

Separation of Fischer-Tropsch Wax from Catalyst by Supercritical Fluid Extraction

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Fischer-Tropsch (F-T) synthesis produces a broad range of products (known as waxes) consisting primarily of paraffins, olefins, and alcohols with carbon numbers ranging from 1 up to about 200, with the “average” wax being a C₆₀. Slurry-phase bubble-column (“slurry”) reactors are superior to the traditionally used fixed-bed reactors for carrying out the F-T reaction. However, the separation of the reactor catalyst from the wax product is an issue that has yet to be resolved. Supercritical fluid (SCF) extraction was first proposed by Roberts for the separation of the catalyst from the wax, followed by fractionation of the wax product itself. As has been demonstrated by White et al. at FETC, a wax that contains only 100 ppm catalyst can be recovered using near-critical hexane. Preliminary process simulation calculations indicate that product fractionation and recovery are most effective at temperatures near the operating temperature of the slurry reactor, that is, 200-300 °C. Therefore, a solvent whose critical temperature is within this range is of primary interest for use as the supercritical solvent. A logical choice is hexane ($T_c = 234.4$ °C; $P_c = 30.25$ bar); being a product of the F-T reaction, it is inexpensive and readily available.

A goal of this study is the development of a thermodynamic model applicable to the F-T wax/supercritical fluid system. However, phase equilibrium measurements at elevated temperatures for systems containing an appropriate supercritical solvent with model components representative of those found in F-T waxes are surprisingly scarce. Thus, the first objective of this study is to measure equilibrium phase compositions for model F-T wax compounds at conditions representative of those in a SBC reactor. Then, both cubic and more theoretically based equations of state will be examined for their ability to model the measured results and extend them to real systems.

Vapor-liquid equilibrium (VLE) compositions have been measured for binary mixtures of hexadecane, hexadecanol, hexadecene, tetracosane (C₂₄H₅₀), squalane (C₃₀H₆₂), and hexatriacontane (C₃₆H₇₄) with n-hexane. A continuous-flow apparatus designed for visual observations of phase behavior at elevated temperatures and pressures was used for the experimental measurements. For each binary system, vapor and liquid equilibrium phase compositions have been measured for four isotherms (ranging from 200 to 350 °C) from a pressure of approximately 6 bar up to the mixture critical point. Mixture critical pressures were obtained by visual observation of critical opalescence, and critical compositions were obtained by direct sampling of the opalescent phase. As can be seen in the figure, the critical-locus curves for the binary systems measured follow the expected trend, and run through a pressure maximum that increases as the size difference between hexane and the wax compound increases. Results for the three hexane/C₁₆-backbone systems indicate that the presence of a double bond on the

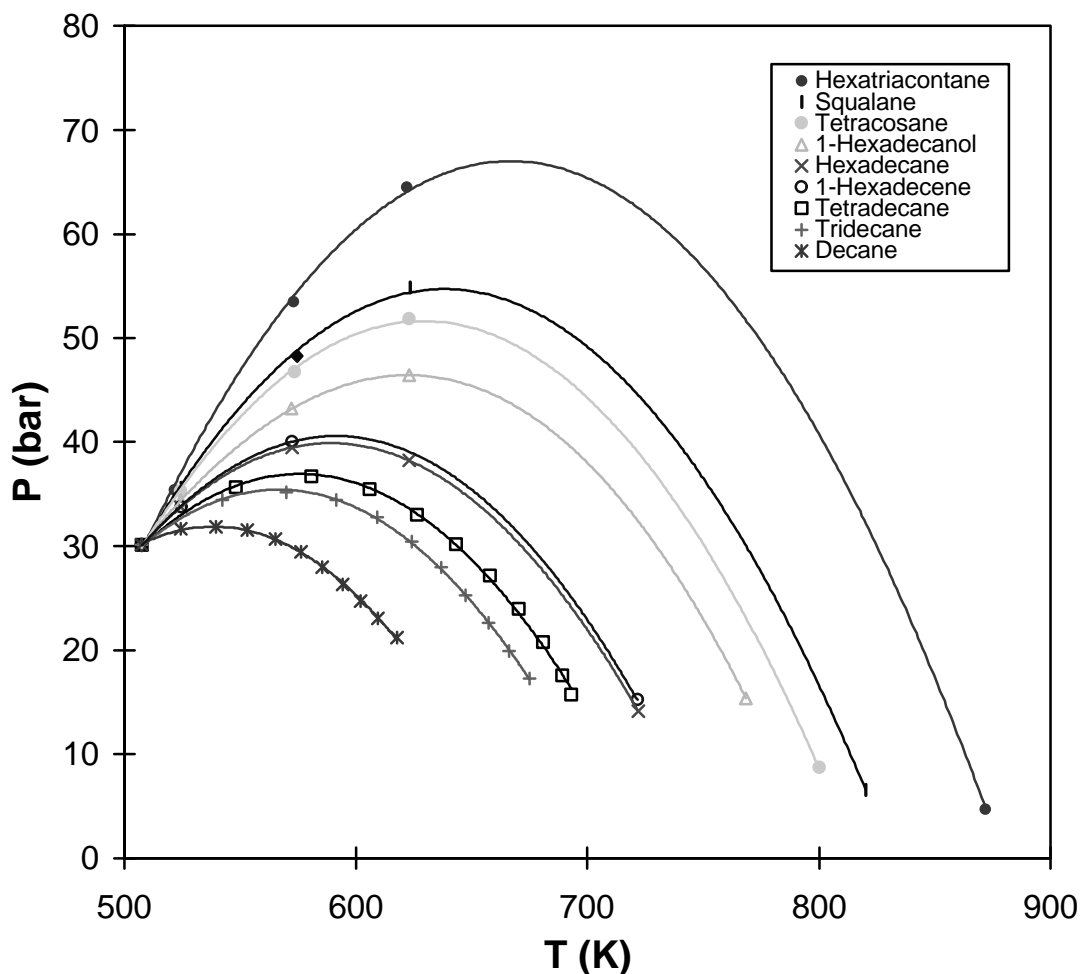


Figure 1. Mixture critical curves for model wax compounds in supercritical hexane.

C_{16} backbone has little effect on phase behavior. However, the significant increase in the size of the two-phase region with the addition of an OH group to the C_{16} backbone indicates that higher molecular weight alcohols must be explicitly considered in modeling the VLE of F-T waxes in supercritical fluids.

Theoretically based equations of state should be ideal for modeling mixtures of small and large alkanes. SAFT accurately predicts the liquid-phase compositions; furthermore, the optimized binary interaction parameters are well-behaved, being virtually constant (i.e., 0.02-0.03) for all systems and temperatures. Thus, the evidence thus far indicates that SAFT is a truly predictive equation for predicting liquid-phase compositions in solvent-wax mixtures over a range of temperatures and pressures. However, the solubility of the wax components in the vapor phase is consistently underpredicted. Peng-Robinson (P-R), on the other hand, fits the three hexane/ C_{16} -backbone systems fairly well, but its ability to correlate hexane/ model wax systems deteriorates for the C_{24+} waxes. In addition, for the C_{24+} waxes the P-R binary interaction parameters vary widely as the temperature is changed within a given binary system.

1. Journal Articles and Presentations arising from this grant:

Joyce, P.C., and M.C. Thies, "Vapor-Liquid Equilibrium for Mixtures of Hexane and Squalane at Temperatures from 469.8 K to 623.3 K", *J. Chem. Eng. Data*, **42**, 321 (1997).

Joyce, P.C., and M.C. Thies, "The Phase Behavior of Fischer-Tropsch Waxes in Supercritical Fluids", Presented at the *AIChE 1997 Spring National Meeting*, March 1997, Houston, TX, paper 55h.

Biales, J.M., Sherrard, D.M., Kilpatrick, P.K., and Roberts, G.W., "A New Approach to Catalyst Recovery and Recycling in Slurry Bubble Column Fischer-Tropsch Reactors", Presented at the *AIChE 1997 Spring National Meeting*, March 1997, Houston, TX, paper 140a.

Joyce, P.C. and M.C. Thies, "Fluid Phase Equilibria for Model Fischer-Tropsch Waxes in Supercritical Hexane", accepted for publication in the Proceedings of the Eighth International Conference on FP&PE for CPD, The Netherlands, April 1998.

Joyce, P.C., and M.C. Thies, "Vapor-Liquid Equilibrium and Critical Points for the Hexane-Hexadecane and Hexane/1-Hexadecanol Systems", *J. Chem. Eng. Data.*, in press, 1998.

Joyce, P.C., Leggett, B.E., and M.C. Thies, "Vapor-Liquid Equilibrium for Model Fischer-Tropsch Waxes (Hexadecane, 1-Hexadecene, and 1-Hexadecanol) in Supercritical Hexane", submitted for publication in *Fluid Phase Equilibria*.

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