ECONOMIC ANALYSIS OF MESOPHASE PRODUCTION BY SUPERCRITICAL EXTRACTION

R.T. Pigott and M.C. Thies
Clemson University, Department of Chemical Engineering
Clemson, SC 29634-0909

Introduction

Although supercritical fluid extraction has been shown to be a useful method for the production of mesophase pitch in the laboratory by Clemson researchers, the economics of this process on a commercial scale have yet to be determined. To this end, a process simulation package (i.e., Aspen Plus®) has been used to evaluate the economic viability of the proposed process.

Modeling Pitch Pseudocomponents

To model systems containing petroleum and/or coal-tar pitches in Aspen Plus® (or "Aspen" for short), pseudocomponents must be defined that adequately describe the pitch. Dickinson of Union Carbide separated A-240 pitch into three fractions by using different solvents, and then chemically characterized these fractions [1]. The molecular structures, molecular weights, and weight percentages of these fractions in the A-240 pitch are shown in Figure 1. In this study, we chose these three pseudocomponents to represent our isotropic feed pitch.

Using these pseudocomponents in Aspen required that several of their physical properties be estimated for input into equations of state. Two methods were considered for estimating these properties. First, group contribution methods from Aspen were used to correlate the molecular structure of the pseudocomponents to their pure component properties T_c, P_c, and ω. Second, a correlation previously developed by Hutchenson for the same purpose was used [2]. As shown in Figure 2, Hutchenson's method is significantly superior to the group contribution method of Gani-Ambrose (the most accurate method available in Aspen) for predicting the phase behavior of pitch/toluene mixtures at supercritical conditions. Thus, Hutchenson's correlation was used in conjunction with the Peng-Robinson equation to model thermodynamic properties in Aspen. To model the phase behavior in the region of liquid-liquid equilibrium, the SAFT equation [3] was used in conjuction with our experimental data for pitch/toluene systems. Viscosities for the pitch pseudocomponents were obtained by fitting the Andrade viscosity model in Aspen to A-240 viscosity data.

Process Simulation

Figure 3 shows a schematic of the supercritical extraction process that was developed in Aspen. A homogenous liquid mixture **1** of isotropic pitch and toluene in a 1:1 weight ratio is pumped up to 94 bar. This feed stream is then heated by a heat exchanger that uses otherwise wasted energy from the process. The resulting stream is then heated to its operating temperature of 595 K **3** with Dowtherm. A solvent stream **2** is also pressurized and heated **4** to its operating conditions of 94 bar and 595 K. Streams **3** and **4** are then combined in a static mixer to meet the specified solvent-to-pitch (S/P) ratio of 3.5:1. The resulting mixture is then sent to a phase separator **PS** where fractionation of the pitch pseudocomponents takes place in a region of liquid-liquid equilibrium at 94 bar and 595 K. The resulting light phase is sent to a flash drum to recover a majority of the solvent and to remove most solvent from the isotropic pitch. The top phase of this flash **5** is compressed, and the excess heat is used for energy recovery in the process. The bottom phase of this flash is sent to a nitrogen stripper **S1** to recover the remaining solvent **6**, and the recovered isotropic pitch **7** is sold back to the refinery. The heavy phase from the separator **PS** is sent to a flash drum to recover a majority of the solvent and devolatilize the mesophase product. The top phase of this flash **8** is then mixed with the top phase of the light-end flash **5**; the resulting mixture is used as solvent for the process, and, along with a small make-up stream, serves as the solvent for stream **2**. The bottom phase of the heavy-end flash is sent through a nitrogen stripper **S2** for the purpose of completely drying the mesophase product. The overhead vapor **9** of the stripper is either burned or treated to recover the solvent. The bottom-phase product **10** from the nitrogen stripper **S2** is the desired mesophase product, and is obtained as a yield of 20% of the feed pitch.

To design the nitrogen strippers **S1** and **S2**, new thermodynamic data had to be measured at Clemson. In particular, gas-liquid chromatography was used to determine Henry's Law constants for toluene dissolved in A-240 pitch. These constants were used as the thermodynamic data input for both the **S1** stripper (probably a good assumption because the top phase is similar to A-240 pitch) and the **S2** stripper (not as good an assumption for mesophase pitch).

Economic Analysis

The economic analysis was performed on a basis of 1,000,000 kg of mesophase per year production rate. The process is designed to operate continuously for 350 days per year over a ten-year plant life. Using a discounted cash flow rate-of-return of 20% and an interest rate of 8%, the following results are obtained: (1) the mesophase product is sold at $4.45/kg, (2) the process has a payback period—time in which it takes to recover the fixed capital investment—of 3.6 years, and (3) the net present value—the worth of the project at the end of its life—is $876,000.

A key assumption in the above economic analysis is that no hazardous wastes are produced in the process. This is a reasonable assumption, provided that clean isotropic pitches are available as feedstock.

Conclusions

An economic analysis of a supercritical extraction (SCE) process for producing mesophase pitch has been performed using the Aspen Plus® simulation package. Aspen's own physical property estimation methods gave only a fair prediction of the physical properties of the isotropic pitch feedstock. Thus, selected experimental data from our laboratory were used for much of the necessary property estimation. Our analysis indicates that the selling price of the SCE mesophase would be $4.45/kg, which compares favorably with the current selling price for AR mesophase of over $7.00/kg.

References

[1] Dickinson EM. Average structures of petroleum pitch fractions by $^{1}H/^{13}C$ n.m.r. spectroscopy. Fuel 1985; 64:704-706.

[2] Hochgeschurtz T, Hutchenson KW, Roebers JR, Liu GZ, Mullins JC, Thies MC. Production of mesophase pitch by supercritical fluid extraction. In: Kiran E, Brennecke JF, editors. Supercritical fluid engineering science. Fundamentals and applications, ACS symposium series 514; Washington, DC: American Chemical Society, 1993: 347-362.

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

Acknowledgments

Research sponsored by the Office of Naval Research under contract N00014-95-1345.

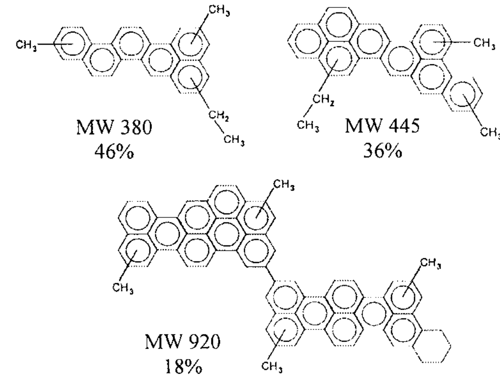

Figure 1: Three pseudocomponents used to represent A-240 isotropic petroleum pitch.

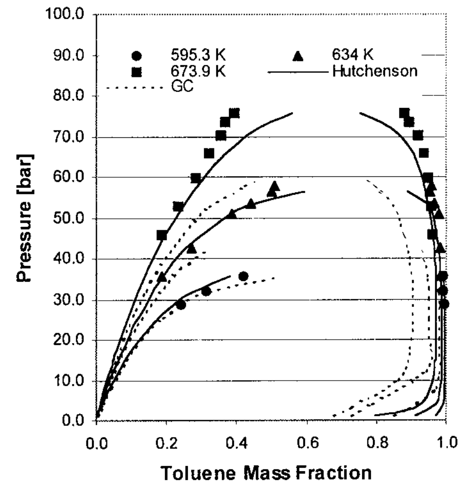

Figure 2: Vapor-liquid equilibrium data for A-240 pitch/toluene mixtures.

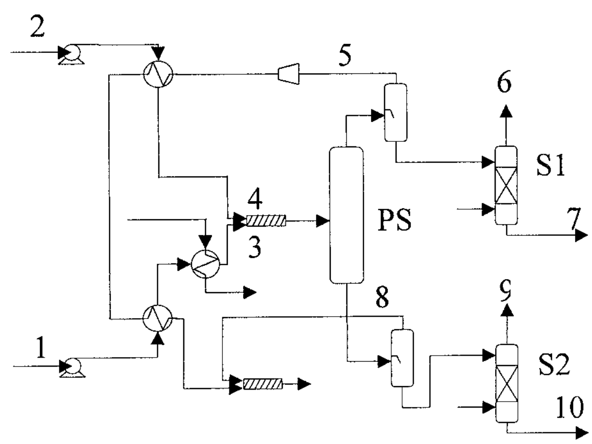

Figure 3: Schematic of the supercritical extraction process.