

REACTIONS OF LOW-RANK COALS WITH PHENOL

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Although the acid-catalyzed reaction of coals with phenol has been investigated for some time, the nature of the products, especially with respect to molecular weights, remains unclear. Heredy investigated the reaction of coals with phenol and boron trifluoride at 100°C, with the objective of selectively degrading the coal macromolecules so that monomeric units could be isolated (1,2). The resulting product from a high volatile bituminous coal was claimed to be soluble to a large extent (61% in phenol). The definition of solubility, however, was simply that the phenol extract was filtered through Celite. The particle size was not measured nor was the absence of a Tyndall effect noted. Molecular weight measurements were carried out on various fractions by ebullioscopic measurements in benzene, benzene-methanol or pyridine. The molecular weight of the phenol soluble material was reported to be 1150 daltons using pyridine ebullioscopy. The chemistry of the reaction is believed to be a transalkylation of the methylene bridging group between two aromatic systems onto a molecule of the phenol. A substantial amount of phenol was chemically incorporated into the products resulting from the treatment.

Stating the same objective as Heredy, Ouchi (3) reacted coals with phenol and p-toluenesulfonic acid as the catalyst at 185°C. Pyridine Soxhlet extraction of the product from a Yubari coal (84.6% C, 6.1% H) resulted in high yields of material. Molecular weights as measured by pyridine boiling point elevation were less than 500.

These acid-catalyzed transalkylation reactions with phenol appear to fragment the macromolecular network of the coals to give extracts which the phenol solvent alone cannot give. The question of the colloidal nature of the extract has been addressed by Larsen (4,5) and Sharma (6). Since the pyridine extracts were found to plug 0.5 micron filters, a significant amount of the material in the extract was colloidal. Centrifugation at 120,000 x g for three hours precipitated the colloidal material. The actual amount of colloidal material present varied with the coal, but was as high as 80%. Gel permeation chromatography of the "truly soluble" material with VPO measurement of collected fractions gave a molecular weight (M_n) distribution which indicated that most of the material had a molecular weight greater than 6000. The early-eluting material appeared to be highly polydisperse, hence the VPO measurements were likely to be inaccurate and overly influenced by the smaller molecular weight material present (7). The conclusion of Larsen was that the soluble products were very large molecules and only limited depolymerization had occurred.

Although Givens's and Larsen's observations and arguments are persuasive, reports of alleged depolymerization continue to appear in the literature. Ouchi (8) has recently claimed to have depolymerized an Australian (Yallourn) brown coal, while advancing the argument that a low-rank coal should behave differently toward the phenolation reaction than the higher rank coals investigated by Larsen. Unfortunately Ouchi did not address the colloidal nature of the products and inappropriately used VPO and size exclusion chromatography for the determination of molecular weights. Thus, his number average molecular weight value of 1120 daltons for the pyridine extract of the product cannot be taken seriously.

The objective of our investigations was to determine the extent to which the cross linking methylene units between aromatic systems are broken down in low-rank coals (Wyodak and Yallourn) during the phenolation reaction with p-toluenesulfonic acid and compare the results with those from the reaction with a bituminous coal. In order to determine the extent of depolymerization, the weight average molecular weight of the products were examined using Rayleigh light scattering. Thus the range of molecular weights above 6000 which were not accessible in Larsen's experiments can be accurately measured with this technique.

EXPERIMENTAL

Phenolation: Wyodak coal (C, 70.9; H, 5.2; N, 0.92; S, 0.60; O, 22.3; maf basis), Yallourn brown coal (C, 69.4; H, 4.9; N, 0.6; S, 0.3; O, 24.8), and Pittsburgh #8 coal (C, 82.0; H, 5.5; N, 2.0; S, 6.8; O, 3.7) were demineralized by heating and stirring for three hours with 1N HCl, filtered and washed with water until free of acid, and dried in vacuum at 110°C for 24 hours. Phenol and p-toluenesulfonic acid monohydrate were heated with the coals according to Ouchi's procedure (8). The reaction products were worked up by distillation in vacuo until the volume was reduced to about one-third. The product was poured into a large excess of water, stirred for 2 hours and filtered. The residue was washed with water until free of acid and steam distilled to remove residual phenol. Last traces of phenol were removed by heating the residue in vacuo at 110°C until constant weight was obtained.

The dried products were extracted with pyridine using Soxhlet extraction under dry nitrogen until there was no color observable in the solvent. The pyridine extract was concentrated to about one third its volume and added to a large excess of 1 N hydrochloric acid and stirred for 3 hours. The precipitate was filtered, washed repeatedly with 1 N hydrochloric acid and then with water until free of acid, and dried in vacuo at 110°C to a constant weight.

Reductive acetylation: The pyridine-soluble phenolation products were reductively acetylated by the method used for humic acids (9). Molecular weight determinations of the reductively acetylated products in THF were carried out as previously described with a KMX-6 low angle laser light scattering photometer (9).

RESULTS

The coals dispersed in the refluxing phenol and acid catalyst (p-toluenesulfonic acid) giving high yields of products. The weight of the product was greater than the weight of starting coal, as described in earlier papers, due to chemical combination of the phenol with the coal. The phenol uptake was inversely proportional to the coal rank. The weight increase for Yallourn brown coal was 86%, whereas the Wyodak subbituminous coal exhibited a 65% weight increase, and for the Pittsburgh #8, a 47% increase was observed.

The infrared spectra of the phenolation products were obtained by photoacoustic spectroscopy and exhibit evidence for the incorporation of phenol; that is, strong O-H, aromatic ring and ether stretching absorptions. The ether stretching absorption could be due to the formation of ethers by a dehydration reaction occurring under these conditions; however, further work is needed to establish the nature of the incorporated phenol in these products.

A large fraction of the phenolated coals became dispersible in pyridine. The phenolation product from Yallourn brown coal was 97% dispersed, the Wyodak product was 87% dispersed and the Pittsburgh #8 products was 84% dispersed. As observed

by Larsen, attempted filtration of the pyridine dispersions using a 0.5 micron Millipore filter resulted in plugging. Thus these products in pyridine should be regarded as organosols or colloids as suggested by Larsen, not as true solutions.

The objective of this study was really to determine the size of the macromolecules making up this dispersion by conversion of the coal-derived material to a soluble form so that we could apply Rayleigh light scattering techniques, which are appropriate for large macromolecules and do not rely on calibration with small molecular species. This knowledge of the molecular weight of the entire fraction of product which is dispersible in pyridine is required for the determination of the extent of depolymerization of the coal in the phenolation reaction. The pyridine dispersed materials were only slightly soluble in THF, a solvent previously used effectively in low-angle laser light scattering photometry (LALLS), and were highly colored, making observation of the Rayleigh scattering difficult.

In order to accomplish the molecular weight determination with LALLS, the pyridine-dispersed material was converted to a less polar and less colored form by reductive acetylation, as we had previously done with the humic acids from lignites. The yields of reductively-acetylated derivatives were nearly quantitative for the phenolation products from all three coals. Photoacoustic infrared spectra of these derivatives indicated complete absence of the hydroxyl stretching absorption and the presence of strong ester carbonyl absorption.

The reductively-acetylated material dissolved completely in THF and the resulting solution could be filtered through a 0.2 micron filter and did not exhibit the intense flashing (Tyndall effect) of the laser light by dispersed particulate matter. The THF solutions of the reductively-acetylated phenolation products had a lower molar absorptivity than the original phenolation products and the Rayleigh scattering could be easily observed.

Rayleigh scattering factors were measured for the dilute THF solutions of the reductively acetylated phenolation products, and corrected by means of the Cabannes factors which were determined for each of the solutions used. These corrected Rayleigh factors gave a linear reciprocal scattering plot (Kc/R_0 vs. c) with an r^2 of 0.99 for the coal derivatives. The weight average molecular weight of the reductively acetylated Wyodak product was 1.67 million daltons, as determined from the intercept of the reciprocal plot. The slope was positive ($A_2 = 3.0 \times 10^{-3}$). The reductively acetylated phenolation product from the Yallourn brown coal had a molecular weight of 2.26 million daltons ($A_2 = 1.3 \times 10^{-3}$). The weight average molecular weight of the reductively acetylated phenolation product from the Pittsburgh #8 was 2.23 million with an A_2 of 4.6×10^{-3} .

DISCUSSION

Molecular weight determinations of derivatives of the phenolation products from both high and low rank coals gave high values in the light scattering determination. These reductively acetylated derivatives of the phenolation products gave true solutions in THF as defined by their ability to pass a 0.2 micron filter and the lack of a Tyndall effect in the laser beam. Furthermore the phenolation products were completely converted to this soluble form by the reductive acetylation, so the entire sample is being examined in the light scattering experiment. This contrasts with the Larsen experiment which separated the dispersed material out by ultracentrifugation and examined the soluble material by VPO, whose limitation in determining the high molecular weight material was discussed by Larsen. Ouchi (8) defined solubility as the lack of a

residue; this does not distinguish a true solution from a colloidal dispersion, and his molecular weight measurements are subject to the same limitations as Larsen's.

Because of the high molecular weights obtained, we conclude that both the low and high rank coals were not extensively depolymerized in the phenolation reaction. The reaction serves to cleave cross-linking bonds to create some mixture of soluble and dispersed particles, probably in the submicron range as in the dispersion obtained by treating Wyodak coal with sodium hydroxide. Thus cleavage of the guaiacyl ether linkages and possibly some activated methylene bridges will accomplish this limited digestion of the coal structure which does not amount to depolymerization or solubilization. Since the coal may not consist of repeating polymer units, perhaps a better generic term for the phenolation reaction is limited digestion or degradation.

The differences in the weight average molecular weights of the three coals may not be significant with respect to the coal structures, since extensive rearrangements of bonds and chemical adduction of phenol occurred in addition to cleavage of labile benzyl ether groups and methylene bridges between the aromatic systems. This complex reaction does not really allow us to count branch points or cross-links that are broken. One must proceed to other synoptic reactions to elucidate the types of cross links or branch points in these coals.

The differences in the second virial coefficient (A_2) obtained from the slope of the reciprocal Rayleigh plot for each coal phenolation product can be attributed to the differences in the Cabannes factors for the coal derivatives. The slope of a Cabannes factor vs. concentration plot is proportional to the coal rank; that is, the Cabannes factors increase more with concentration for the Pittsburgh #8 derivative than they do for the Wyodak, which in turn increase more than the Yallourn derivative. Thus, at higher concentrations the Rayleigh factors are more corrected and therefore proportionately smaller for the Pittsburgh #8 product, and the slope of the reciprocal plot is therefore greater. The high Cabannes factors are probably due to the presence of larger polynuclear ring systems in the product from the bituminous coal which result in greater anisotropic scattering.

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