR with experimental data for the vapor-phase compositions of the hexane/squalane system.
Figure 7. Variation of optimized $k_{ij}$'s versus solvent reduced temperature when the solute is smaller than $C_{20}$. (Data for the the $C_5/C_{16}$, $C_5/C_{18}$, and $C_7/C_{19}$ systems from Nederbragt and De Jong [3]; data for $C_2/C_{20}$ from Peters et al. [4])
Figure 8. Variation of optimized $k_{ij}$’s versus solvent reduced temperature when the solute is larger than $C_{24}$. (Data for the $C_3/C_{34}$ system from Peters et al. [5])