FRACTIONATION AND CHARACTERIZATION OF HEAVY PETROLEUM PITCH FRACTIONS

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Introduction

Previous work has shown that supercritical extraction can be used to produce mesophase pitch and provide good control of the mesophase properties. Further research is needed to learn how the molecular compositions of mesophases affect their final physical properties. In this work, we report on the investigation of a stagewise technique to fractionate mesogenic fractions present in isotropic pitch for characterization. The fractions were characterized using various analytical techniques.

Experimental

Method of stagewise fractionation

An isotropic petroleum pitch obtained by the heat soaking of decant oil is fractionated using a series of single-stage flashes. A schematic diagram of the fractionation process is shown in Figure 1; a basis of 100g of feed pitch is chosen for llustrative purposes. All fractionation stages are carried out in the liquid-liquid equilibrium (LLE) region using toluene as the solvent at a constant temperature of 620 K and a solvent-to-pitch (S/P) ratio of 2.0. The selected pressure for the first fractionation stage produces LLE, with about 95 g of pitch in the toluene-rich light phase, and 5 g of pitch in the pitch-rich heavy phase. The precipitated 5 g of pitch is the product of the first stage, while the extracted 95 g of pitch in the top phase becomes the feed for the 2nd stage. The 2nd stage of fractionation is operated at the same temperature and S/P ratio as in the first, but at a lower pressure. These conditions also produce LLE, but with about 90 g of pitch in the top phase, and 5 g of pitch in the bottom phase. The extraction process continues, decreasing the pressure so as to obtain another 5 g of pitch precipitate, until the region of vapor-liquid equilibrium is reached.

Extraction and characterization

A continuous-flow apparatus, with a maximum operating temperature and pressure of 673 K and 300 bar, respectively, was used for the fractionation of the pitches. The detailed description of this apparatus and the information regarding the materials and chemicals used can be found else where [1].

The softening points of both top- and bottom-phase samples were estimated using a Fisher-Johns Melting Point Apparatus (Model no. 12-144). The carbon and hydrogen content of the pitches was determined by elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN). The mol wt distributions were determined with a Waters 150C ALC/GPC chromatograph equipped with a 100 Å PLgel® column and an intrinsic viscosity detector. 1,2,4-Trichlorobenzene (TCB) was used as the mobile phase. A calibration curve, generated from polynuclear aromatic standards, was used to convert the retention times to mol wts. Birch reduction was used to hydrogenate pitch fractions to increase their solubility in TCB.

Results and Discussion

Five pitch fractions (or cuts) were produced in the LLE region as the pressure was decreased from 138 bar in stage one to 46 bar in stage five. Further decreasing the pressure (by about 2 bar) causes a transition in the top phase from the liquid state to the vapor state. Each cut represents about 5% of the feed pitch. The softening points of the heavy pitch cuts are shown in Figure 2. Previous researchers have found that the softening point is roughly proportional to the mol wt of the pitch fraction. Figure 2 shows that the softening points of the bottom-phase fractions decrease as the fractionation proceeds. This implies a decrease in the mol wt and is consistent with previous observations. Elemental analysis was conducted to obtain the carbon-to-hydrogen atomic ratios (C/H ratios) of the heavy pitch fractions. A decreasing C/H ratio indicates a decreasing aromaticity and, for petroleum pitches, a decreasing average mol wt. This trend can be seen in Figure 3. Figure 4 shows that the solubility of heavy pitch cuts in TCB increases from as low as 5% to above 92% after the hydrogenation treatment. The measured molecular weight distributions of these three hydrogenated fractions are shown in Figure 5.

Conclusions

The stagewise fractionation with supercritical toluene was successful in fractionating the heaviest portion of petroleum pitch, something that to our knowledge has not previously been done. Initial results indicate that hydrogenation greatly increases the solubility of heaviest fractions for characterization.

References:

[1] Zhuang MS, Thies MC, Extraction of petroleum pitch with supercritical toluene: experiment and prediction. Energy & Fuels 2000; 14: 70-75.

Acknowledgments

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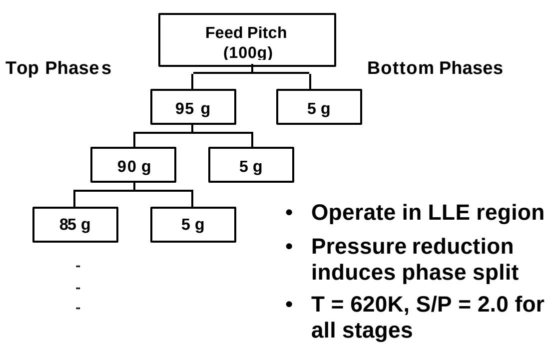

Figure 1. Conceptual chart of stagewise fractionation.

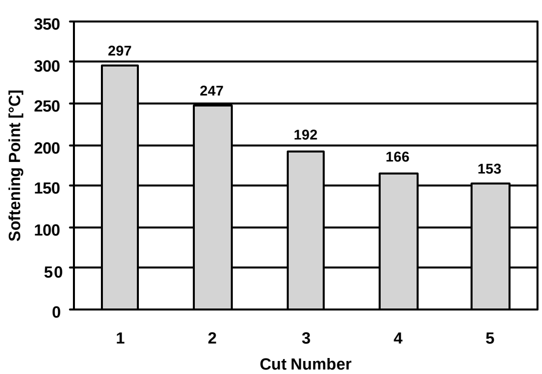

Figure 2. Softening points of bottom-phase cuts.

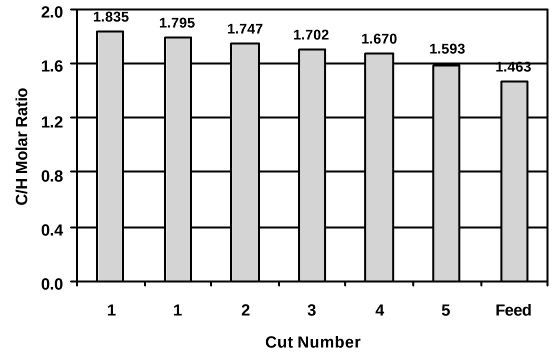

Figure 3. C/H atomic ratio of bottom-phase cuts.

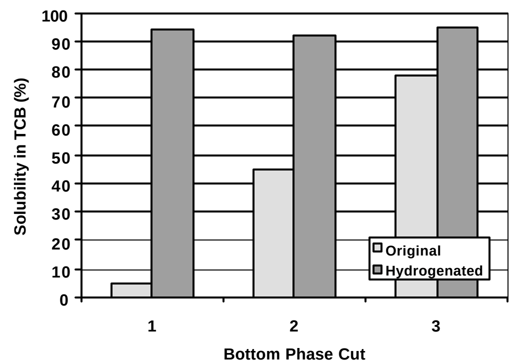

Figure 4. Solubility of heavy pitch fractions in TCB.

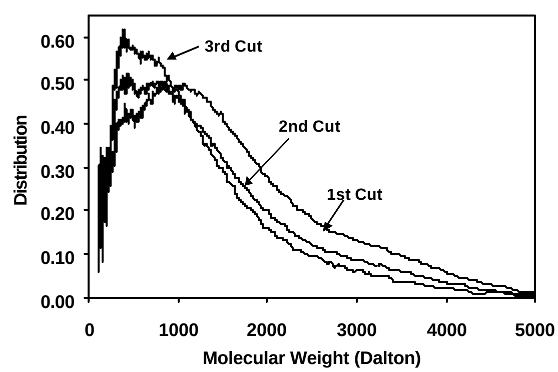

Figure 5. MWD of hydrogenated heavy pitch fractions.