MIXTURES OF PETROLEUM MACROMOLECULES: THEIR FRACTIONATION, CHARACTERIZATION, AND PHASE BEHAVIOR

W. F. Edwards, L. Jin, and Mark C. Thies*
Clemson University
Department of Chemical Engineering
Center for Advanced Engineering Fibers and Films
Clemson, SC 29634-0909
E-mail: mcths@clemson.edu
FAX: (864) 656-0784

Abstract. Dense-gas extraction is being investigated for the fractionation of petroleum macromolecules, with an emphasis on those carbonaceous pitches that can serve as precursors for advanced carbon materials. For this investigation, we synthesized a model pitch from pure anthracene so that a relatively well-defined material would be available for study. A dense-gas extraction apparatus was designed and constructed for semi-continuous operation at temperatures and pressures to 400 °C and 200 bar, respectively. The unit was designed for the fractionation of 3-10 g of pitch per run and can be operated isothermally; with a linear, positive temperature gradient; or with a linear, negative temperature gradient across the length of the column. If properly applied, such a gradient can be expected to generate a liquid reflux stream and thus improve the purity of the overhead cuts that are obtained. Experiments were carried out using either supercritical pentane or toluene as the extractive solvents, with temperature gradients (ΔT's) of –20, 0, and +20 °C being evaluated. MALDI-TOF-MS was used to determine the molecular weight distribution of selected overhead cuts, and of the residue remaining in the stillpot. Results to date indicate that the technique has potential for the separation of pitches into their constituent oligomers. A pure monomer cut was obtained with pentane and a ΔT of –20 °C, while a pure dimer cut was isolated by using toluene as the extractive solvent.

1. INTRODUCTION

Petroleum pitches are produced by polymerizing decant oil, a byproduct of the fluid catalytic cracking (FCC) of petroleum distillates, by heat soaking, and serve as important raw materials for the production of high-performance carbon products, such as carbon fibers [1]. Generally speaking, these pitches consist of polynuclear aromatic hydrocarbons with methyl and ethyl side chains and have a broad molecular weight distribution (MWD) ranging from less than 300 to above 3000. When processing carbon products from a pitch-based precursor, the molecular composition of the pitch (i.e., the MWD and the molecular structures present) acquires special importance, as composition directly affects the physical properties of the pitch and ultimately affects the properties of the carbon products themselves. For example, certain heavy pitch molecules (also called mesogens; normally with MW > 800) will spontaneously form discotic liquid crystals (or mesophase) when they are isolated from the lighter pitch molecules; previous workers have found that the heaviest 10-20% of petroleum pitch forms up to 100% mesophase when isolated and serves as an excellent precursor for high-performance carbon products, such as fibers [1].

Over the past decade, researchers [2-4] have investigated new processing techniques for controlling the properties of mesophase pitch, with the goal being an improvement in the physical properties of the final carbon products. An assumption inherent in their work is that dramatic improvements in the properties of advanced carbon materials (or dramatically reduced costs for a given level of performance) are possible if the molecular makeup of the starting mesophases can be manipulated. In fact, a long-term goal of researchers at the Center for Advanced Engineering Fibers and Films at Clemson is the molecular design of advanced materials such as high-performance carbon products. Unfortunately, the quantitative analysis of pitches is a difficult task, as they (and in particular the mesophases) are only partially soluble in even aggressive solvents, such as toluene and trichlorobenzene. Thus, the applicability of techniques such as GPC, NMR, and GC-MS is limited. Clearly, one needs to be able to first measure the molecular properties of pitches (e.g., MWD) before one can attempt to control them.

In this study, we are pursuing a two-pronged approach to this dilemma: (1) the fractionation of pitches into their oligomeric constituents by dense-gas extraction (DGE) and (2) the molecular characterization of pitches by MALDI-TOF-MS. The use of dense-gas extraction for fractionating compounds of low volatility was first proposed by Zosel [5].

2. MATERIALS

For this study, we synthesized a carbonaceous pitch from pure anthracene so that we would be working with (to the extent possible) a relatively well-defined pitch. The procedure for making the anthracene pitch is given elsewhere [6]. Toluene (99.8%, HPLC grade) and *n*-pentane (99.5%, HPLC grade) were supplied by Fisher Scientific and were used as the extractive solvents for DGE. Carbon disulfide (ACS reagent grade; Fischer Scientific) and 7,7,8,8-tetracyanoquinodimethane (TCNQ; 98%, Aldrich) were used for Simulated Distillation GC and MALDI analyses, respectively.

3. EXPERIMENTAL

A schematic of our dense-gas extraction apparatus is given in Figure 1. The unit is operated in the semi-continuous mode and was designed to fractionate g-sized quantities of pitch at temperatures to 400 °C and pressures to 200 bar. Its central feature is an extraction column constructed from three, 316 SS high-pressure manifolds custom-made to our specifications by High Pressure Equipment Co. The first manifold (0.69” i.d. x 12” long) serves as the stillpot and contains a hollow cartridge with a sintered bottom for holding 3-10 g of pitch. The second manifold (0.69” i.d. x 18” long) is screwed into the top of the first manifold and is packed with 16” of Propak 0.16-in. SS distillation packing (Scientific Development, State College, PA). The third manifold is identical to the second, is screwed into the top of the second manifold, and provides an additional 12” of packing for a total of 28”. A hot/cold finger is screwed into the top of the third manifold and consists of a 100W heater cartridge fitted into a 0.5” o.d. aluminum finger. An internal thermocouple located at the end of the cartridge is insulated from the heating section for both temperature indication and control of the finger.

Special care was taken in the design and construction of the heating and insulation setup to ensure that a linear temperature gradient could be established across the length of the column. The entire column is surrounded by a machined casing of 1.0-in. thick aluminum to help provide even heating. Nine 4” o.d. band heaters (Watlow, Thinband Model, 300 or 500W) varying from 3” to 5” wide are secured around the aluminum cladding, with the entire assembly being covered with insulation. The temperature of each of the three column sections is controlled with three independent temperature controllers (Omega, Model CN77343), with the controlling thermocouples being inserted directly into the column interior. Additional indicating thermocouples (not shown in Figure 1) are used to monitor the temperature along the entire column length.

For a typical run, the bottom of the column is charged with 3-10 g of anthracene pitch previously reduced to a powder by mortar-and-pestle grinding. A constant flow rate of solvent (typically pentane or toluene at 4 mL/min) is then started to the bottom of the column, with the preheater heating the solvent up to within 1 °C of the desired operating temperature (usually within 20-40 °C of the critical temperature of the solvent). The dense-gas, supercritical phase then flows through the sintered bottom of the feed cartridge, which serves to evenly distribute the solvent through the pitch charge. Here, extraction of a portion of the pitch occurs. Next, the dense-gas phase containing solvent and extracted pitch rises into the two packed sections of the column. The temperature of the stillpot, column, and finger are controlled so as to establish isothermal operation, a linear, positive temperature gradient (+ΔT), or a linear, negative ΔT across the column from the stillpot to the finger at the top of the column.

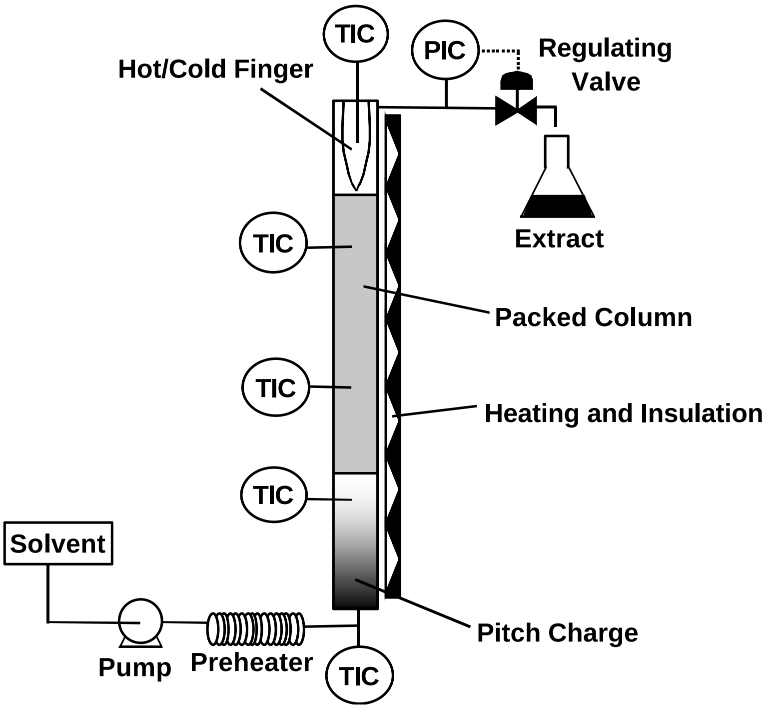

Figure 1. Schematic of the dense-gas extraction apparatus for fractionating carbonaceous pitches.

Depending on column operation and the phase behavior of the system of interest, such a temperature gradient can be expected to generate a liquid reflux that first forms as liquid condensate on the hot/cold finger, flows down the column, and increases the purity of the overhead cuts that are obtained. Typically, the bottom of the column is maintained at a constant temperature, with the top of the column at the same, lower, or higher temperature, depending on whether a zero, negative, or positive temperature gradient is desired.

After exiting the top of the column, the supercritical gas and uncondensed pitch components are throttled through a regulating valve to ambient pressures. The valve and associated lines from the column are heat-traced to avoid plugging due to pitch solidification. Pressure control to within ± 0.1 bar is accomplished through a regulating valve (Autoclave Engineers, Model 30VM4082-GY) and stepping motor unit (ECM Motor Co., Model 5471) interfaced to a pressure transducer (Heise, 0-5000 psig, Model HPO) using Labview (National Instruments) data acquisition and motion control software. Samples are collected after expansion to ambient conditions in a flask cooled with an ice bath.

4. RESULTS AND DISCUSSION

For our first studies, we are evaluating both pentane (T_c = 196.5 °C, P_c = 33.74 bar) and toluene (T_c = 318.6 °C, P_c = 41.13 bar) as extractive solvents. For the initial set of experiments with toluene, a solvent flow rate of 4 mL/min was employed, and 4 g of pitch were charged to the stillpot. The stillpot temperature was set to 340 °C, and temperature gradients of +20 °C, 0 °C, and –20 °C were investigated in three separate runs. So-called "survey runs" were conducted, in which the system was maintained at a constant pressure until the extraction rate (as observed by the color of the collected extract) decreased significantly. The pressure was then incremented upwards approximately 3 bar and maintained at this new operating pressure until the extraction rate again significantly decreased. Beginning at a pressure of about 15 bar, the process of incrementing the pressure upwards was repeated until pressures of about 60 bar were attained. Matrix assisted, laser desorption, ionization time-of-flight (MALDI) mass spectra for the $\Delta T = +20$ °C run are shown in Figures 2 and 3. For extract cut No. 7, obtained at an operating pressure of 34.5 bar, we see that an essentially pure dimer cut (centered around 350 Daltons) is obtained, with essentially no higher oligomers and very little monomer (at around 200 Daltons) in the cut. In contrast, we see that the residue recovered in the stillpot after the run contains only traces of monomer and dimer, with trimer through hexamer being the dominant species.

5. CONCLUSIONS

Dense-gas extraction is being investigated for the fractionation of mixtures of petroleum macromolecules, with a focus on carbonaceous pitches that can serve as precursors for advanced carbon materials. DGE experiments were performed on anthracene pitch, using pentane and toluene in the vicinity of their respective pure component critical temperatures as solvents. Initial results are most encouraging, as purities significantly exceeding what can be obtained by silica gel chromatography are already being obtained, at both reduced effort and in greater yield.

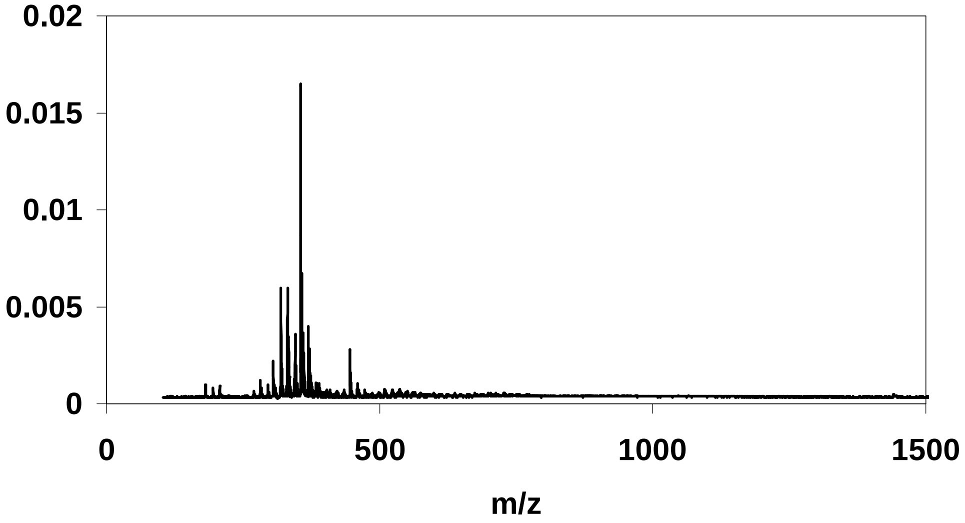

Figure 2. MALDI spectrum for cut no. 7 (P = 34.5 bar) of a DGE run with anthracene pitch, using toluene as the extractive solvent. A ΔT of +20 °C was employed.

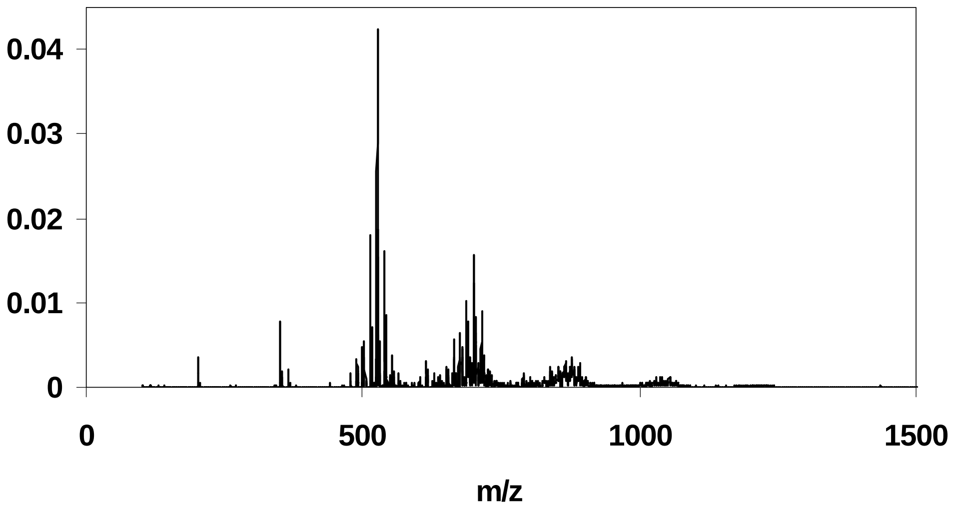

Figure 3. MALDI spectrum for stillpot residue from the above DGE run.

ACKNOWLEDGMENTS

This work was supported by the ERC Program of the National Science Foundation under Award Number EEC-9731680, Conoco Inc., and the U. S. Army Research Office (Grant No. DAAG55-97-1-0376).

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