

## CONVERSION OF LOW-RANK COALS AND LIGNINS TO PHENOLIC PRODUCTS BY CATALYTIC HYDROGENOLYSIS IN AQUEOUS BASE

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### INTRODUCTION

Direct methods of coal conversion to liquids have been studied in depth since the initial experiments were conducted in the late 19th century; however, the identification of methods to lower reaction severity has been slow. Earlier work, as discussed by Schobert,<sup>1</sup> successfully achieved conversion to liquids using very high reaction temperatures and hydrogen pressures (>450 °C and >5000 psi). Reactions at somewhat lower severity (i.e., lower temperature and pressure) were achieved by the use of various catalysts and solvents. These catalyzed reactions can occur at ~400-425 °C and hydrogen pressures (initial) of ~900-1000 psi (2500-3000 psi at temperature) in 30-60 minutes. Even under these reaction conditions, economic viability in today's petroleum market still has not been achieved. Researchers continue to seek avenues to further reduce reaction severity.

Some research has shown that for lower rank coals, particularly lignites, reaction severity can be reduced.<sup>2-6</sup> It is thought that the mechanism that drives coal reactions in the 350-450 °C range is the thermolysis of C-C bonds and particularly C-O bonds; lower rank coals contain more oxygen functionality, and therefore, these coals tend to react at the lower end of this temperature region because C-O bonds are weaker than C-C bonds. Derbyshire, *et al.*,<sup>2,3</sup> and Jackson, *et al.*,<sup>7,8</sup> have achieved conversions of ~90% for low rank coals when using various hydrogenation catalysts (Ni/Mo) at lower reaction temperatures of ~400 °C and reaction times of 30-60 min. Understanding the complexity of the macromolecular structure and the mechanisms of liquefaction of low-rank coals is important in order to optimize the production of valuable liquid products. The main limitation to lowering the reaction severity of coal liquefaction processes is identifying a reaction method that is not completely dependent on the thermolysis of C-C and C-O bonds for depolymerization.<sup>2-6</sup> Lewis acids (e.g., SnCl<sub>4</sub>, ZnCl<sub>2</sub>) do accomplish coal cleavage at slightly lower temperatures (~350 °C and 1 h reaction time).<sup>9-14</sup> Unfortunately, large quantities of catalyst must be used and the chlorides in these compounds cause significant reactor corrosion.<sup>9-14</sup>

The present primary energy project at UTPB relates to the reductive depolymerization of biomass polysaccharides to C<sub>5</sub> and C<sub>6</sub> hydrocarbons.<sup>15</sup> Since coal essentially represents a degraded biomass, it is envisioned that the reactions used to fractionate biomass into polyols and lignins, and to further react the latter, might be equally successful when applied to low rank coals. The reaction conditions initially employed were based on Russian reports of sequential catalytic hydrogenolyses in acid and base. This was done to first convert carbohydrates to C<sub>5</sub> and C<sub>6</sub> polyols at 185 °C and 700 psi (initial) and then lignin into phenolic materials at 280-320 °C and 700-900 psi hydrogen (initial), respectively.<sup>16</sup> Because of the very high conversions of raw biomass by the "biomass-to-polyol" process and because of some similarities in the structures of lignin and lignites, we expected similar sequential reactions could have a significant effect on the conversion of low rank coals to liquids. We chose to focus on the base hydrogenolysis omitting a prior acid hydrogenolysis, as this step had the greatest effect on the lignin in biomass.<sup>16</sup> This paper focuses on reacting DECS-1 coal and lignin at 240, 270, and 300 °C, 700 psi (initial) for 6 h in NaOH solution and subsequent characterization of the products by solution NMR and pyrolysis-GC/MS.

### EXPERIMENTAL

The coal was obtained from the Pennsylvania State University Coal Sample Bank (COPL), denoted by DECS-1. The coal rank of DECS-1 as determined by the COPL is subbituminous C. Elemental analysis for the coal and the solids (acids) from the NaOH-solubles was done by Galbraith. For the coal, the elemental analysis was carbon % (C) - 58.7, hydrogen % (H) - 4.7, nitrogen % (N) - 1.0, sulfur % (S) - 1.2, and oxygen % (O) (by difference) - 18.1. The ash content is 16.3%. The lignin used is a commercial hydrolytic lignin obtained from Aldrich Chemical Company.

Reactions of coal with NaOH were carried out in a 1-gallon Parr stirred autoclave. The reactions were run at 240, 270, and ~300 °C under 700 psi hydrogen (initial) atmosphere using a carbon-supported ruthenium catalyst (Ru/C) purchased from Aldrich (5% Ru). About 20 g of coal or lignin was loaded with 2 g of catalyst (Ru/C) and 2 L of 1.5% (wt) NaOH. Reactions were run at the designated temperature for ~6 h although initial heating and final cooling of the reactor could take

several hours depending on the final temperature. The contents of the reactor were filtered and the solid washed with water to remove all of the base (until pH ~7).

Figures 1 and 2 are schematics of the procedure used to extract all of the soluble organic products resulting from the reaction. Neutral oils were obtained by washing the initial solids and aqueous layer (including rinse water) with methylene chloride  $\text{CH}_2\text{Cl}_2$  (see Figure 1). The NaOH-solubles were acidified with concentrated  $\text{H}_2\text{SO}_4$  to pH ~2 and heated to ~80°C to promote coagulation and filterability; the precipitated solids (acids) were then filtered (see Figure 2). All the solids from the initial filtration procedure and the acidic solids were extracted (using sonication) with  $\text{CH}_2\text{Cl}_2$  followed by extraction (using sonication) with tetrahydrofuran (THF). The percent conversion was determined from the difference between the initial weight of the dry coal and catalyst and the final dry weight of solid residue and catalyst, per initial amounts.

All organic products were analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  solution NMR. Samples were dissolved/filtered in chloroform ( $\text{CDCl}_3$ ) or dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) and spectra obtained by a Bruker 250 MHz Avance DPX NMR.

Pyrolysis-GC/MS was performed with a Hewlett Packard (HP) 18580A pyroprobe interfaced to a (HP 5890/5970) GC/MS. Chromatography was carried out on a 25 m x 0.22 mm i.d. x 1.0  $\mu\text{m}$  film thickness column coated with a BPX5 phase (modified to 5% phenyl siloxane). The GC oven temperature was programmed to increase from 40°C, initially held for 2 min., at a rate of 4°C/min to 300°C (maintained for a further 30 min). The samples pyrolyzed were the DECS-1 raw coal and the solids (acids). On pyrolysis at 850°C about 55-60% of both samples was vaporized.

## RESULTS AND DISCUSSION

### *Percent of Coal Extracted*

Figure 1 is a schematic of the initial treatment of reactor contents, whilst Table 1 shows the total conversion and the material balance information. For all reactions, >90% of the organic matter from DECS-1 was extracted and/or dissolved. About 85-95% of the coal was extracted into the aqueous base solution. As the temperature increases, then the amount of coal extracted into the aqueous base slightly decreases. For reactions at 240 and 270°C, the other materials extracted from the remaining catalyst/organic/ash residue ( $\text{CH}_2\text{Cl}_2$ - and THF-soluble compounds) amounted to about 4-5%. However, at 300°C, the  $\text{CH}_2\text{Cl}_2$ - and THF-soluble compounds increase to 15%. This suggests the reaction chemistry is indeed changing with increasing temperature and this may account for the higher proportion of neutral compounds and less of the acidic compounds at higher temperature, i.e., more thermolytic reduction (see Table 1).

Figure 2 is a schematic of the product work-up of the NaOH-solubles. Table 2 shows a breakdown of the product into fractions. The NaOH-solubles were acidified with  $\text{H}_2\text{SO}_4$  to a pH of ~2. The solution then formed a dark brown precipitate that was briefly digested (to coagulate solids) at 80°C before filtering. The remaining filtrate was a clear, pale yellow solution with a strong phenolic odor. The 240°C reaction had the highest percent NaOH-solubles, 95%, with 49.7% solids and 45.8% (determined by difference) of material either left in solution or gaseous reaction products. At 270°C, a lower amount of coal was solubilized by the base, 87.5%, but a much greater proportion, 72.7%, were solids. At 300°C, only 84.5% of the coal was solubilized by the base, but only 34.9% precipitated out. Since the majority of the coal was extracted into the base solution, determining the product character of this fraction is important in understanding the reaction chemistry. However, elucidation of the composition of both the solid and water-soluble materials has proved to be complicated and is to-date not complete. Clearly, phenols (A2 acids) and carboxylic acids (A1 acids) would be expected to be dissolved into aqueous base but polyfunctional compounds remain in the water layer even after neutralization. The variability in the ratio of precipitated acids versus water-soluble compounds is also being addressed. Results from the present methods of analysis are outlined below.

### *NaOH-soluble Products*

Most of the work completed has been done on the 240°C reaction solids from the acidification of the base solution. The elemental analysis of the NaOH-soluble solids from the 240°C reaction is 64.7% C, 5.4% H, 1.4% N, 1.2% S, 1.1% ash, and 26.2% O (by difference). The H/C ratio is 1.0 and the O/C ratio is 0.3, compared to the coal H/C, 0.98 and the O/C, 0.23. The H/C of the product is essentially the same as the coal whilst the O/C ratio is significantly higher than that of the coal, suggesting at 240°C hydrolysis mostly accounts for the strong oxygen increase and not much hydrogenation has occurred. In fact, more hydrogen is consumed at higher temperature.

None of the solids (acids) proved soluble in  $\text{CH}_2\text{Cl}_2$  or other less polar solvents. The material is therefore thought to be very polar and possibly also of very high molecular weight, albeit a reduction of the large macromolecules in the coal to smaller oligomers is anticipated. Solution GC/MS analysis revealed little molecular information from the solid NaOH-soluble product. This material did prove soluble to varying degrees in THF, DMSO, and pyridine. Solution  $^1\text{H}$  NMR was obtained using the

polar solvent DMSO-*d*<sub>6</sub>. The <sup>1</sup>H NMR is shown in Figure 3 (a). The main feature of the proton NMR is the noticeable -OH or -CH-O- functionality. Unfortunately, the concentration of this solution was not high enough for <sup>13</sup>C NMR detection.

Figure 3 (b) and (c) shows the pyrolysis-GC/MS of DECS-1 coal and of the solid product from the NaOH-solubles. Significantly fewer aliphatic and large aromatic compounds are detected from the NaOH-solubles than from the parent coal. These compounds may be present in a different fraction obtained by extraction with other solvents. The compounds in the pyrolysis-GC/MS of the NaOH-soluble product have been identified as predominantly alkylated aromatic compounds with or without -OH functionality. Work will be continued to more accurately determine the structure and/or molecular weight of the NaOH-soluble solid products and will likely include direct MS of the solids with chemical ionization and gel chromatography for polymer size distributions.

The liquids that remain in the water have not yet been completely isolated. Following exhaustive extraction with CH<sub>2</sub>Cl<sub>2</sub>, some color and odor remained in the water indicating that not all of the organic was extracted. Work continues to more efficiently extract the compounds from the water so as to complete the material balance. Once released these products will also be analyzed by GC/MS. Organic acids and alcohols will first be derivatized to less polar and more volatile esters. Several derivative methods are being screened, e.g., acetylation according to Thring *et al.*<sup>17</sup>

### Comparative Reactions

As stated earlier, these reactions of coal were suggested as an extension of lignin reactions in the literature, so a comparative reaction with lignin was done under these conditions. In our case, however, as noted in Tables 1 and 2, less lignin reacted than the coal reaction at 240 °C. Lignin reactions at higher temperatures are also planned.

The amount of coal extracted under these reaction conditions is remarkable as most reactions at these temperatures produce little if any product. For example, Garcia and Schobert<sup>18</sup> showed with coals of high organic sulfur content that about 8.8 % THF-soluble material could be extracted at 250 °C. This increases up to ~50 % at 325-350 °C when using a molybdenum catalyst in a hydrogen atmosphere (the reactor used in this case was a "tubing bomb" type and caution in comparing this to a stirred autoclave must be noted). Most coal liquefaction reactions produce high conversions at 400-450 °C, and most of the product is composed of lighter molecular weight materials than produced in the reactions reported here. One research group, Hulston *et al.*,<sup>7,8</sup> used NaOH or NaAlO<sub>2</sub> combined with a hydrogenation catalyst (Ni/Mo) at 365 °C to produce significantly higher conversions to CH<sub>2</sub>Cl<sub>2</sub>-soluble products than when using the Ni/Mo catalyst alone, but the increase in conversion is noted with low-rank coals only. It is also expected for our reaction conditions that coals of rank higher than subbituminous will not convert as easily because of the significantly lower oxygen content of bituminous and anthracite coals. While the ultimate goal of high conversion efficiency of coal into small phenolic liquids has not yet been achieved, a significant amount of liquefaction and a remarkably high conversion to more soluble/extractable products (with little mineral matter left in the organic material) has been realized. Further analytical data are required to show the extent of conversion to small (liquid) molecules.

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Table 1: Conversion information for reactions of DECS-1 and lignin.

Temp °C <sup>a</sup>	Feed	Reactor Load (g)	% NaOH-solubles <sup>b</sup>	% Other <sup>c</sup>	Total	Psi
240	DECS-1	20	95.5	4.7	100	700
270	DECS-1	20	87.5	5.7	93.4	700
306	DECS-1	20	84.2	15.8	100	500
240	Lignin	20	78.9	9.0	87.9	700

- a All reactions were 6 h at temperature shown; does not include ramp times.
- b Includes any gas that may have been generated because this is determined by difference.
- c Methylene chloride-solubles + tetrahydrofuran-solubles.

Table 2: Yield information for the NaOH-soluble portion of the coal. This fraction was acidified with H<sub>2</sub>SO<sub>4</sub> to a pH of about 2 and solids filtered out (see Figure 2 for flow diagram).

Temp °C <sup>a</sup>	Feed	% NaOH-solubles <sup>b</sup>	% Solids	% H <sub>2</sub> O-solubles <sup>c</sup>	Total
240	DECS-1	95.5	49.7	45.8	100
270	DECS-1	87.5	72.7	14.8	93.4
306	DECS-1	84.2	34.9	49.3	100
240	Lignin	78.9	31.5	47.4	87.9

- a All reactions were 6 h at temperature shown; does not include ramp times.
- b Includes any gas that may have been generated because this is determined by difference.
- c H<sub>2</sub>O-solubles are the compounds that remain in solution but also includes any gas that may have been generated.

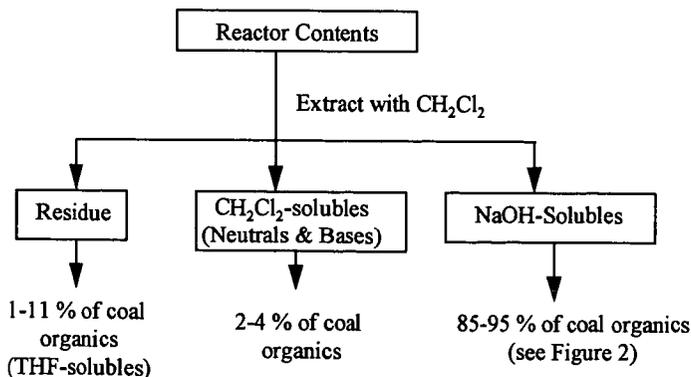


Figure 1: Initial product work-up of coal from reactor. The residue also contains ash and recovered Ru/C catalyst.

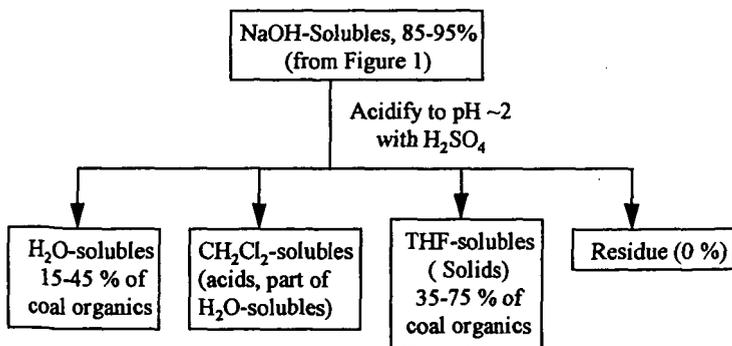


Figure 2: Schematic of product work-up of the aqueous NaOH fraction, the major portion of the coal.

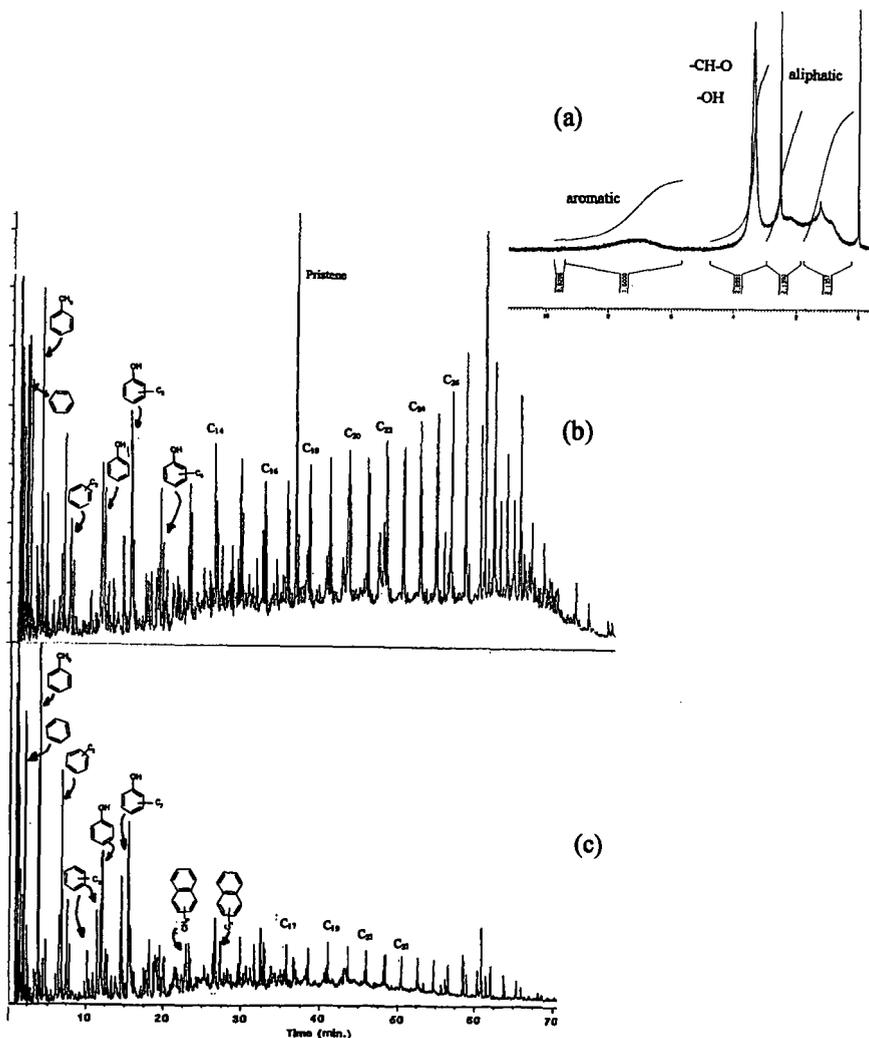


Figure 3: Spectra for: (a) <sup>1</sup>H NMR of NaOH-soluble solids (acids), (b) pyrolysis-GC/MS of DECS-1, and (c) pyrolysis-GC/MS of NaOH-soluble solids (acids).