Transactions of the Illinois State Academy of Science
(1983), Volume 76, 1 and 2, pp. 237-245

Water Solubilization of North Dakota Lignite Via Reductive Carboxylation

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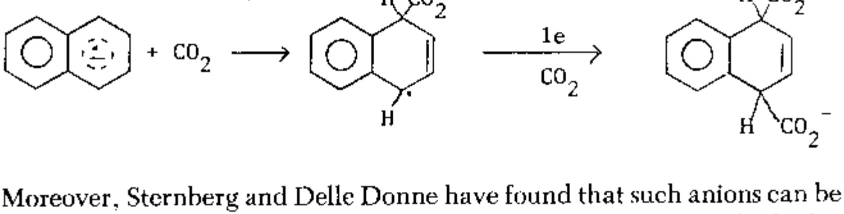
ABSTRACT

The reductive carboxylation of North Dakota lignite was accomplished using an autoclave to react lignite with potassium metal under various temperature and solvent systems. The characterization of the alkali-soluble acids generated and the insoluble residue was accomplished by several titrometric techniques as well as elemental analyses.

INTRODUCTION

The solubilization of coals in alkaline aqueous solutions has been reported for the high pressure reaction of Illinois Bituminous #6 coal with sodium metal in the presence of carbon dioxide. Such solubilization was attributed to the substitution of carboxyl ($-CO_2H$) groups onto the various aromatic structures which comprise coal (Duty, 1981). These carboxyl groups may be substituted onto aromatic rings through two main pathways — direct reaction and Kolbe-type reactions.

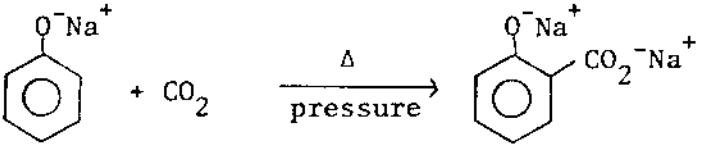
The use of alkali metals such as sodium or potassium for the generation of radical anions in aromatic systems has been known for many years. Wawzonek showed that these radical-anions react with carbon dioxide in aprotic solvents to produce a carboxylated aromatic structure by the production of 1,4-dicarboxy-1,4-dihydro-naphthalene from the naphthalenide anion (Wawzonek, 1959) as shown below:



(1)

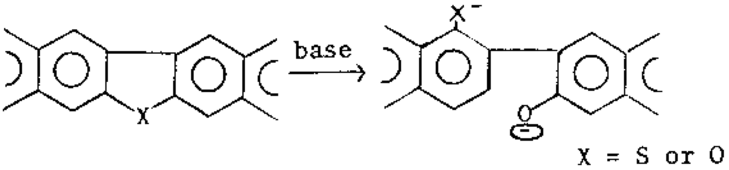
Moreover, Sternberg and Delle Donne have found that such anions can be produced in coal by reduction of the coal with potassium metal in tetrahydrofuran (THF) using naphthalene as an electron-transfer agent. These anions were alkylated by treatment with ethyl iodide (Sternberg, 1974). Therefore, upon generation of such radical anions in coal, it seems likely that direct reaction of these with carbon dioxide is likely to occur.

The Kolbe reaction, which was reviewed by Lindsey (Lindsey, 1957), has been known for over 100 years is shown below. Such reactions involve substitution by a carboxyl group ortho to an existing phenolic group as follows:



(2)

Such phenolic groups have been shown to occur in many types of coal, including North Dakota lignite (Blom, 1957). Furthermore, such sites may be formed by cleaving various ether linkages present in coal with alkali metals. These reactions have been experimentally substantiated by Sternberg, *et al.* (1974). Phenolic groups may also be formed by cleaving dibenzothiophene and dibenzofuran structures which are also found in coals (Hayatsu, 1975) as follows:



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Whether by direct reaction with carbon dioxide or through phenolic intermediates or both, North Dakota lignite can be expected to generate a substantial amount of water-soluble acids.

MATERIALS AND METHODS

Reduction and Carboxylation of North Dakota Lignite

Ten grams of solvent-refined North Dakota lignite (200 — 250 US mesh) was dried at 100°C for 2 hours. Approximately 10 g of potassium metal was cut and weighed in a drybox under a nitrogen atmosphere desiccated by P_2O_5. In the solvents toluene and tetrahydrofuran, 10.000 g of biphenyl was added as the electron transfer agent. The biphenyl and coal were placed in an Autoclave Engineers Model WP-5000 autoclave equipped with a 900 rpm steel paddle stirrer. The potassium was covered with solvent and transferred to the autoclave. Table 1 summarizes reaction conditions including solvent, temperature, gases employed, and length of reaction. The autoclave was sealed and purged with nitrogen gas. Reactions 3-5 were not purged with nitrogen but were purged and pressurized immediately with carbon dioxide. The thermocouple which controlled the temperature was inserted into the autoclave body. After the reaction was complete the autoclave was cooled and the contents removed. Isopropyl alcohol (500 ml) was added to the autoclave to decompose any unreacted potassium, and the mixture was stirred for approximately 30 minutes. The contents were removed and this solution was rotary evaporated to remove solvents. The autoclave was washed also with 5% aqueous potassium hydroxide. This was saved for later use as the basic reflux solvent for solubilizing the black acids.

Separation of Biphenyl and Neutral Compounds from Lignite

The dried autoclave contents were refluxed for 3-6 hours with 750 ml of a 3:1 (v/v) mixture of ether/benzene. The insoluble materials from this reflux were separated by centrifugation using a Sorvall SS-3 Model GLC-1 high-speed centrifuge (10,000 rpm). These were dried and weighed. The ether/benzene solution was collected and the volume was adjusted to 1.000 l. Ten ml of this was taken for HPLC analysis of recovered biphenyl. The remainder was rotary evaporated, dried, and weighed to determine the amount of neutral compounds.

Separation of Acids from Water-Insoluble Residue

The ether/benzene insolubles were placed in a 1.00 l boiling flask and refluxed for 3-6 hours with the 5% KOH solution (0.500 l) which was used to wash the autoclave. The insoluble material remaining was isolated by high-speed centrifugation, dried, and weighed. The supernatant solution was acidified by Congo Red with concentrated HCl. Acids, which precipitated slowly from the acidified solution, were collected by centrifugation, washed several times with distilled water, dried, and weighed. The pH of the final supernatant was adjusted to 7.0 using potassium carbonate. It was extracted with three-200 ml portions of ether, which were dried with $MgSO_4$. The ether was evaporated, leaving amphoteric compounds which were weighed.

Equivalent Weight Determination of Black Acids

Approximately 1 N NaOH was standardized by pH titration with 1.000 N HCl using a Sargent Welch Model HG Automatic Titrator. About 0.25 g of acid sample was weighed to within ± 0.0001 g and dissolved in 10.00 ml of the standardized 1.000 N NaOH solution. This was degased for one hour with N_2 in a vessel previously described (Duty, 1978) and titrated with the 1.000 N HCl. From the difference between the blank NaOH curve and those of the acids in NaOH, the equivalent weight of the acid sample could be determined. The accuracy of the method was determined by finding the equivalent weight of 1,2,4-benzene-tricarboxylic acid, which has an equivalent weight of 70.

Total Acidity and Carboxyl Group Tests

The total acidity of each water-insoluble residue was determined as outlined by Schafer (1970). This was accomplished by stirring the sample (about 0.250 g) in a solution 0.200 N in barium hydroxide and 0.800 N in barium chloride. The residue was separated from the supernatant by filtration under nitrogen, and the residue was washed with a solution 0.1 N in barium chloride and 0.03 N in sodium hydroxide. After washing with distilled water, the residue was boiled for twenty minutes in 20.00 ml of 0.495 N perchloric acid. After filtration, the residue was discarded and the filtrate was diluted exactly to 250.0 ml in a volumetric flask. Twenty ml of this solution was back-titrated using 0.108 N barium hydroxide connected to the Sargent-Welch titrator previously described. All handling of solutions was carried out under a blanket of nitrogen. From the titration data, total acidity as meq/g was calculated.

Carboxyl group determinations were conducted according to the procedures established by Schafer (1970). About 0.25 g of sample was weighed and placed into a 250 ml boiling flask into which was added 100 ml of a 1 N solution of barium acetate. The pH of this solution was adjusted to 8.25 using 0.108 N barium hydroxide. After 4 hours of refluxing under nitrogen, the solutions were titrated back to the endpoint of 8.25 using the titrator and base previously used. From the titration data, carboxyl groups per gram were determined. Phenolic group content was obtained by the difference between total acidity and carboxyl group values for each sample.

Elemental Analysis of Water-Insoluble Residues and Black Acids

The ash content of each sample was determined by accurately weighing about 0.2 g of the sample into previously dried and weighed crucibles. These samples were ashed in a Thelmco Model GRP muffle furnace at 850°C for 4-6 hours. Percent ash was calculated by weighing the crucible after ashing and finding the weight of ash.

The elemental analyses of acids and residues were conducted by the Micro Analysis Corporation of Wilmington, Delaware. Percent (weight) carbon, hydrogen, nitrogen, and sulfur were obtained. The sum of these plus the ash content were assumed to be the total elemental content except for oxygen. Percent oxygen was obtained by subtracting this sum from 100%.

RESULTS AND DISCUSSION

The overall extent of solubilization in the various reactions was expressed as percent solubility. This quantity was defined as the weight percent of the original lignite for which the insoluble residue did not account. These values are given as well as the material balances of the five reactions in Table 2.

The variations encountered with lignite as a substrate under the reaction conditions are well illustrated by the range of percent solubilities seen in Reactions 3-5. Also, the choice of solvent plays a minor role in percent solubility. In reaction 1, which was carried out in tetrahydrofuran (THF), the percent solubility was 57.8%. In reaction 2, the lignite showed the highest solubility, but this probably was due to the increase in temperature. Chiri (1981) reported an increase in percent solubility of 18.9% from 100°C to 200°C for bituminous coal (Ill. #6) in the solvent toluene. Reactions 3-5 gave a mean percent solubility of 45.1 ± 2.9% and were carried out in toluene (Lavin, 1982).

The greatest amount of direct evidence for carboxylation is the actual isolation of black acids from aqueous alkali extract of the reactions. Furthermore, the material balances all show an increase in weight of coal products from the original starting lignite. The primary reason for this weight gain is uptake of CO_2 and the subsequent incorporation of this into carboxyl groups. Most evidence for the extent of carboxylation was obtained by indirect methods such as titrometric and elemental analysis measurements. The extent of carboxylation is indicated by the increase of the carboxyl groups in the insoluble residue over the starting lignite. The total acidity and carboxyl group determinations were obtained for each by the difference of total acidity and carboxyl group values.

The marked loss in phenolic group content from unreacted lignite to insoluble residue is due to the conversion of these groups to phenolic acids (reaction 2) which are generated during the course of the reaction. Evidence for these phenolic acids is illustrated in Table 2 where the carboxyl group content increases over unreacted lignite and the phenolic content decreases.

Further evidence of carbon dioxide incorporation in lignite structures is the increase in percent oxygen in both residue and acid when compared to starting lignite. The elemental analysis data for the acids and residues of reactions 1-5 are given in Table 4. Increases in percent oxygen are seen in all acids and residues, indicating that new oxygen-containing functional groups have been added to the coal structure. Rather interesting is the fact that the acids generated from Reactions 1 and 2, which yielded the greatest percent solubility, had the lowest percent oxygen. Reasons for this will be offered later in this report.

From elemental analysis, carboxyl group, and phenolic group data from the insoluble residues, the number of carboxyl and phenolic groups per 1000 carbon atoms was calculated as well as the atomic H/C and O/C ratios. These are presented in Table 5.

These triplicate runs showed remarkable similarities even though the overall percent solubility of each reaction varied from the mean by as much as five percent. (Errors are inherent in this kind of research due to the variable nature of the lignite substrate.) The extent of aromatization in these residues may be compared to that of the unreacted lignite by comparing H/C atomic ratios. Since the H/C ratio of demineralized moisture free (*dmmf*) lignite is considerably lower, one may conclude that the polymeric aromatic structures of the lignite are somewhat disrupted by the carboxylation process (see reaction 1). Therefore, the extent of disruption may very well control the extent of solubilization.

Equivalent Weight of Black Acids

The equivalent weights of the black acids were determined by the titration method described previously. These are shown in Table 6. These data indicate that an inverse relationship generally exists between percent solubility and the equivalent weight of the acids generated. In this reaction, the equivalent weight is a measure of how extensively a substrate is carboxylated. The lower the equivalent weight, the more carboxyl groups are added per unit weight. However, considering the data in Table 4, the two reactions generating acids of the lowest equivalent weight also generated acids having the lowest percent oxygen. This may seem paradoxical, but if one computes percent oxygen in one equivalent of acid due to the carboxyl group and subtracts this from total percent oxygen in each acid, one obtains a percent oxygen contribution from other functional groups. The majority of these other groups are phenolic groups. Table 7 shows these results.

The percent oxygen from other functional groups shows an inverse relationship with percent solubility without exception when the data in Tables 2 and 7 are compared. Since the percent oxygen from other groups is mainly comprised of phenolic group contributions, this may be a measure of "phenolic efficiency" which is solvent dependent. Since there are two paths available for carboxylation to occur (reactions 1 & 2), the data from Table 7 suggest that carboxylation occurs more readily on aromatic carbanions (reaction 1) and, consequently, reflects a lower percent oxygen content. In the toluene solvent, the percent oxygen content suggests carboxylation occurred more on the phenolic sites (reaction 2) than the aromatic sites which is reflected in a higher oxygen content "from other groups" as revealed in Table 7.

One observation made from Table 4 was that percent sulfur markedly decreased in both acids and residues with respect to the starting lignite. This was evidenced macroscopically by the detection of H_2S upon opening the autoclave following the reactions.

An additional observation from Table 4 is that the percent ash in the residue is much higher — nearly five times — than that in the acids. This indicates that the formation of acids indeed is a result of extensive disruption of the aromatic superstructure which is characteristic of lignite. This leads one to conclude that the structure of the insoluble residue is that of a core containing trapped insoluble inorganic compounds surrounded by a carboxylated surface.

SUMMARY

The carboxylation of North Dakota lignite was conducted under a variety of reaction temperatures. The greatest solubility was obtained by using naphthalene as molten solvent and electron transfer agent at 200°C. Triplicate reactions were conducted in toluene, and the percent solubility varied from the mean by about 5%. Total acidity, carboxyl group, and phenolic group determinations were made for all insoluble residues. These yielded insight into the intrinsic extent of carboxylation. Elemental analysis data pertaining to residues and acids were obtained as were the equivalent weights of the acids. From this, it seemed that, as equivalent weight decreased, percent oxygen actually decreased. From a variety of calculations, it was seen that this was actually a measure of how many phenolic groups per unit weight are needed to induce the substitution of a carboxyl group. From decreases in percent sulfur from lignite to products as well as a very large difference in percent ash in acids compared to residue gave insight as to the structures of these moieties.

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Table 1. Autoclave Reactions

Reaction #	Solvent	Temperature	Gas(es) Employed
1	THF	100°C	N_2 (5 days) CO_2 (2 days)
2	Naphthalene	200°C	N_2 (5 days) CO_2 (2 days)
3	Toluene	100°C	CO_2 (5 days)
4	Toluene	100°C	CO_2 (5 days)
5	Toluene	100°C	CO_2 (5 days)

Table 2. Percent Solubility and Material Balance

Reaction No. and Solvent	Temp (°C)	Wt. Insoluble Residue (g)	Wt. of black acids	Total Wt. of All Fractions	% Solubility
1 (THF)[a]	100	4.219	3.78	11.642	57.8
2 (Naph)[a]	200	3.238	4.80	b	67.8
3 Ø CH_3	100	5.913	5.11	13.899	40.8
4 Ø CH_3	100	5.091	4.43	12.376	49.1
5 Ø CH_3	100	5.496	4.46	13.015	45.4
lignite[c]	100	0.807	0.306	1.113	19.3
lignite[d]	100	0.893	0.268	1.161	10.7

[a] 10 g of lignite and 10 g of potassium.

[b] The material balance for the second reaction is obtainable since the neutral fraction contained the solvent naphthalene which could not be separated from the neutral compounds.

[c] 1 g. of lignite and 50 ml toluene

[d] 1 g. of lignite. 1 g. of potassium and 50 ml toluene

Table 3. Total Acidity and Carboyxl Group Data for Insoluble Residues

Reaction	Total Acidity[a] (meq/g)	Carboxyl Groups[a] (meq/g)	Phenolic Groups[d] (meq/g)
1	4.59 ± 0.04	1.80 ± 0.02	2.79
2	5.10 ± 0.12	1.90 ± 0.03	3.20
3	4.64 ± 0.18	1.61 ± 0.03	3.03
4	4.59 ± 0.04	1.55 ± 0.06	3.04
5	4.78 ± 0.02	1.65 ± 0.07	3.31
Unreacted Lignite	6.11[b]	0.78[c]	5.32

[a] average ± average deviation - two determinations
[b] average of three determinations (Lavin, 1982)
[c] average of eight determinations (Lavin, 1982)
[d] obtained by difference

Table 4. Elemental Analysis Data for Reaction Products

Reaction		%C	%H	%N	%S	%Ash[a]	%O[b]
1	Acids:	66.16	4.45	1.021	0.52	0.986	26.86
	Residue:	64.78	3.49	0.56	0.28	4.63	16.26
2	Acids:	66.09	4.13	0.991	0.58	0.906	27.30
	Residue:	66.31	3.44	0.58	0.33	4.56	24.78
3	Acids:	56.75	4.29	1.021	0.32	0.935	36.68
	Residue:	59.90	4.40	0.929	0.21	4.76	30.73
4	Acids:	63.45	3.81	1.233	0.59	0.772	30.15
	Residue:	60.06	4.01	0.922	0.57	4.84	29.60
5	Acids:	59.48	4.84	1.076	0.51	0.811	33.28
	Residue:	60.34	5.12	0.710	0.48	4.83	28.52
	Unreacted Lignite:	65.71	3.77	0.78	0.89	8.95	19.90

[a] Average of two determinations
[b] By Difference

Table 5. Carboxyl and Phenolic Groups per 1000 Carbon Atoms for Residues

Reaction	Carboxyl Groups/1000 C	Phenolic Groups/1000 C	H/C	O/C
3	32.3	60.7	0.88	0.38
4	31.0	60.5	0.76	0.37
5	32.8	62.2	1.02	0.35
Unreacted Lignite	14.2	97.1	0.69	0.30

Table 6. Equivalent Weight of Black Acids

Reaction	Equivalent Weight (g)[a]
1	226 ± 3
2	215 ± 3
3	267 ± 2
4	259 ± 6
5	257 ± 3
1,3,5-benzenetricarboxylic acid	71.9 ± 2.2

[a] sample size was 0.1000 g of acid

Table 7. Percent Oxygen from Various Functional Groups

Reaction	% 0 from Carboxyl Groups	% 0 from Other Groups
1	14.16	12.70
2	14.88	12.40
3	11.99	24.69
4	12.36	17.79
5	12.45	20.83