

DISSOLUTION OF THE ARGONNE PREMIUM  
COAL SAMPLES IN STRONG BASE\*

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INTRODUCTION

The objective of this study is to solubilize the Argonne Premium Coal Samples in order to facilitate analysis by mass spectrometry, FTIR and NMR. Earlier, in a search for relatively mild methods for solubilizing coal, we discovered that treating coals with potassium hydroxide in ethylene glycol at 250°C to be quite an effective approach.<sup>1</sup> Under these conditions, secondary reactions which may obscure the distribution of the basic building blocks of the coal structure are not expected to occur. At higher temperatures, such as those used in more traditional liquefaction processes (> 400 °C), secondary reactions such as the formation of polycyclic aromatic and heteroaromatic compounds dominate.

A focus of our approach to characterization of coals is desorption-pyrolysis high resolution CI and EI mass spectrometry and laser desorption mass spectrometry (LDMS). It has been shown by PyMS that the yields and the distribution of products is superior for coal extracts compared to the original whole coals.<sup>2,3</sup> There appears to be few secondary reactions occurring and many molecules, which are released in analysis of the extract, are trapped in the solid matrix of the coal and never observed. In addition, soluble materials are more amenable to LDMS.<sup>4</sup>

The glycol/KOH system was chosen since in early work up to 93% of the product was soluble for lower-rank bituminous coals.<sup>1</sup> Others have solubilized coals under basic conditions. Ouchi and co-workers<sup>5</sup> used ethanolic - NaOH at temperatures ranging from 260 °C to 450 °C. More recently, Stock and co-workers have discussed the use of Lochmann's base (potassium tert-butoxide, n-butyl lithium in heptane at reflux) which is especially effective for the higher rank coals.<sup>6,7</sup> Also, a base hydrolysis is included in a low severity liquefaction scheme devised by Shabtai and co-workers.<sup>8</sup>

Table VII-1. Elemental analyses for the coal samples.

Sample	Name	%C (dmmf)	H	Per 100 Carbons		
				N	S	O
8	Beulah-Zap Lignite	74.1	79.5	1.35	0.36	20.9
2	Wyodak-Anderson SubB	76.0	85.6	1.28	0.23	18.0
3	Herrin hvCB	80.7	77.2	1.51	1.15	13.0
6	Blind Canyon hvBB	81.3	85.7	1.67	0.17	10.8
4	Pittsburgh hvAB	85.0	76.7	1.69	0.40	7.96
7	Lewiston-Stockton hvAB	85.5	76.3	1.62	0.30	8.93
1	Upper Freeport mvB	88.1	66.0	1.55	0.32	6.59
5	Pocahontas lvB	91.8	58.5	1.25	0.21	2.04

## EXPERIMENTAL

The following procedure was applied to all eight of the Argonne Premium Coal Samples. Approximately 20 g of coal was stirred in 100 ml concentrated HCl and 100 ml 48% HF under a N<sub>2</sub> atmosphere in a teflon container for at least 48 hours. After dilution to 1.5 l with distilled water, it was filtered through acid-hardened filter paper, the residue was washed off the paper and, subsequently, filtered through a sintered glass funnel, washed acid-free and vacuum dried at 100 °C for 16 hours. An ash determination was made on the dried product.

The demineralized coal was refluxed in pyridine for 10 hours. After cooling, the residue was separated by centrifuging and decantation. The residue was stirred in 5% HCl heated to 80°C for 2 hours, filtered, washed acid-free with distilled water, then methanol and, finally, vacuum dried at 100 °C for 16 hours. The pyridine solution was roto-evaporated to dryness and the pyridine soluble material was treated in the same manner as the insoluble; hot 5% HCl but no methanol rinse.

Ten grams of the pyridine extracted residue was added to a 100 ml solution of 10 g KOH and dissolved in ethylene glycol in a 300 ml stirred Parr reactor. The reaction mixture was heated to 250 °C for 2 hours and cooled. After dilution to 1 l, the mixture was heated to 60 °C and filtered, washed alkaline-free, and the residue vacuum dried at 100 °C for 16 hours.

The residue was then successively extracted by refluxing for 2 hours in hexane, 1:1 benzene-methanol, and pyridine. The filtrates were roto-evaporated to dryness and vacuum dried at 60 °C for 16 hours. The pyridine soluble and insoluble residues were washed as described above with 5% HCl and vacuum dried at 100 °C for 16 hours.

## RESULTS AND DISCUSSION

The solubility yields from the KOH in glycol reaction are shown in Figure 1. The pyridine soluble yields are a combination of the yield of pyridine solubles prior to the reaction added to the pyridine solubles produced during the reaction of the extracted coal. This reaction produces (typically less than 1%) of very small, non-polar molecules which would be soluble in hexane. Indigenous molecules of this type would have been removed prior to the reaction by the initial pyridine extraction. Apparently, the extensive bond breaking which occurs at higher temperatures such as in pyrolysis and liquefaction is not taking place under those reaction conditions. In addition, the recovery weights were very close to 100% for all of the samples. Very little sample weight was lost to small molecules or gained from the addition of the solvent to the products.

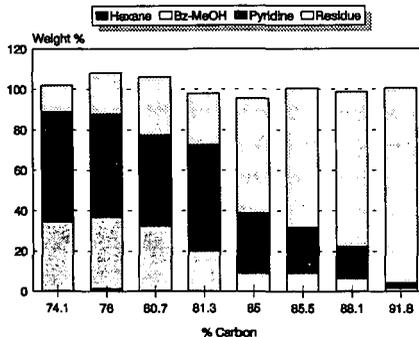


Figure 1. Yields from the ethylene glycol-KOH treatment of the Argonne Premium Coals.

A much more definitive trend is seen for the decrease in soluble product yields as a function of increasing rank than in the previous study.<sup>1</sup> In the original study, surprisingly, only 60% of the lignite products were soluble. However, this lignite coal was highly oxidized and had not been stored under premium conditions as is the case with the present samples. This procedure is obviously very effective for the lower rank coals. There are significant yields of benzene/MeOH solubles in the three lowest rank coals. These mixtures are typically much more amenable to characterization than the pyridine extracts.

There is good correlation with oxygen content as is shown in Figure 2. This is expected since it is likely that cleavage of ether linkages is one of the important mechanisms of solubilization. The Utah coal is much more reactive than expected from its oxygen content. However, this coal tends to be much more reactive than one would expect from its rank, such as in vacuum pyrolysis.<sup>2</sup> Also, this result implies that oxygen functionality is only partially responsible for the mechanisms of solubilization for this reaction.

The Lochmann's base reaction yields the opposite rank trend compared to the KOH/glycol approach. For the subbituminous coal, which has been methylated, the pyridine solubility increases only to 44% from 35%,<sup>6</sup>

while for the high rank Pocahontas coal (APCS 5), pyridine solubility increases dramatically from 2.5% to 55% upon treatment with the base.<sup>7</sup> These results suggest that these two different base treatments can be used in parallel to produce a very soluble set of samples for the complete set of Argonne Premium Coal Samples. Mass spectral data from both LDMS and DCIMS, along with FTIR data, are being analyzed for this complete set of samples from the KOH glycol solubilization.

#### ACKNOWLEDGMENT

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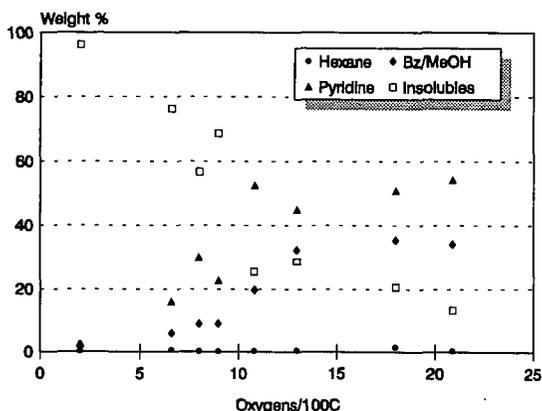


Figure 2. Yields as a function of oxygen content for the ethylene glycol-KOH reaction.

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