

SEPARATION OF FISCHER-TROPSCH WAS FROM CATALYST BY SUPERCRITICAL EXTRACTION

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## Executive Summary

Phase equilibrium experiments for the n-hexane/tetracosane ( $nC_{24}H_{50}$ ) system have been completed. Tetracosane was chosen as a model wax component for two reasons. First, it is the largest alkane that has a measured critical point. With both pure component critical properties and vapor pressures available, the Peng-Robinson equation was evaluated for its ability to model systems containing a straight-chain hydrocarbon up to 24 carbons long. Second, by comparing tetracosane with squalane (2,6,10,15,19,23-hexamethyltetracosane), it was possible to examine the effect of branching on phase behavior. Vapor and liquid equilibrium compositions and mixture critical points were measured for the n-hexane/tetracosane system at 199.8, 251.1, 300.3, and 349.8 °C at pressures ranging from 6.18 to 51.83 bar. Liquid- and vapor-phase compositions are estimated to be accurate to  $\pm 2\%$  and  $\pm 3\%$ , respectively. The measured temperatures and pressures are accurate to  $\pm 0.2$  °C and  $\pm 0.14$  bar.

Both SAFT and the Peng-Robinson equations of state were used to model the measured data. SAFT adequately describes the liquid-phase compositions but overpredicts the mixture critical points and underpredicts the wax solubility in the supercritical fluid, giving similar results as were found for the  $C_6/C_{16}$  system. Peng-Robinson was found to underpredict the mixture critical points. Predictions of the liquid-phase compositions at the two higher temperatures were inadequate, but vapor-phase fits were generally good for all temperatures. Unfortunately, the binary interaction parameters required to obtain these fits can take on large, physically unreasonable values (i.e., up to  $-0.20$ ) and vary significantly with temperature; thus their predictive value is limited. In contrast, the optimized interaction parameters for the SAFT equation are small and nearly constant (i.e., 0.02-0.03) over the entire temperature range. Thus, within the limitations of SAFT, one can with good confidence estimate vapor and liquid compositions at any temperature over the range examined.

## 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  $C_{100}$ , 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. Additional details of the task structure are given below.

### 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  $C_{36+}$  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 1c. Design and Construction of New Apparatus

No effort planned for this quarter.

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

Vapor-liquid equilibrium experiments for the n-hexane/tetracosane ( $nC_{24}H_{50}$ ) system have been completed. Measured compositions and corresponding pressures for the n-hexane/tetracosane binary at 199.8, 251.1, 300.3, and 349.8 °C are given in Table I and are depicted on a pressure-composition diagram in Figure 1. Mixture critical pressures and compositions are also reported at the three higher temperatures. For clarity, the vapor-phase composition of the 199.8 °C isotherm is plotted separately in Figure 2. Note that the inflection in the vapor-phase curve of Figure 2, which must exist according to theory, is detected, indicating the good quality of the measured results at even the lowest concentrations.

For the liquid phase, the three samples collected at a given temperature and pressure were typically reproducible to better than  $\pm 1.0\%$  deviation in tetracosane composition. For the vapor phase, the samples were typically reproducible to  $\pm 1.5\%$  in the minor component tetracosane. In one instance ( $T = 199.8$  °C;  $P = 17.42$  bar) a higher deviation (i.e.,  $\pm 6\%$ ) was observed because the vapor-phase composition changes dramatically with small increases in pressure as the vapor pressure of hexane is approached (see Figure 2). Thus, the pressure fluctuations ( $\pm 0.14$  bar) inherent in a flow apparatus reduce the accuracy of this measurement. Temperature and pressure uncertainties for a given isotherm were always less than  $\pm 0.2$  °C and  $\pm 0.14$  bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are believed to be accurate to  $\pm 2$  and  $\pm 3\%$ , respectively.

Table I. Vapor-liquid equilibrium properties for the n-hexane/tetracosane system.

P/bar	x (C <sub>24</sub> )	y (C <sub>24</sub> )	P/bar	x (C <sub>24</sub> )	y (C <sub>24</sub> )
T = 199.8 °C					
6.18	0.5315	0.000460	13.08	0.2036	0.000257
7.91	0.4504	0.000406	14.80	0.1276	0.000201
9.63	0.3586	0.000348	16.53	0.0606	0.000142
11.35	0.2758	0.000301	17.42	0.0325	0.000094
T = 251.1 °C					
7.91	0.629	0.00389	25.14	0.182	0.00298
11.35	0.501	0.00319	28.59	0.124	0.00352
14.80	0.408	0.00287	32.04	0.066	0.00446
18.25	0.328	0.00270	35.28	0.015	
21.70	0.254	0.00272			
T = 300.3 °C					
7.91	0.6914	0.0185	32.11	0.2672	0.0134
14.80	0.5486	0.0127	38.93	0.1856	0.0177
18.25	0.4750	0.0119	44.10	0.1224	0.0274
21.70	0.4130	0.0116	46.72	0.0591	
25.14	0.3649	0.0118			
T = 349.8°C					
7.91	0.7676	0.0652	42.38	0.2721	0.0457
14.80	0.6380	0.0430	45.83	0.2334	0.0530
21.70	0.5160	0.0367	48.59	0.2007	0.0630
28.59	0.4286	0.0359	51.83	0.1109	
35.49	0.3499	0.0386			

The results for the n-hexane/tetracosane system were compared to the n-hexane/squalane (2,6,10,15,19,23-hexamethyltetracosane) system to examine the effect of branching on phase behavior. Figure 3 shows a pressure-temperature diagram of the critical-point curves for both systems. The critical point of pure squalane was estimated by the method of Constantinou [1], and the critical point of tetracosane is available in the recent literature [2]. Although squalane has six more methyl groups than tetracosane, the mixture critical points of the two systems do not differ greatly. This implies that the backbone of squalane governs its phase behavior. It is of interest to note that these results are consistent with the molecular simulation results of Zhuravlev and Siepmann [3] for pure C<sub>30</sub>H<sub>62</sub> isomers. They showed that the critical properties of squalane agreed more closely with tetracosane than with triacontane (nC<sub>30</sub>).

#### Task 2a. Modeling VLE Data with Cubic Equations of State

The experimental data for the n-hexane/tetracosane binary were modeled using the Peng-Robinson (P-R) equation of state (EOS). Optimized binary interaction parameters were determined for each isotherm by minimizing the following objective function (OF):

$$\text{OF} = \sum_i \left| \frac{(x_i[\text{exp}] - x_i[\text{calc}])}{x_i[\text{exp}]} \right| + \sum_i \left| \frac{(y_i[\text{exp}] - y_i[\text{calc}])}{y_i[\text{exp}]} \right|$$

where  $x$  and  $y$  are the minor component compositions of the liquid and vapor phases, respectively. Table II shows the optimized binary interaction parameters and the average absolute percent deviation between the calculated and measured compositions for P-R. The acentric factor for  $C_{24}$  was regressed from vapor pressure data [4] using the program by Hutchenson [5]. Calculated and experimental data are shown in Figure 4 for the liquid phase, and in Figure 5 for the vapor phase for the three isotherms above the critical point of hexane. P-R gives adequate results when modeling the two lower temperature isotherms, and vapor-phase predictions at all temperatures are good. However, the liquid-phase compositions for the two higher temperature isotherms are poorly represented, and all mixture critical points are underpredicted. Furthermore, as seen below, the binary interaction parameters required to obtain these fits can have highly negative (and thus physically unreasonable) values, and they vary significantly with temperature. Thus, their predictive value is limited. These results indicate that P-R may be starting to fail in its ability to model VLE for the systems of interest as the carbon number of the wax compound exceeds 20.

Table II. Optimized binary interaction parameters for the P-R equation and deviations between experimental and calculated results.

Temperature (°C)	Optimized $k_{ij}$	AAPD in $x^a$	AAPD in $y$
199.8	-0.01	11.1	14.4
251.1	-0.04	11.0	7.5
300.3	-0.11	22.1	5.1
349.8	-0.20	33.0	2.2

$$^a \text{AAPD} = \sum_i \left| \frac{(x_i[\text{exp}] - x_i[\text{calc}])}{x_i[\text{exp}]} \right| \times 100\%$$

### Task 2b. Examination of Theoretically Based Equations of State

The Statistical Associated Fluid Theory (SAFT) EOS has also been used to model the data for the  $C_6/C_{24}$  binary. Interaction parameters were optimized as described for P-R. The optimized binary interaction parameters and the average absolute percent deviation between the calculated and measured compositions for the SAFT equation are shown in Table III. The results for this binary are similar to previous modeling efforts

with SAFT. SAFT adequately represents the liquid-phase compositions but overpredicts the mixture critical points and underpredicts the solubility of the model wax in hexane. Calculated and experimental data are shown in Figure 6 for the liquid phase, and in Figure 7 for the vapor phase for the three isotherms above the critical point of hexane. It should be noted that the parameters for tetracosane used in SAFT were calculated using the correlation proposed for n-alkanes by Huang and Radosz [6]. A better fit to the data would be expected if the SAFT parameters were regressed directly from pure component vapor pressure and liquid density data for tetracosane, as was done with P-R.

Although SAFT does have limitations, it is generally superior to P-R for correlating the experimental data for the C<sub>6</sub>/C<sub>24</sub> system. Furthermore, SAFT may be the better model for predicting the phase behavior of hexane with the higher carbon number components of F-T waxes. In contrast with P-R, the optimized binary interaction parameters for SAFT are small, positive, and nearly constant (compare Tables II and III). Therefore, SAFT would be more capable of predicting phase behavior at any temperature. It is also of interest to note that the binary interaction parameters for C<sub>6</sub>/nC<sub>24</sub> are similar to those found for the C<sub>6</sub>/nC<sub>16</sub> binary. Future VLE measurements are planned for the hexane/hexatriacontane (nC<sub>36</sub>) system, and will determine whether SAFT parameters continue to be well-behaved for even larger F-T waxes.

Table III. Optimized binary interaction parameters for the SAFT equation and deviations between experimental and calculated results.

Temperature (°C)	Optimized k <sub>ij</sub>	x error (%)	y error (%)
199.8	0.02	15.7	14.9
251.1	0.02	16.7	21.9
300.3	0.03	8.1	16.3
349.8	0.03	4.4	14.4

$${}^a \text{AAPD} = \sum_i \left| \frac{(x_i[\text{exp}] - x_i[\text{calc}])}{x_i[\text{exp}]} \right| \times 100\%$$



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

Work will be reported next quarter.

#### **Plans for Next Quarter**

Binary phase equilibrium experiments for the system n-hexane/1-hexadecene are being initiated and will be followed by measurements for the hexane/hexatriacontane system.

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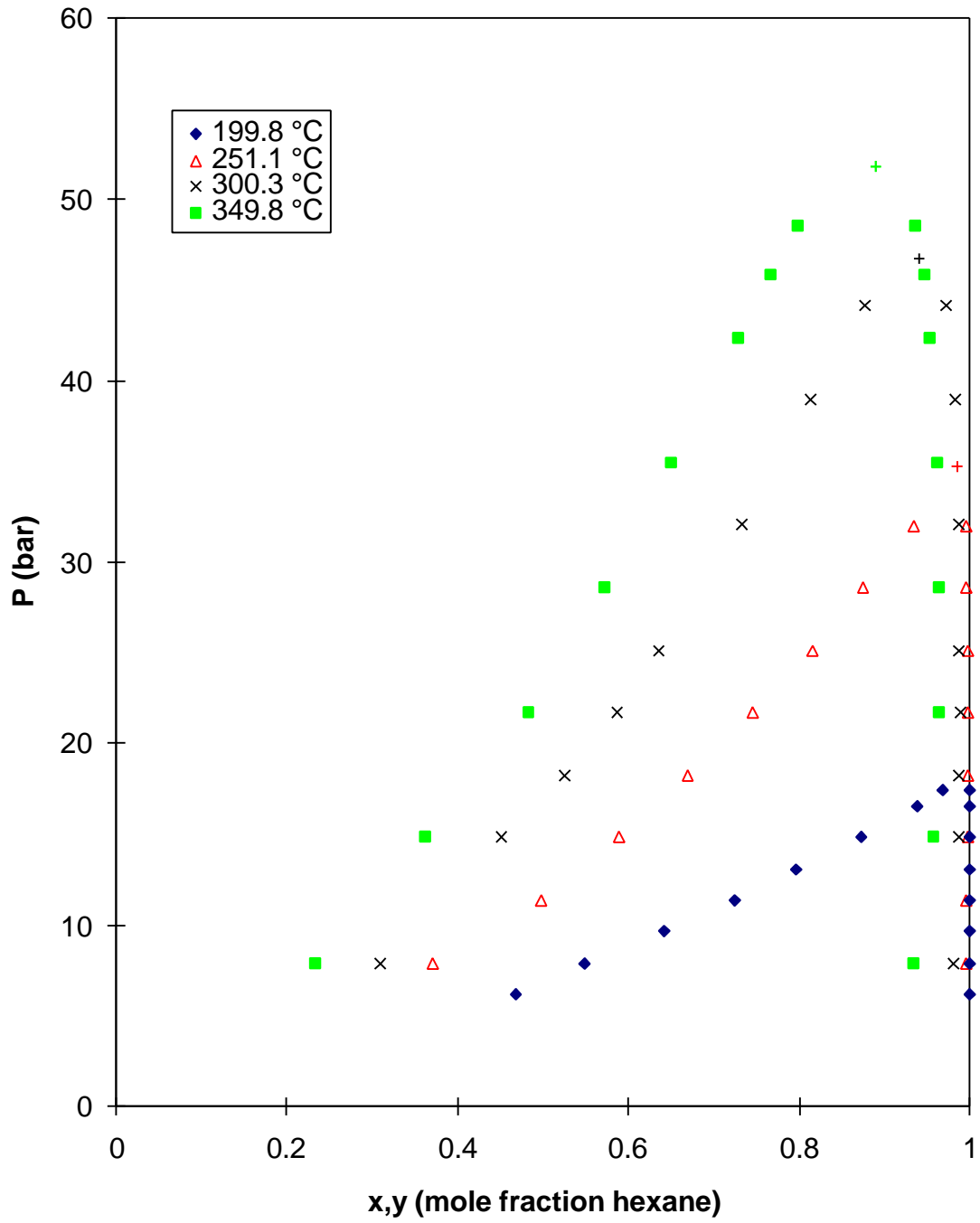


Figure 1. Pressure vs composition diagram for the n-hexane/tetracosane binary at 199.8 °C, 251.1 °C, 300.3 °C, and 349.8 °C. The + are the mixture critical points.

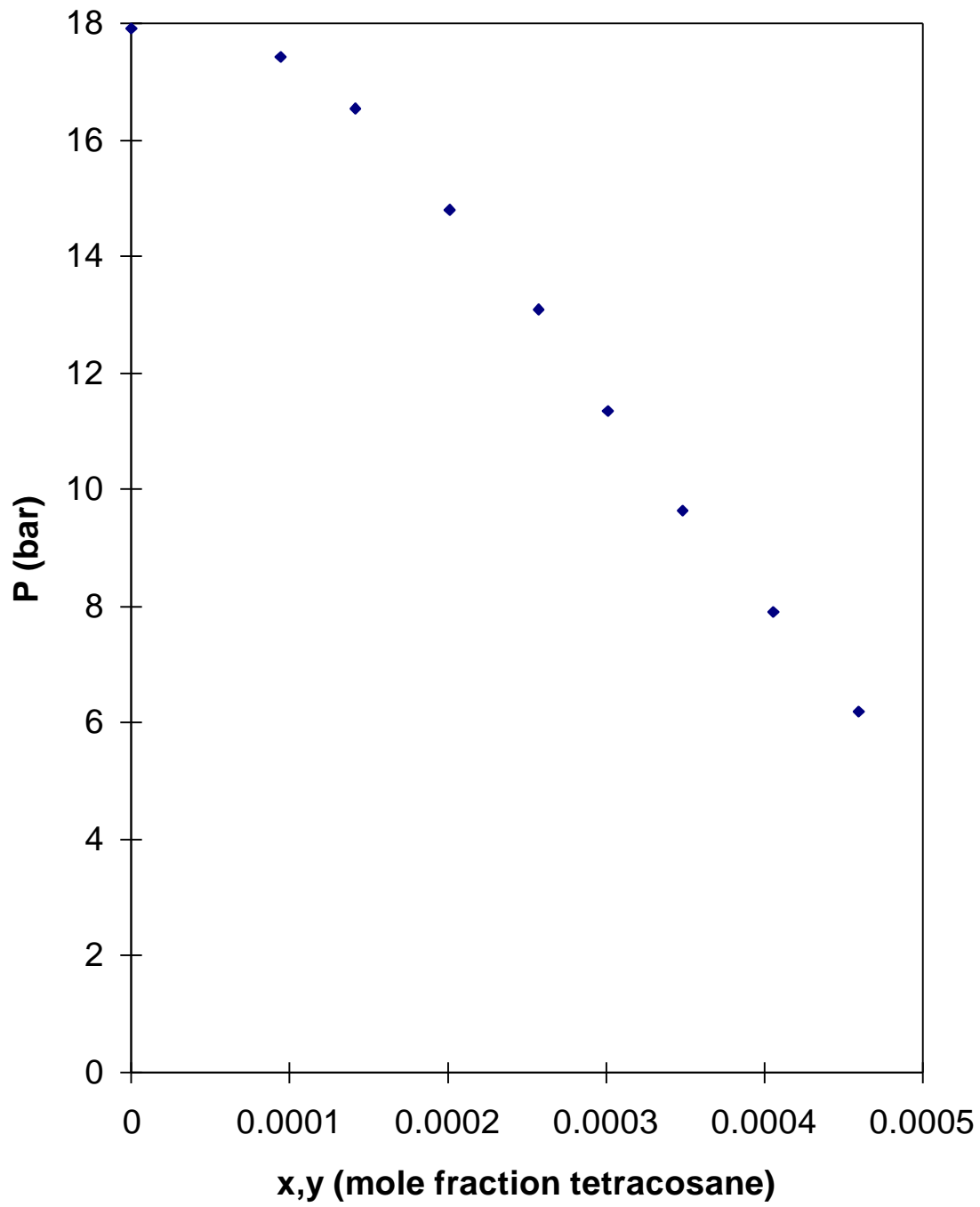


Figure 2. Vapor-phase compositions at 199.8 °C.

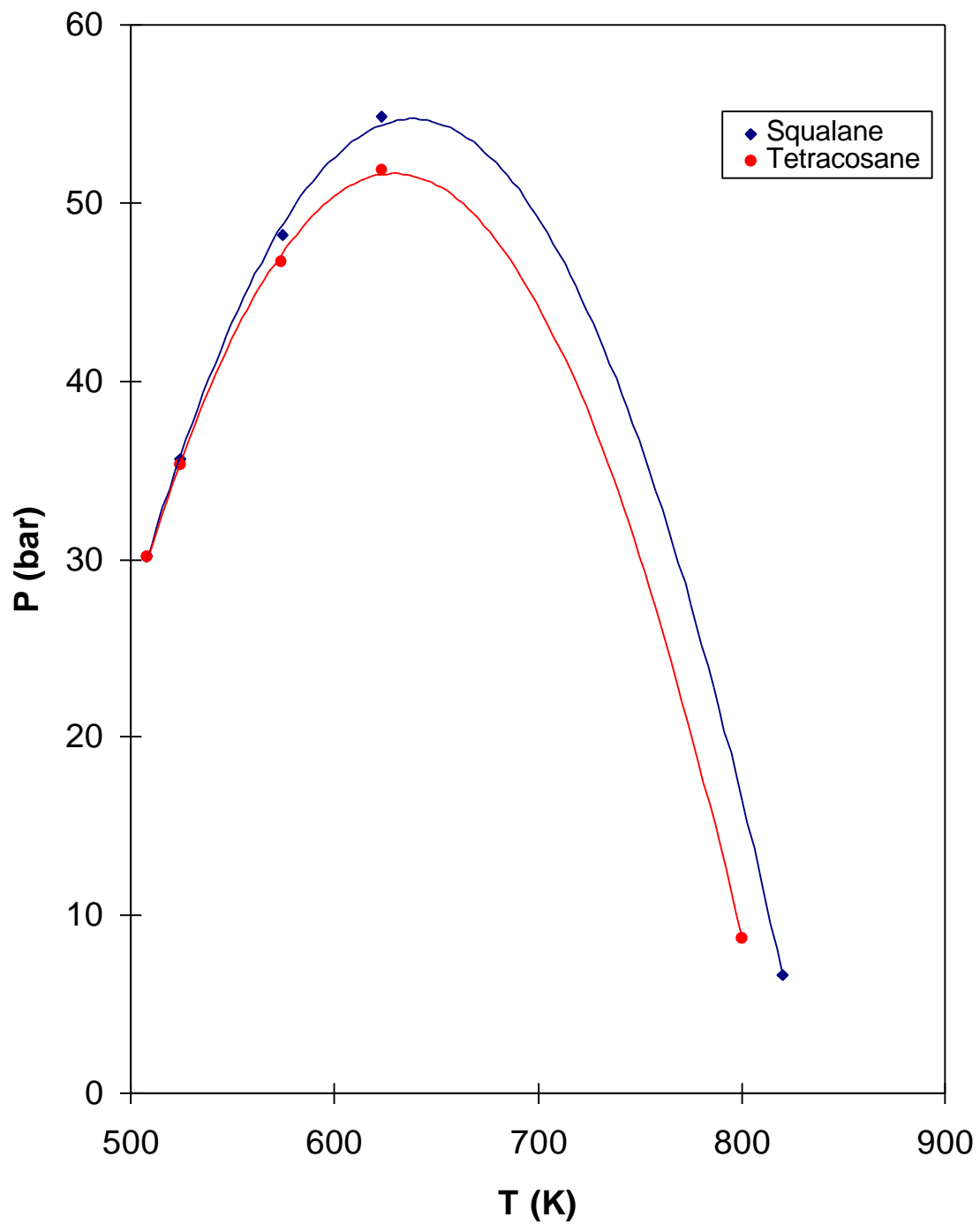


Figure 3. Critical-locus curves for squalane and tetracosane with hexane.

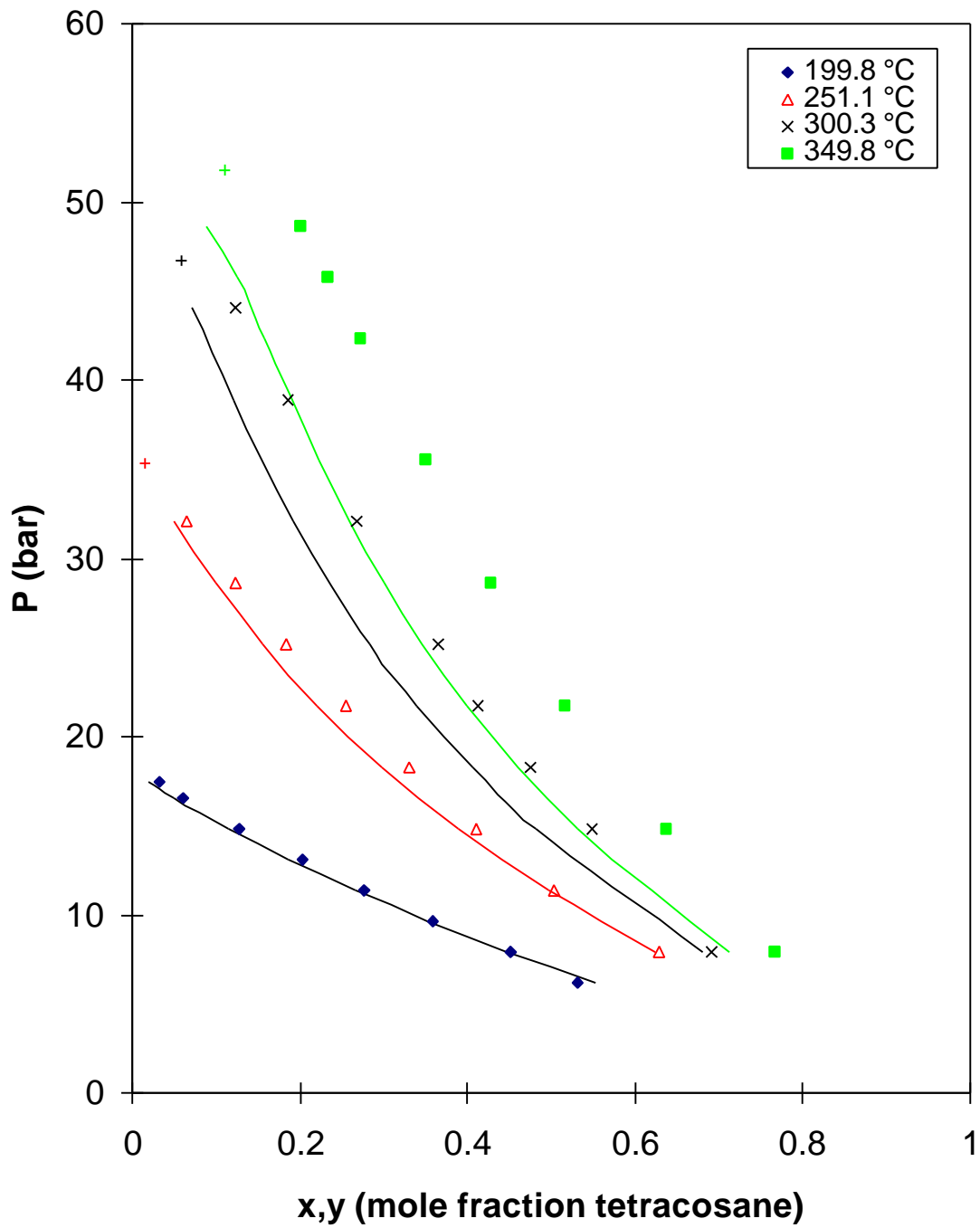


Figure 4. Comparison of Peng-Robinson calculations with experimental data for the liquid-phase compositions. The + are mixture critical points.

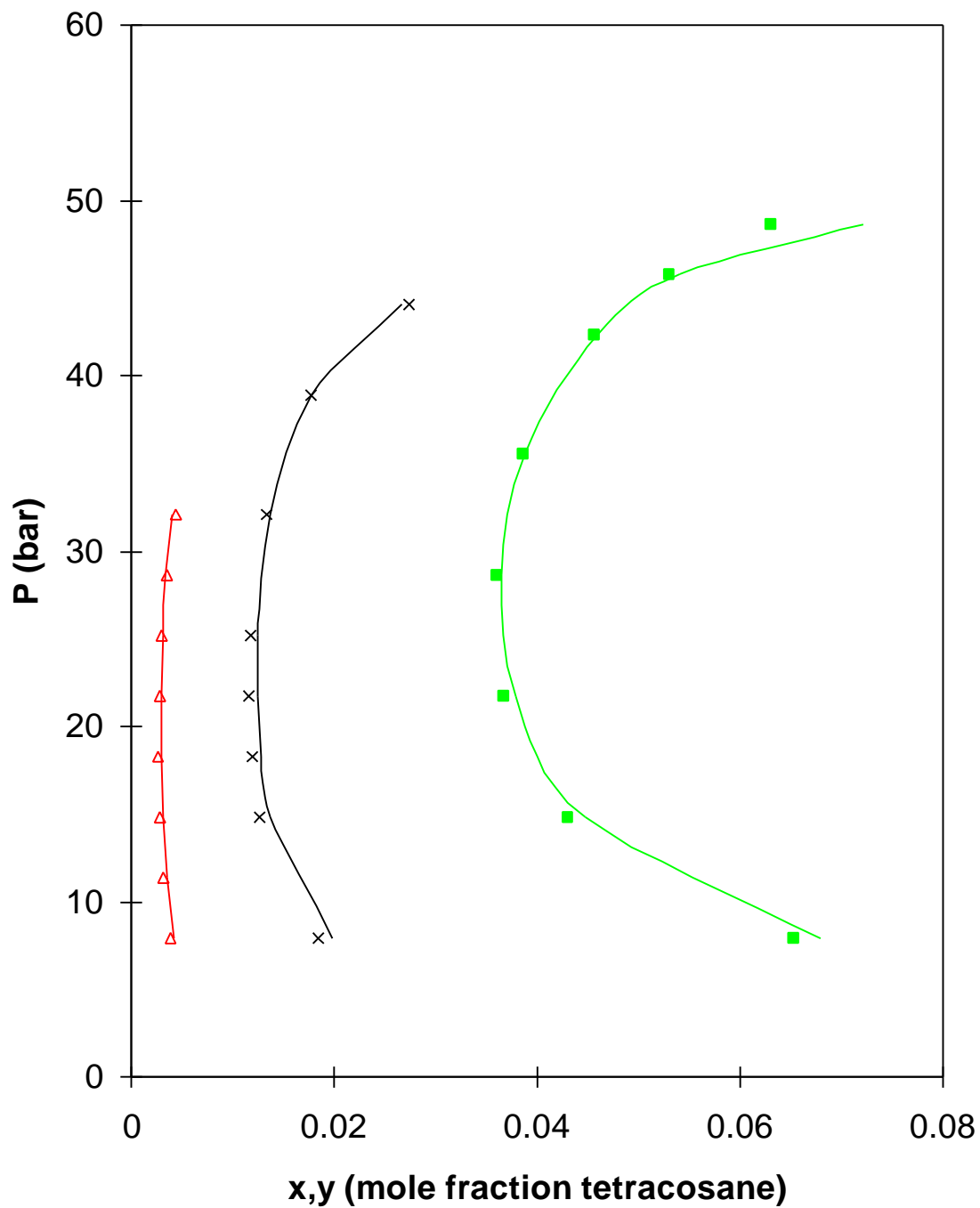


Figure 5. Comparison of Peng-Robinson calculations with experimental data for the vapor-phase compositions.

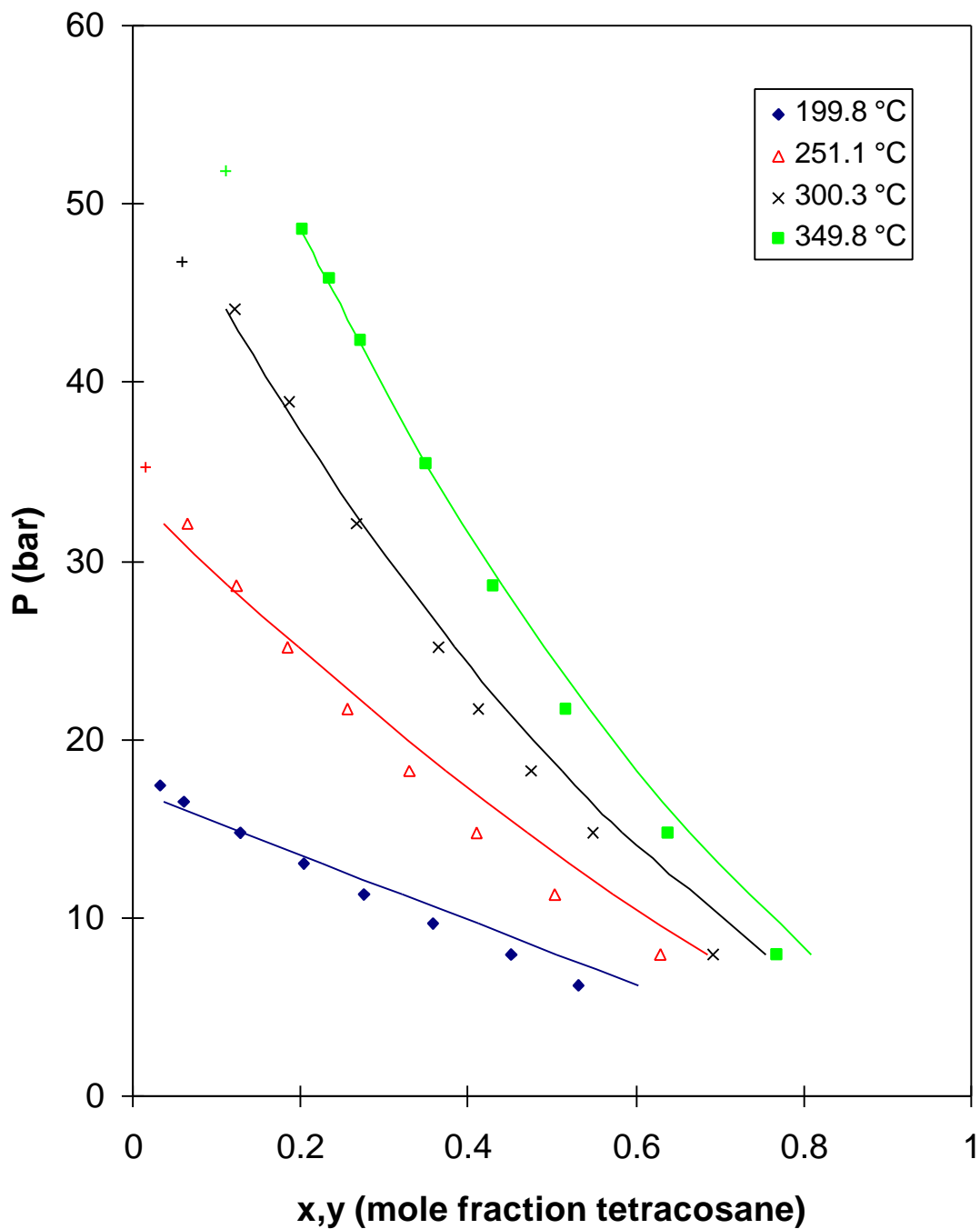


Figure 6. Comparison of SAFT calculations with experimental data for the liquid-phase compositions.

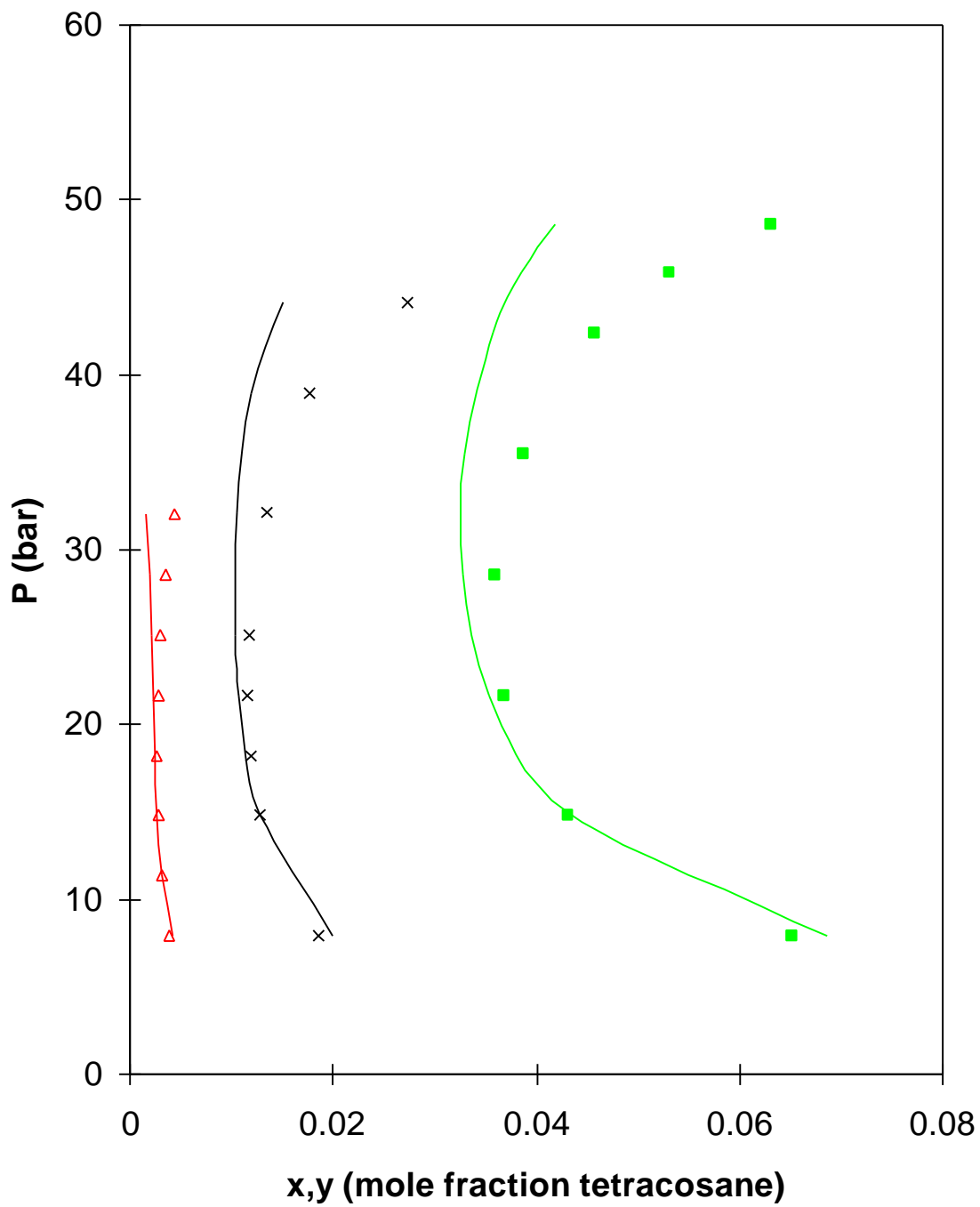


Figure 7. Comparison of SAFT calculations with experimental data for the vapor-phase compositions.