

Chemical Structure of Heavy Oils Derived from Coal Hydrogenation

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Introduction

Structural characterization using high resolution nuclear magnetic resonance, NMR, and elemental analysis was first applied to coal pyrolysis products by Brown and Ladner¹. Other investigators 2-5 have extended these studies to coal hydrogenation products and coal extracts. Parameters such as the fraction aromaticity, f_a , the degree of substitution on aromatic rings, σ , the hydrogen to carbon ratio in a hypothetical unsubstituted aromatic ring system, H_{ar}/C_{ar} , the ring index, R_a , the length of alkyl substituents on aromatic rings, $H_o/H_{\alpha} + 1$, and the molecular weight of the unit structure, M_u , can all be calculated. In this study, heavy oils from coal hydrogenation using $ZnCl_2$ catalyst have been characterized by structural analysis techniques.

Experimental

Hiawatha, Utah coal (45% VM, d.a.f.b.) was hydrogenated at 950°F and 1800 psi H_2 pressure. Three (3) samples with catalyst concentrations of 1.5, 3.0 and 6.0 percent zinc as zinc chloride were hydrogenated. The heavy oils were extracted with NaOH and H_2SO_4 to produce neutral oils. The neutral oils were separated into a hexane-soluble fraction and an asphaltene fraction by extraction and the hexane-soluble oil was separated into saturated and aromatic oils by liquid chromatography using a silica gel column. Yields of various products are shown in Table 1. The asphaltene and aromatic oil fractions were further separated by gel permeation chromatography, GPC. GPC elution curves are shown in Figure 1.

Proton NMR spectra were measured for each GPC fraction at 100 M Hz. Molecular weights were determined by vapor pressure osmometry and elemental composition by C, H and N analysis.

Results and Discussion

The GPC elution curves shown in Figure 1 show a shift to smaller molecules as the catalyst concentration increases. (Larger molecules elute first in GPC). Molecular weight measurements verify that the larger molecules are eluted first in all cases.

The NMR spectra show a continuous shift in the properties of the molecules with elution volume. The larger molecules for both the aromatic oil and asphaltene samples have a large fraction of the hydrogens bound to aliphatic carbons β or further from aromatic rings, H_o . As the elution volume increases, hydrogens bound to aromatic carbons, H_{α} , and hydrogens bound to carbons α to aromatic rings, H_{α} , increase. Structural analysis was performed using the equation of

Brown and Ladner¹⁻². Results of these calculations are shown in Figures 2-4. Molecular weights are also shown in Figure 4.

The aromatic oil fractions show a large change in the carbon aromaticity and in the length of alkyl substituents on the aromatic ring. The degree of substitution of ring carbons varies from 0.5 to 0.2. The average number of aromatic rings in the unit structure is 1.5 to 3. The molecular weights calculated for the unit structure agrees with the measured values. The larger molecules, eluted at low elution volumes, appear to be composed of small ring systems with long aliphatic substituents. As the elution volume increases, the alkyl side-groups become shorter resulting in larger values of fa and lower molecular weights.

The asphaltene fractions show a similar trend as the aromatic oils except that the aliphatic branches are much shorter and Ra and fa are higher. The molecular weight of the unit structure is significantly less than the measured molecular weight, indicating that the actual molecules are dimers or trimers of the unit structures determined by structural analysis.

The effect of increasing the concentration of the zinc chloride catalyst is to decrease the yields of asphaltene and benzene-insoluble heavy oil with a corresponding increase in the yields of hexane-soluble oil. The average molecular weight of asphaltene and aromatic oils is also decreased. There is no other major structural change in the heavy oil product of coal hydrogenation. Fractions eluted at the same elution volume show the same properties independent of the catalyst concentrations used to produce the oils.

References

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Table 1
Products from Extraction of Heavy Oil

| | Percent Yield | | |
|-----------------------------|---------------|-------------|-------------|
| | Sample 0.015 | Sample 0.03 | Sample 0.06 |
| Heavy Oil (% of coal) | 25.6 | 31.8 | 31.3 |
| Asphaltene (% of heavy oil) | 17.3 | 6.6 | 6.0 |
| Oil | 34.0 | 63.6 | 62.2 |
| Saturates | 8.9 | 11.9 | 6.9 |
| Aromatic | 91.1 | 88.1 | 93.1 |
| Acidic (% of heavy oil) | 9.5 | 17.4 | 12.9 |
| Basic (% of heavy oil) | 1.5 | 1.8 | 2.2 |
| Residue (% of heavy oil) | 28.4 | 5.3 | 3.3 |
| Loss | 9.3 | 5.3 | 12.9 |

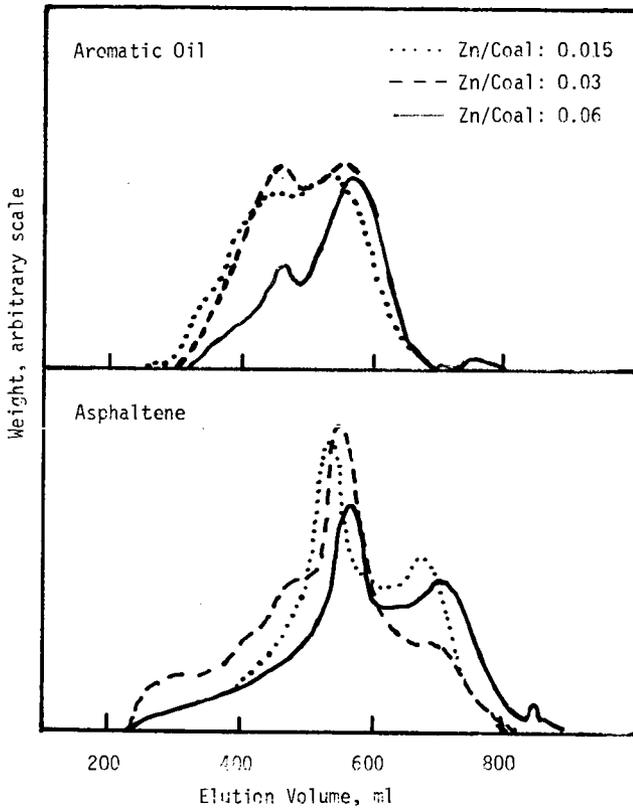


Figure 1. GPC Chromatograms

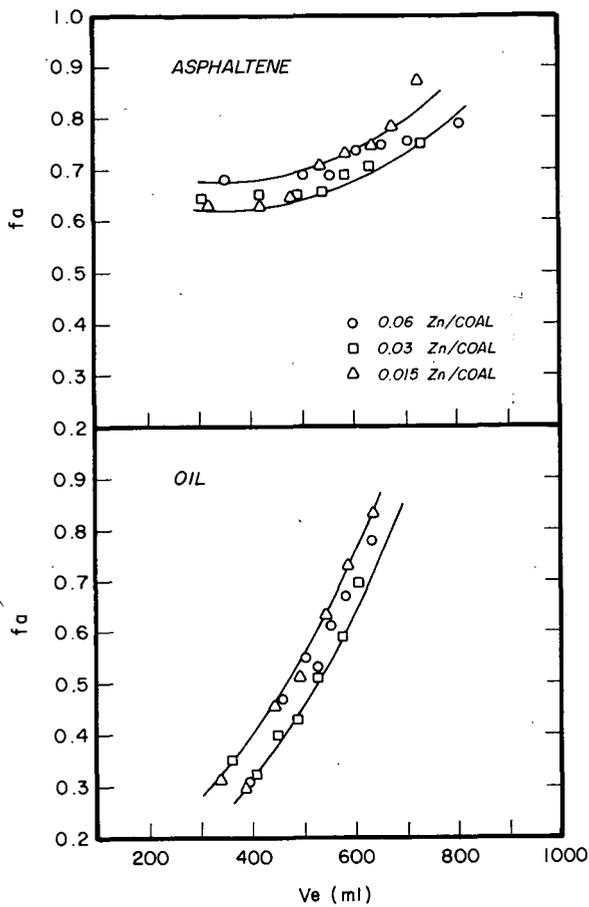


Figure 2. Carbon aromaticity vs. elution volume for oils and asphaltenes.

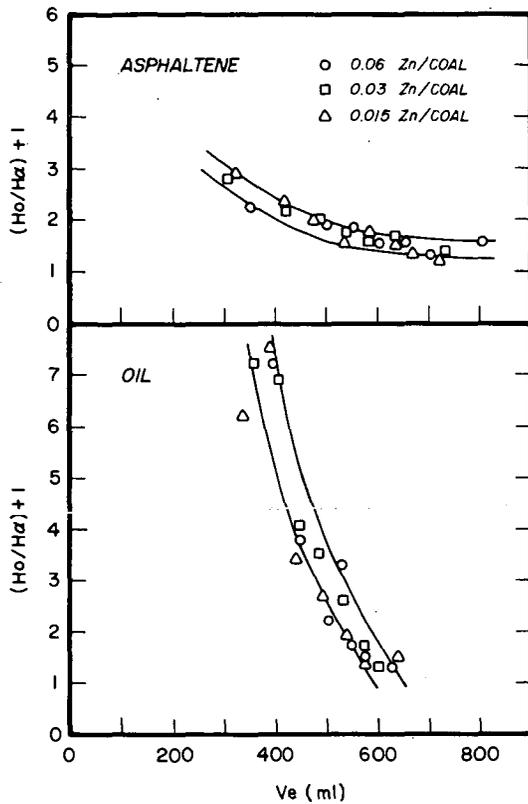


Figure 3. The average length of aliphatic carbon chain vs. elution volume for oils and asphaltenes.

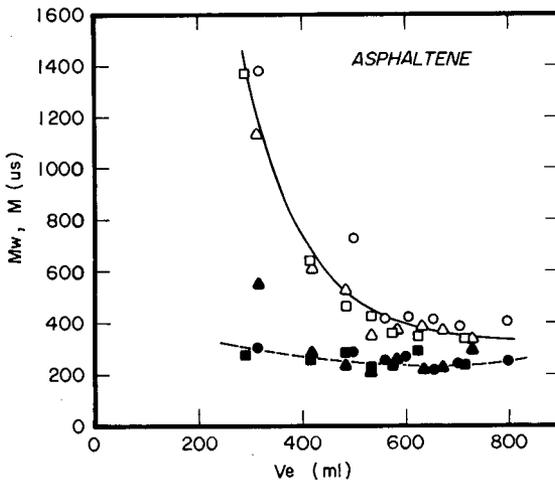
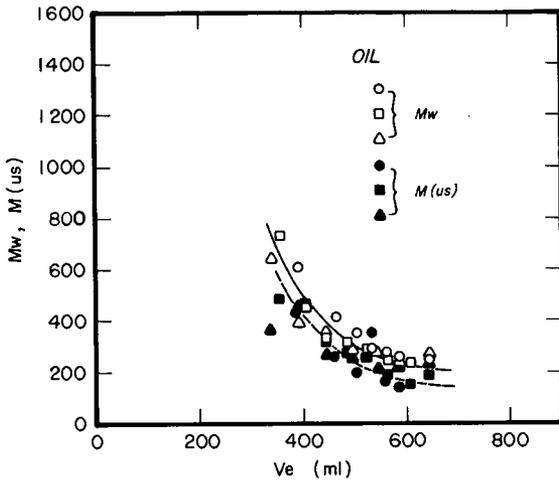


Figure 4. Experimental and calculated molecular weights vs. elution volume.