

THE DISSOLUTION OF LIGNITE IN ANHYDROUS LIQUID AMMONIA

R. L. Harris, L. H. Simons and J. J. Lagowski

Department of Chemistry, The University of Texas, Austin, TX 78712

INTRODUCTION

The rapid depletion of gaseous and liquid fossil fuels has focused attention on the problems associated with using the existent vast quantities of coal-substances for equivalent purposes, e.g. the production of energy and as a source of useful carbon compounds. Although our primary interest here is in the latter area, the ideas presented may have useful implications in certain aspects of the former.

The general strategy involves using the unusual solvent properties of liquid ammonia as a means to solubilize relatively large fractions of coal-substances at low temperatures and thereby providing (1) a method of obtaining potentially useful carbon-containing compounds directly and (2) information on the chemical nature of the original coal-substance.

The Chemical Nature of Coal-Substances

It is generally conceded that coal-substances originated primarily from plants through a series of evolutionary changes. The plant matter is transformed sequentially into humic acid, peat, lignite, subbituminous coal, bituminous coal, and anthracite. During this series of transformations, the carbon content increases while the oxygen content decreases. The precise chemical composition of coal-substances is unknown (indeed it may be unknowable in the chemical sense) because it may be derived from a variety of sources by numerous combinations of physical and/or chemical processes which lead to a nearly continuous variation of mixtures of carbon-containing (1) compounds. Nonetheless, a combination of techniques has led to the identification of broad classes of compounds present in coal-substances; viz., waxes, resins, terpenes, cellulose, protein, flavonoids, tannins, lignins, alkaloids and sterols as deduced from solvent extraction studies, (2) precursors of the heterocycle nitrogen bases, obtained by vacuum distillation of coal tar, (3) and humic acids (4). A large portion of carbon present in coal occurs in the form of saturated 6-membered condensed ring systems (naphthenes) linked together by oxygen bridges (4). Chemical analysis involving a variety of standard methods (5) has shown that coal-substances contain -OH groups (predominantly as phenolic units), carboxylic (as metal salts), ether, and carbonyl groups in varying proportions depending upon the rank of the sample; nitrogen (6) is believed to exist almost completely in cyclic structures whereas sulfur (6d, 7) appears as thioethers (-S-) or bis thioethers (-S-S-) groups. A model structure (8) for the coal-substance which summarizes the relationship among the known functional groups, consists of 6-7 aromatic ring clusters held together by saturated carbon chains (1-4 atoms long), ethers, sulfides, disulfides and biphenyl groups; the model suggests a predominantly 2-dimensional structure in the vicinity of the 6-7 aromatic rings, but the individual aromatic sections are not necessarily co-planar.

The Solvent Properties of Liquid Ammonia

Solubility in a two-component system involves a consideration of the attractive forces which exist between solute and solvent, solvent and solvent, and solute and solute; the attractive forces in the first instance favor the solubility of one substance in another, whereas the last two types of interactions oppose solubility. Because of its moderate dielectric constant, high dipole moment, ability to hydrogen bond, and relatively high basicity, liquid ammonia is a remarkably versatile solvent (9). The potential of ammonia to react with certain functional groups to produce soluble products also provides an additional advantage in the solubilization processes.

A consideration (9) of the polarity of the ammonia molecule as well as the dispersion forces generated by it suggest that ammonia should be a good solvent for covalently bound polar groups. In addition, arguments (9) based on internal pressure considerations (10) indicate that aromatic hydrocarbons and molecules containing polarizable atoms should exhibit a reasonable degree of solubility in liquid ammonia. Molecules which contain highly polar functional groups such as the carbonyl moiety (aldehydes, ketones, acid amides, and esters) that can interact strongly with the solvent dipole might be expected to interact strongly with ammonia. In addition, an enhancement of solubility would be expected in the presence of groups which can form hydrogen bonds to ammonia ($X-H \cdot \cdot NH_3$, e.g. alcohols, primary, and secondary amines) or be hydrogen-bonded by ammonia ($X \cdot \cdot \cdot HNH_2$, e.g., ethers, tertiary amines, oxygen functions, and nitrogen heterocycles). Lastly, molecules possessing acidic hydrogen atoms such as carboxylic acids or phenolic groups react with liquid ammonia to form ammonium salts which should be soluble in liquid ammonia.

The solubility principles developed here are illustrated by the data summarized in Table 1; these data are selected examples of a more extensive series available (9).

It is from this point of view that we decided to investigate the possibility of dissolving substantial fractions of coal substances in liquid ammonia under mild conditions using Rockdale (Texas) lignite for our preliminary experiments.

EXPERIMENTAL

The apparatus used for extraction of Rockdale (Texas) lignite with pure liquid ammonia is shown in Figure 1. The lignite ground to 100 mesh is placed in a Whatman extraction thimble which is then sealed by a staple. Sealing the extraction thimble prevents accidental mixing of the solid, unextracted lignite with ammonia. The thimble is placed in a conventional Soxhlet extractor; a condensing Dewar placed on top of the Soxhlet extractor and an empty flask placed below. The entire apparatus is purged with anhydrous gaseous ammonia; then a dry ice slush is added to the Dewar condenser on top, allowing the ammonia to condense and drip from the Dewar condenser onto the sample in the thimble. As extraction continues, an insulating layer of ice condenses on the outside of the apparatus. After six to ten hours the extraction is complete (25% by weight) for ca. 100 mesh samples. Extraction was conducted on samples weighing up to 50 grams.

After extraction of the lignite was complete, the precipitated tar from the ammonia solution, and the brown-black ammonia solution were let stand in air until only solid residue remained. The lignite remaining in the extraction thimble (75%) we term "treated lignite", whereas that which dissolved in the ammonia we term the ammonia extract.

Proton magnetic resonance spectra on d_6 -DMSO solutions of the ammonia extract were obtained using an NT200 spectrometer.

Infrared spectra of the samples prepared as KBr pellets were obtained with both Beckman IR5A and Beckman IR9 spectrometers.

Elemental analysis was conducted at Schwarzkopf Microanalytical Laboratory, Inc.

OBSERVATION AND RESULTS

The addition of ammonia gas to the system described in Figure 1 led to warming of the lignite sample. Later, when the first drops of liquid ammonia fell on the lignite, the outside of the Soxhlet extractor became quite hot. It was at this time that spattering of the lignite sample took place in open extraction thimbles which led us to the current method of sealing the thimbles. After about 10-20 minutes, the Soxhlet extractor was cooled by the liquid ammonia to below room temperature.

An extraction was attempted at room temperature using a pressure bomb. After several days, the mixture was filtered at room temperature, yielding 26% extract and 74% solid residue (treated lignite). Whereas the solid extract obtained from extraction at -33°C was a brown powder; the solid obtained at room temperature was black and lustrous. However, when the -33°C ammonia extract was dissolved in DMSO, which was then allowed to slowly evaporate, the appearance of the resulting product was identical to the room temperature reaction.

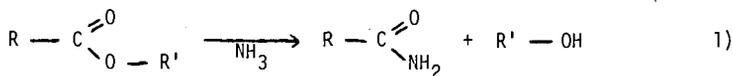
Preliminary GC-mass spectroscopic data indicated that the DMSO soluble extract contains well over 100 compounds, none of which could be resolved sufficiently for identification. Proton magnetic resonance spectroscopy revealed absorptions at 7.5, 1.2 and 0.9 τ (downfield from TMS). The ratio of the area of the 7.5 τ absorbance to the sum of the areas of the 1.2 τ and 0.9 τ absorbances, which is usually assigned as the ratio of aliphatic to aromatic protons, was ~1.3 for the ammonia-soluble fraction.

Elemental analysis (Table 2) suggests that at least some components in the lignite react with liquid ammonia, since both the extract and the treated lignite exhibit increased nitrogen content as well as increased atomic H/C ratios. The increased content of sulphur in the extract suggests preferential extraction of those portions of the lignite with a high hetero-atom content.

The solubility behavior of the treated lignite and the ammonia extract shows gross differences from the solubility behavior of the untreated lignite. The untreated lignite and treated lignite are not totally soluble in any solvent attempted, but they are both partly soluble in pyridine. The treated lignite has enhanced solubility in DMSO and dimethylformamide, which are considered good solvents for high molecular weight substances. The ammonia extract is at least partly soluble at room temperature in all solvents tested except water.

DISCUSSION

As mentioned in the introduction, one important consideration in these experiments is the solubility characteristics of functional groups in ammonia. We might expect that the lower rank coal-substances like lignite, which have a higher oxygen content, presumably in the form of functional groups that enhance solubility, would have a moderate solubility in ammonia. Another consideration is the ability of ammonia to react with certain functional groups, breaking a large unit into two smaller moieties. For example, ammonia reacts with esters (12) to create alcohols and amides (scheme 1) both of which should exhibit high ammonia solubility. If esters, or



similar compounds, are constituents of coal, ammonia will react, breaking the coal into smaller fragments. A recent study (11) on Texas lignite showed that hydrogenation of this coal-substance provides phenols, thus supporting the possibility that some of the linking groups in Rockdale (Texas) lignite are esters or ethers. Further support can be inferred from the observation that a saturated DMSO solution of the ammonia extract is more highly colored than a saturated solution of untreated lignite in DMSO. This observation implies that upon extracting with ammonia reactions took place, changing the nature of the remaining lignite as well as the ammonia extract, and creating more soluble moieties.

Yasukatsu Tamai and co-workers (12,14) treated bituminous coal with liquid ammonia; no more than 4% of the coal was actually extracted into the ammonia at 100-120°C. It is interesting to note that the coals they used had atomic hydrogen to carbon ratios of from 0.55 to 0.98. The ammonia extract always had a significantly higher atomic H/C ratio, whereas the treated coal maintained approximately the same

H/C ratio as the untreated coal. The same general trends are found for our lignite experiments (Table 3), although lignite has a much higher H/C ratio, thus perhaps explaining the greater amount extracted by ammonia. It should be noted that our method provided continuous extraction of 100 mesh particles whereas Matida, et.al. (13) extracted larger particles by 5 successive contacts of pure ammonia for one hour each. A priori, our method would be expected to extract more than this even at the lower temperature involved, but not as great a deviation as is observed. The difference must be accounted for in the chemical difference between lignite and bituminous coal.

There are similarities to our lignite-ammonia extract and the coal-ammonia extracts of Tamai and co-workers; infra-red bands at 3300, 1720 and 1660 cm^{-1} are characteristic of the ammonia extract obtained from coal. In our experiment the methanol soluble portion of the extract has broad bands at 1640 cm^{-1} with a shoulder at 1700 cm^{-1} , and 3400 cm^{-1} with a shoulder at 3200 cm^{-1} ; the C-H stretches are all below 3000 cm^{-1} . The ammonia extract itself had a strong band at 1380 cm^{-1} , a small broad band at 1460 cm^{-1} , large broad bands at 1620 cm^{-1} and 1700 cm^{-1} , large bands at 2950-2980 cm^{-1} and a large broad band at 3400 cm^{-1} .

The primary difference in the infrared spectra of the untreated lignite and of the ammonia extract was the growth of the band at 1380 cm^{-1} and a decrease in the ratio of heights of the bands at 3400 cm^{-1} to those at 2950 cm^{-1} , indicating an increase of alkyl group hydrogens to hetero-atom hydrogens in the ammonia soluble portion compared to the treated lignite portion. Of course, the treated lignite portion showed an increase in height of the band at 3400 cm^{-1} relative to the bands at 2950 cm^{-1} .

Even though the infrared results seem to indicate an increase in the aliphatic content of the ammonia extract relative to the OH and NH content, the NMR results indicate more aromatic protons than aliphatic.

CONCLUSION

It is clear that the original lignite structure can be modified and lignite separated into its component moieties by treatment with liquid ammonia. The usefulness of liquid ammonia to better identify lignite components has been demonstrated. The solubility of different coals should be further tested; the identity of the species dissolved in the ammonia should be more explicitly identified. We are currently engaged in both types of experiments.

ACKNOWLEDGEMENTS

We acknowledge the generous support of the Center for Energy Studies at The University of Texas and The University Coal Laboratory.

Table 1
Solubilities of Selected
Compounds in Liquid Ammonia

<u>Substance</u>	<u>Solubility</u>	<u>Reference</u>	<u>Atomic H/C</u>
C_6H_6	Moderately Soluble	a	1.00
$C_6H_5CH_3$	Slightly Soluble	a	1.14
$C_6H_5CH=CH_2$	Soluble	a	1.00
$C_6H_5CONH_2$	Soluble, 35%	b	1.00
$C_6H_5CH_2CO_2CH_3$	Miscible	b	1.11
$C_6H_5OCH_3$	Miscible	a	1.14
$(C_2H_5)_2O$	Miscible	a, c	2.50
$(C_4H_9)_2O$	Soluble	d	2.25
$C_6H_5NH_2$	Miscible	a	1.17
C_6H_5OH	Very soluble	a	1.00

a) E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, 20, 820 (1898).

b) F. de Carli, *Gazz. Chim. Ital.*, 57, 347 (1927).

c) G. Gore, *Proc. Roy. Soc. (London)*, 20, 441 (1872).

d) F. A. White, A. B. Morrison, and E. g. E. Anderson, *J. Am. Chem. Soc.*, 46, 961 (1924).

Table 2
Solubilities of Lignite¹

<u>Solvent</u>	<u>Untreated Lignite</u>	<u>Treated Lignite</u>	<u>Ammonia Extract</u>
methyl sulphoxide	I ²	P	S
pyridine	P	P	S
acetone	I	I	P
methanol	I	I	P
water	I	I	I
chloroform	I	I	P
propylene carbonate	I	I	P
dioxane	I	I	P
acetonitrile	I	I	P
ethylenediamine	P ³	I	S
nitrobenzene	I	P	P
dimethylformamide	I	P	S

¹All solubilities except where noted at room temperature. S = totally soluble, ca. 1 mg. in ca. 1 ml; P = solvent becomes colored, but not all of the lignite dissolves; I = no discoloring of the solvent is observed.

²If the lignite is maintained in contact with DMSO at 100°C., the DMSO becomes colored. Concentrated solutions of the soluble lignite in DMSO are much less colored than concentrated solutions of the ammonia extract in DMSO.

³Lignite appears to react with ethylenediamine.

Table 3
Elemental Analysis

<u>Samples</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>Ash</u>	<u>Atomic H/C</u>
Rockdale lignite ¹						
Untreated lignite ²	51.70	4.85	1.03	1.27	12.0	1.12
Treated Lignite ²	53.37	5.18	2.71	1.72	11.8	1.16
Ammonia Extract ²	46.46	5.36	4.45	2.74	9.0	1.37
Mazachi coal ³						
Untreated coal	83.9	6.9	1.5	-	-	0.98
Treated coal ⁴	83.0	6.0	1.9	-	-	0.86
Ammonia Extract ⁵	87.2	10.1	1.4	-	-	1.38

¹Rockdale (Texas) lignite has been reported to contain up to 30% oxygen.

²Analysis by Schwarzkopf Microanalytical Laboratory.

³M. Matida, Y. Nishiyama and Y. Tamai, Fuel 1977, 56, 177.

⁴One hour in liquid ammonia at 120⁰ C.

⁵One hour contact with untreated coal.

EXTRACTION APPARATUS

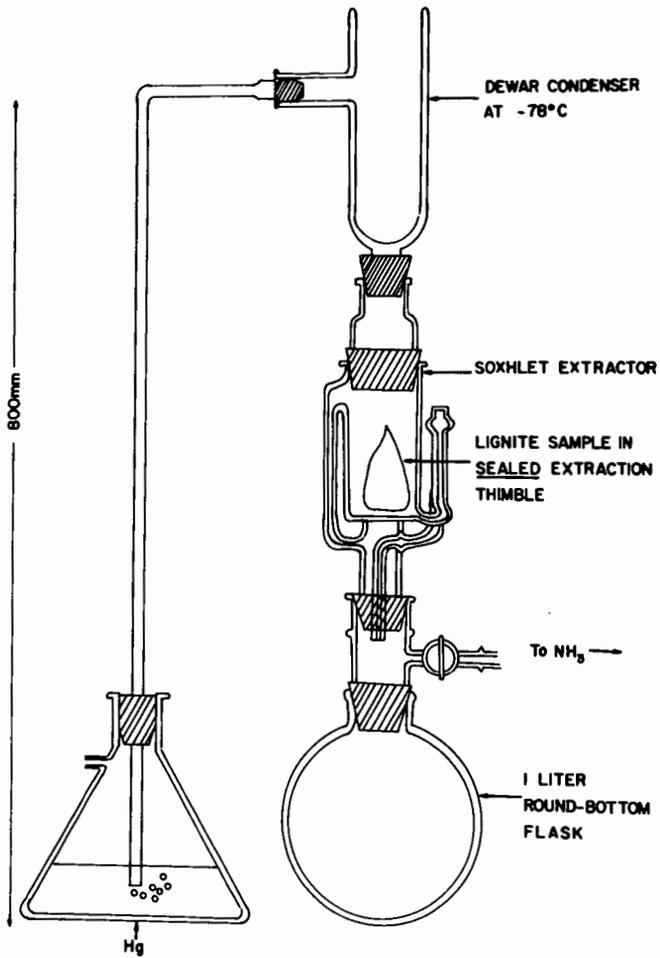


FIGURE 1. The apparatus used for extraction of Rockdale (Texas) lignite.

REFERENCES

1. For a review see D. D. Whitehurst, "Organic Chemistry of Coal," John W. Larsen, Ed., Chapter 1, American Chemical Society, 1978.
2. M. S. Kiebler in "The Chemistry of Coal Utilization," H. H. Lowrey, Ed., Vol. I, p. 677, Wiley & Sons, New York, 1945.
3. a) A. Pictet, O. Kaiser, and A. Labourchere, *Compt. Rend.*, 165, 113 (1917).
b) C. H. Fisher, *U.S. Bur. Mines Bull.*, 412, 31 (1938).
4. C. F. Brown and A. R. Collett, *Fuel*, 17, 359 (1938).
5. a) W. Fuchs and W. Strengel, *Brennstoff-Chem.*, 10, 303 (1929).
b) M. Ihnatowicz, *Prace Glow ego Inst. Gornective (Katowice)*, *Komm.*, 1952, 125.
c) L. Blom, L. Edelhausen, and D. W. van Krevelen, *Fuel*, 1957, 36.
6. a) W. Francis and R. V. Wheeler, *J. Chem. Soc.*, 127, 2236 (1925).
b) C. W. Shacklock and R. J. Drakeley, *J. Soc. Chem. Ind. (London)*, 46, 478T (1927).
c) A. E. Beet, *Fuel*, 19, 108 (1940).
d) L. Horton and R. B. Randall, *Fuel*, 26, 127 (1947).
7. a) A. Lessner and A. Nemes, *Brennstoff-Chem.*, 16, 101 (1935).
b) S. J. Gusey, *J. Appl. Chem. (USSR)*, 17, 362 (1944).
c) L. Wnekowska, 3rd. Intern Conf. on Coal Science, Valkenberg, 1959.
8. a) D. W. Krevelen, "Solvent Extraction of Coals" in *Coal-Topology, Chemistry, Physics, and Construction*, Chapter 10, Elsevier, New York, 1967.
b) G. R. Hill and L. B. Lyon, *Ind. Eng. Chem.*, 54, 36 (1962).
c) "Liquefaction and Chemical Refining of Coal," A Battelle Energy Program Report, July, 1974.
9. J. J. Lagowski, *Pure and Appl. Chem.*, 25, 429 (1971).
10. J. H. Hildebrand, *J. Chem. Ed.*, 25, 74 (1948).
11. C. V. Philip and R. G. Anthony, *Am. Chem. Soc., Div. Fuel Chem.* 1977, 22(5), 31.
12. A. Tomita, T. Tano, Y. Oikawa and Y. Tamai, *Fuel* 1979, 58, 609.
13. J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, p. 338, McGraw-Hill, New York, 1968.
14. M. Matida, Y. Nishizama and Y. Tamai, *Fuel* 1977, 56, 177.