

# DENSE-GAS FRACTIONATION FOR THE MOLECULAR CHARACTERIZATION OF INSOLUBLE PETROLEUM PITCHES

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## Introduction

Petroleum pitches are formed by the thermal polymerization of decant oil, a high MW aromatic oil that is a byproduct of the catalytic cracking of petroleum distillates. The resultant pitch has a broad molecular weight distribution (MWD) ranging from about 200 to 2000 amu. These pitches and fractions thereof have been found to be valuable feedstocks for the preparation of carbon artifacts [1]. The final properties of the resultant products, such as high thermal conductivity carbon fibers or carbon-carbon composites, are significantly affected by the MWD of the pitch precursors. For example, the formation of isotropic and anisotropic phases has a significant effect on the resultant materials, and the formation of these phases is particularly sensitive to the MWD of the pitch. Unfortunately, a quantitative study of the effect of pitch MWD on final carbon products has been inhibited by a lack of narrow MW fractions, that is, well-defined standards representative of the components in pitch, available for study.

In this study, we examine the use of dense-gas extraction (DGE) for producing narrow MWD fractions from two pitches, a commercially available petroleum pitch and a model pitch formed by the polymerization of anthracene. The DGE concept, which was invented by Zosel [2], uses a dense-gas extractive solvent and a reflux-inducing temperature gradient imposed on a packed column to form a multistage, semibatch extraction. The overhead vapor is collected as extract, and the unextracted residue is also a product of the process.

To date, there is really no effective separation method that has been developed for the fractionation of pitches. Chromatographic methods such as GPC cannot be applied to the solvent-insoluble fraction and have given poor resolution [3]. Conventional solvent extraction methods have similar deficiencies. Warzinski [4] and Shi [5] applied DGE to coal- and petroleum-derived residues, respectively, but only qualitative information on the fractions produced was reported.

## Experimental

A semibatch, multistage, DGE unit was designed and constructed to study the fractionation of pitches. The apparatus, which is shown in Fig. 1, is rated for 400 °C and

200 bar and can hold a charge of up to 15 g of pitch. The equipment consists of a pump and preheater for supplying solvent, a 1.8 cm i.d. x 115 cm tall column that contains a stillpot, a 70-cm high section of packing, and a reflux finger at the top. A regulating valve is used to control the column pressure by metering the flow of overhead product exiting the column. The construction of this apparatus is described in greater detail elsewhere [6].

In preparation for an experiment, the stillpot is charged with up to 15 g of the pitch to be studied, and then the apparatus is purged with nitrogen as it is heated to the desired operating temperature. A preheated, dense-gas solvent (in this work, toluene) is supplied to the bottom of the stillpot, where a portion of the pitch charge is extracted. The extract exits the stillpot and enters a packed column where a temperature change causes a condensation of a liquid phase. This liquid phase forms the counter-current reflux that aids in purifying the overhead product, which is collected over time. At the conclusion of the experiment, the column is allowed to cool and the unextracted residue is collected from the stillpot for analysis with the overhead fractions.

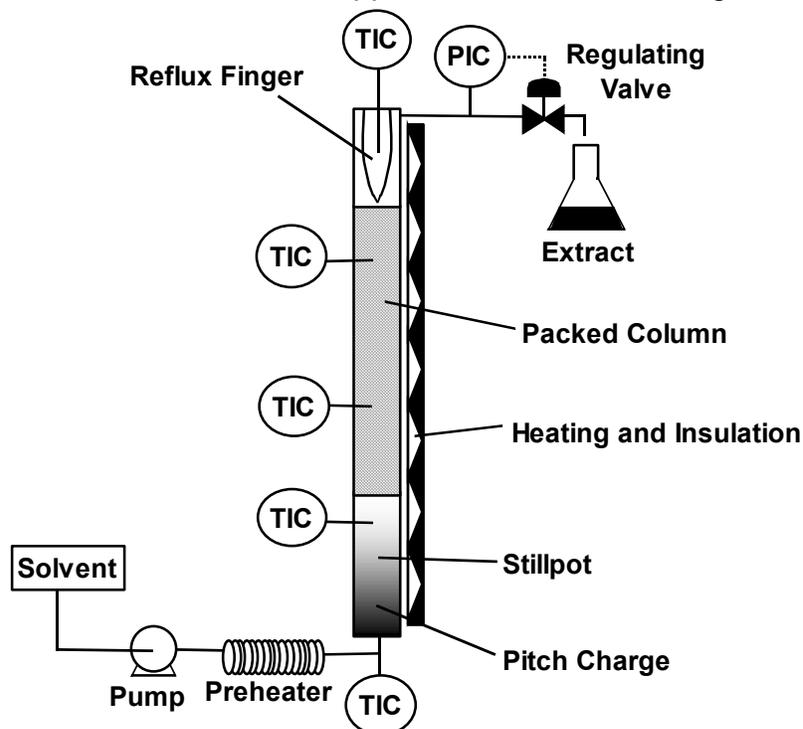


Figure 1. Schematic of the DGE apparatus.

In this work, two pitches were studied, (1) a petroleum pitch supplied by ConocoPhillips (see Fig. 2), and (2) a synthetic pitch formed by the thermal polymerization of anthracene (Fig. 3). In the experiments with the petroleum pitch, the stillpot is charged with about 10 g of pitch and the DGE process is operated at an initial pressure for a period of three hours to extract lower MW material. The pressure is then increased to extract a pure sample of higher MW material. For the study of anthracene pitch, the extraction process was broken into two

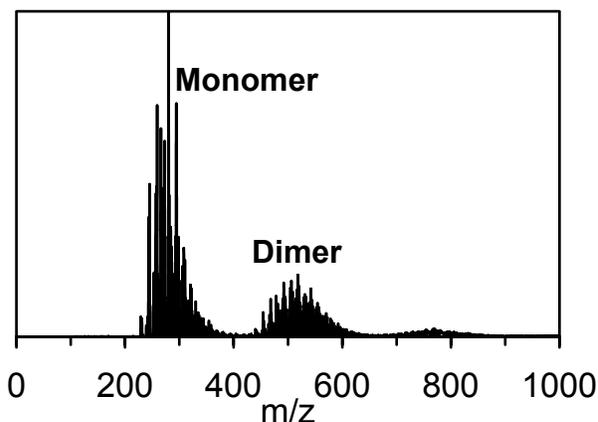


Figure 2. MALDI mass spectrum of the petroleum pitch feedstock.

steps, where the lower-pressure extraction was concluded and the residue analyzed, before this residue is extracted at a higher pressure to collect a pure overhead fraction. This allowed us to optimize each step of the extraction independently.

Matrix assisted laser desorption/ionization (MALDI) mass spectrometry (MS) was used for characterization of the fractions obtained by DGE. The methods used for sample preparation, instrument operation, and analysis are given elsewhere [7]. As can be seen in the spectra of the feed pitches (Figs. 2 and 3), the pitches studied are oligomeric in nature, with broad MWDs that are dominated by low MW species (for reasons discussed elsewhere, species of MW < ~250 are not detectable by MALDI). Higher oligomers are not visible due to their low concentrations. Here, species that constitute the oligomers are grouped, and purities are reported in terms of MALDI area fraction. A relationship between area and mass fraction has yet to be established by researchers [7].

## Results and Discussion

Dense-gas extraction was used to obtain a ~90% pure fraction of dimer species from the petroleum pitch feedstock. In this experiment, the column was operated with a temperature gradient such that the stillpot was held at 320 °C and the temperature increased to 360 °C at the reflux finger. The extraction was carried out at a pressure of 44.1 bar for three hours to remove the monomeric species before raising the pressure to 52.7 bar to collect a dimer-rich fraction. The fraction shown in Figure 4 was taken over the final 30 min of operation (i.e., after three hours at 44.1 bar and 1.5 hours at 52.7 bar). Similar experiments were performed for the purpose of obtaining a pure trimer fraction; however, the removal of dimer species hindered performance, allowing for collection purities of only about 40% (dimer content in this fraction was still >40%).

For the fractionation of anthracene pitch by DGE, the experiments were changed such that the first step, where a lower pressure is used to remove low MW material, is a

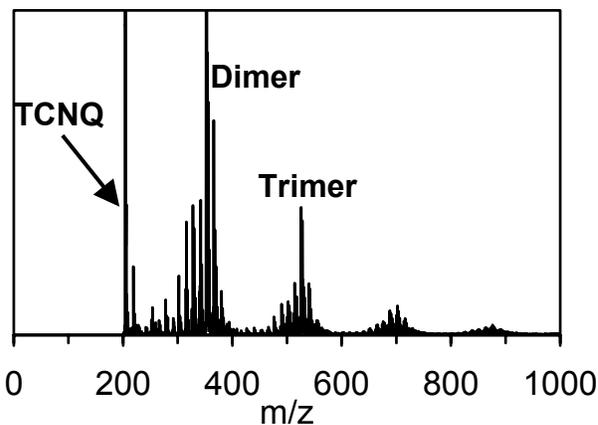


Figure 3. MALDI mass spectrum of the anthracene pitch feedstock.

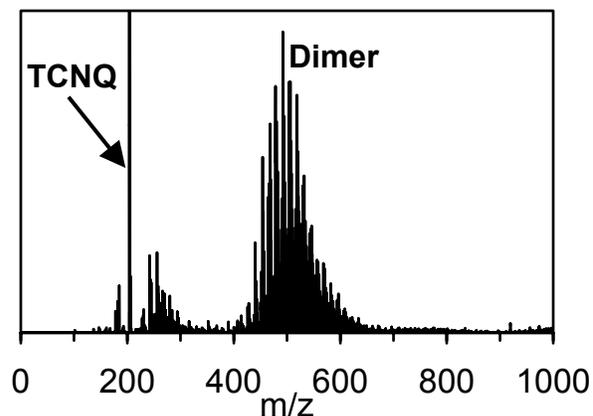


Figure 4. MALDI mass spectrum of ~90% pure dimer collected from the petroleum pitch

separate experiment from the second step, where an increased pressure is used to capture a pure fraction. This allows the low MW removal step to be optimized independently. To this end, DGE was used to strip the monomer species from the anthracene pitch feedstock, yielding a monomer-free feed for the collection of a dimer-rich fraction. The temperature gradient in the DGE column was set so that the stillpot was held at 340 °C and the temperature decreased through the column to the reflux finger, which was held at 300 °C. By extracting the 15 g charge for a period of 2 hr, the monomer content in the residue was reduced to ~ 1 wt % (by gas chromatography). This residue was used as the feed to a second DGE experiment, where a ~95% pure dimer sample was obtained. During this experiment, the column temperature gradient was set such that the stillpot was held at 330 °C and the temperature increased to 360 °C at reflux finger. The pressure was maintained at 35.5 bar, and the overhead product reached 95+% purity during the sixth and seventh hours of operation. The dimer-rich overhead product and the residue from this experiment are compared in Figure 5. The above experiments and results are described in more detail elsewhere [6].

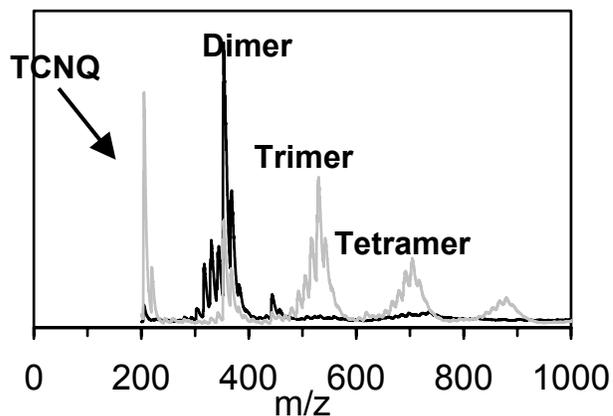


Figure 5. MALDI mass spectrum comparing ~95% pure anthracene pitch dimer fraction (black) to residue (grey).

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