FRACTIONATION AND THERMODYNAMIC MODELING OF PETROLEUM PITCH WITH SUPERCRITICAL TOLUENE

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Introduction

The properties of carbon fibers depend on the chemical and physical characteristics of the mesophase used. Previous work has shown that a supercritical toluene extraction technique can be used to obtain mesophase pitch by fractionating isotropic petroleum pitch [1]. Unfortunately, exploratory experiments to determine the most appropriate operating conditions for producing various mesophases are difficult and time-consuming. In this paper we investigate the ability of SAFT, a modern equation of state developed for poorly defined mixtures [2], to guide our experimental work.

Experimental

A continuous-flow apparatus is available at Clemson both for measuring fluid-phase equilibria and for producing pitch fractions [1]. This apparatus was used to measure liquid-liquid equilibrium phase compositions for mixtures of Conoco petroleum pitch with supercritical toluene at temperatures of 600 K, 620 K, and 640 K and at solvent-to-pitch (S/P) ratios of 2.0 and 3.0, respectively. The reported temperatures are believed to be accurate to within ±2 °C. The reported pressures are believed to be accurate to ±2 bar. Molecular weight distributions of the feed pitch were determined by gel permeation chromatography (GPC).

Modeling

We begin the development of our thermodynamic model by representing the MWD of the feed pitch as a mixture of 3 normal distributions, see Figure 1. Using these distributions, the Gauss-Chebyshev Quadrature method was then used to generate 21 pseudocomponents (7 for each of the normal distributions) for representing the feed pitch. These pseudocomponents and toluene were then input into SAFT, which was used to model the supercritical extraction process. Binary interaction parameters (i.e., k_{ij}'s) were obtained by fitting SAFT to the experimentally obtained phase compositions.

Results and Discussion

Figure 2 shows that $k_{1,j}$'s (i.e., the interaction parameters between toluene (i =1) and pitch) are well behaved with respect to the MW and are essentially independent of temperature and pressure. Thus, the predictive ability of SAFT was tested by using one arbitrary set of k_{ij}'s for all operating conditions. In particular, k_{ij}'s calculated at 620 K and an S/P ratio of 3.0 were used to predict the results for other temperatures and S/P ratios. The effects of temperature and pressure on the phase compositions of the petroleum pitch-toluene system at S/P ratios of 3.0, and the ability of SAFT to predict these effects, are shown in Figure 3. Note that the wt % toluene in both the light and heavy phases decreases as the pressure increases; the same trend was observed for all the operating temperatures and both S/P ratios investigated. In Figure 4, the measured and predicted extraction yield (i.e., wt fraction of feed pitch extracted into the toluene-rich top phase) at an S/P ratio of 3.0 is shown as a function of temperature and pressure. (Note that the yield of pitch product is equal to 1.0 minus the extraction yield.) Finally, the effect of S/P ratio on the extraction yield is shown in Figure 5; reasonable predictions of the yield are obtained. Although additional measurements at other operating conditions are required to more definitively determine the predictive ability of SAFT, the evidence to date is encouraging, especially when on considers the simplified assumptions that were made in characterizing the pitch.

Conclusions

The SAFT equation can be used to predict both the solvent phase compositions and mesophase yields obtained in our supercritical fractionation process. The required input for these predictions are the MWD of the feed pitch and the operating conditions of temperature, pressure, and S/P ratio.

References

[1] Dauche, FM, Bolanos G, Blasig A, Thies MC, Control of mesophase pitch properties by supercritical fluid extraction. Carbon 1998; 36: 953-961.

[2] Huang SH, Radosz M, Equation of state for small, large, polydisperse, and associating molecules. Ind. Eng. Chem. Res. 1990; 29: 2284-2294.

Acknowledgments

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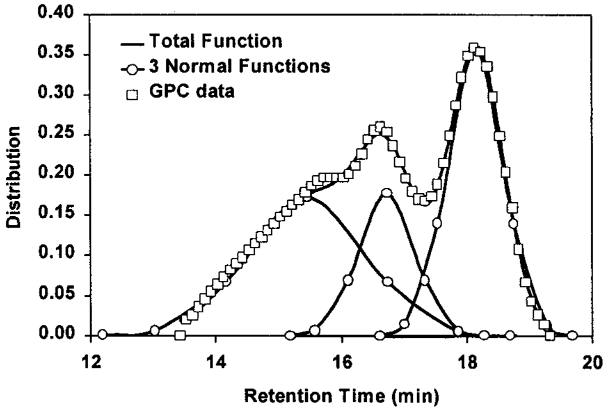

Figure 1. MWD of the feed pitch by GPC.
Log$_{10}$ MW = [6.13394 – 0.19659*(ret. time)]

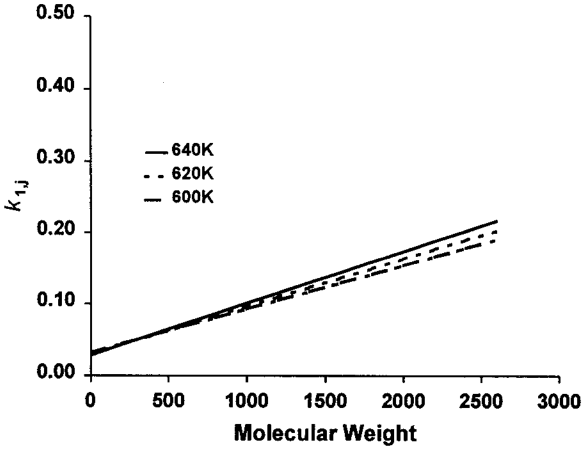

Figure 2. $k_{1,j}$ as a function of MW.

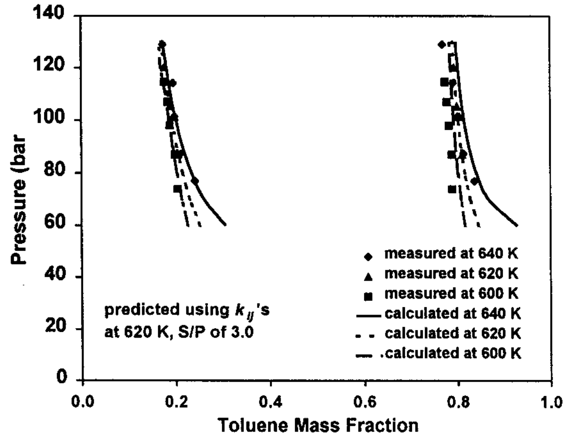

Figure 3. Equilibrium phase compositions at an S/P ratio of 3.0.

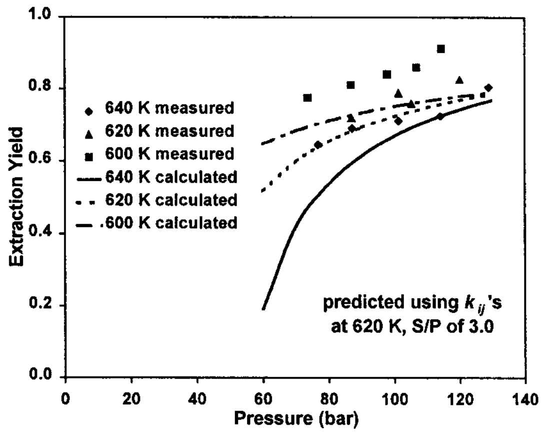

Figure 4. Extraction yields at different temperatures and pressures at an S/P ratio of 3.0.

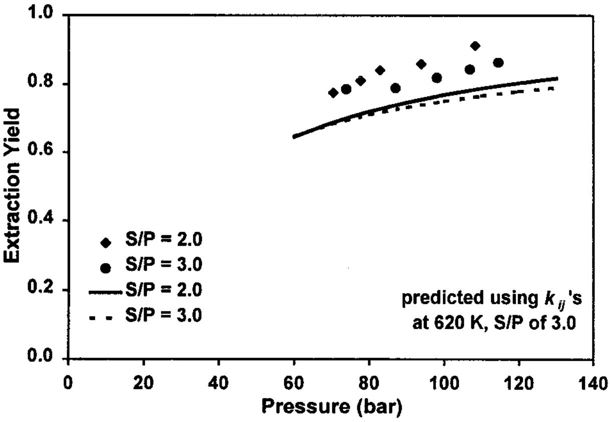

Figure 5. Effect of S/P ratio on the extraction yield at a temperature of 600 K.