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## A Study of the Humic Acids of North Dakota Lignite

David M. Mason

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A STUDY OF THE HUMIC ACIDS  
OF  
NORTH DAKOTA LIGNITE

6/3

by  
David M. Mason  
B.S. in Chemical Engineering, Montana State College,  
1934

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A thesis submitted to the faculty of the College of  
Engineering of the University of North Dakota in partial  
fulfillment of the requirements for the degree of Master  
of Science in Chemical Engineering.

June 6, 1935

University of North Dakota



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This thesis, presented by David W. Mason as  
a partial fulfillment of the requirements for the  
degree of Master of Science in the University of  
North Dakota, is hereby approved by the Committee in  
charge of his work.

Ivan Larnie  
Cecil W. Byers  
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273241

#### ACKNOWLEDGEMENT

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## INTRODUCTION

During the last ten years or more humic acids have been the subject of much investigation, especially in Europe, with regard to their role in the formation of coal and their influence on the briquetting and coking properties of coal. It was decided that the School of Mines of the University of North Dakota should engage in some research on this subject.

This thesis deals primarily with the humic acids of a North Dakota lignite, and, more specifically, their extraction with alkalis, together with a study of the hydroxy content of the coal and humic acids.



## LITERATURE REVIEW

### Constitution and Origin.

Humus substances, according to Oden, (15) are "those yellowish-brown to dark brown substances of unknown constitution which are formed by the decomposition of organic substances, either naturally under the influence of atmospheric agents or in the laboratory by chemical action, especially of acids and bases. They show marked affinity for water and, if they are not soluble or dispersable in water, at least show distinct evidences of swelling".

He then defines humic acids as "those humus substances which can split off hydrogen ions and can give typical salts with strong bases with the formation of water".

According to Kaunert's (1) classification three forms of humus substances may be distinguished:

1. Humic acids, which are soluble in cold alkali solutions.
2. Humins, soluble only in hot alkali solutions.
3. Humus coal, insoluble in alkali solutions under increased temperature and pressure.

Stack (1) has designated these three groups as  $\alpha$ ,  $\beta$ , and  $\gamma$  humic acids respectively.

Humic acids are most richly represented in peat, which is almost entirely composed of them, and in the brown coals of Germany, some of which are known to contain as much as 60% of them. Coals somewhat higher in rank, such as North Dakota lignite and the dull and bright brown coals of central Europe contain little or no humic acid and are composed mostly of humins. Higher rank coals, bituminous and anthracite, represent the humus coals.



Humic acids are considered to be the product of the first stage of the process which has changed the vegetation of past ages into coal. According to the Fischer and Schrader (16) lignin theory of the origin of coal, the cellulose of plant remains disappears as a result of the action of bacteria or enzymes, being transformed into simple aliphatic acids, while the lignin resists decay but is changed into the alkali-soluble humic acids. Considerable evidence has been found in support of this theory, especially in regard to the similarity of chemical structure of lignin to humic acids.

The nature of the change from humic acid to humin has been the object of some investigation. Erdman (3) assumed that anhydrides and lactones which could be saponified only by hot alkali were formed. Hans Stach (1) carried out methylation tests, consisting of the methylation by diazomethane of the original coal, of the humic acid extracted therefrom, and of the coal residue left after extraction, and subsequent quantitative determination of the methoxyl group,  $\text{OCH}_3$ , in them. Diazomethane reacts with acid groups (phenolic hydroxyl and carboxyl) to replace  $-\text{OH}$  by  $-\text{OCH}_3$  groups.



It will not react with lactones or anhydrides, nor with alcoholic or aldehyde groups except when the rest of the molecule is substituted strongly negatively. Stach found that the coal residue after extraction showed almost as high a content of phenolic hydroxyl and carboxyl groups as the humic acids themselves. He concluded that their insolubility in alkali was due not to anhydride and lactone formation, but to a colloidal ageing similar to that in the change of



$\alpha$  stannic acid to  $\beta$  stannic acid, which is believed to take place by an increase in the size of the colloidal particles. The  $\alpha$  form, which is more easily peptized by alkali, changes into the  $\beta$  form on standing under water or dilute acid.

From his investigations Stach concludes that coalification proceeds in three phases: a biochemical, a colloidal, and a geochemical process.

In the biological stage the lignin of plant remains is demethylated and oxidized, producing the humic acid of peat.

In the colloidal stage the highly hydrated humic acids are dehydrated and aged, leading to the humic acids of peat and brown coal difficult soluble in alkali.

Under the influence of geologic pressure and heat ageing proceeds quickly. The moisture content of the coal continues to decrease, there is a slight increase in carbon content and decrease in number of carboxy and hydroxy groups, and it becomes almost entirely insoluble in cold alkalies.

The further course of the maturation of coal is a process not well understood but includes the loss of oxygen from other groups as well as carboxy and hydroxy oxygen.

Stach (1) obtained values of methoxy content of methylated humic acids from different coals ranging from 14.4% to 19.4%, with most of them lying between 14 and 16%. Taking 15% as the average methoxy value, he obtained an equivalent weight of 190.5. These values are for total methoxy. He also determined ester methoxy by treatment of the humic acid with a solution of hydrogen chloride in methyl alcohol. These values of ester methoxy content ranged from 5.4% to 10.4%, while values of ether or phenolic methoxy content, obtained by difference, ranged from 10.35% to 7.93%, and generally were higher.



er than those of the ester methoxy. Humic acid from an Ilse brown coal of Germany, which yielded methoxy derivatives of 7.95% ester methoxy and 8.03% ether methoxy was also used to prepare an acid chloride of 10.14% chlorine. The carboxy equivalent weight, calculated from the ester methoxy derivative, was 376, and calculated from the acid chloride, 331. The preparation of the ester methoxy and acid chloride derivatives was considered to be conclusive proof of the acid nature of humic acid, about which there was at one time some question.

By the analysis of carefully dialyzed calcium humate and by potentiometric and conductometric titrations of humic acid by sodium hydroxide, Sven Oden (4) obtained values for the equivalent weight of a humic acid prepared from peat. These values ranged from 320 to 345.

Oden was also able to determine, by viscosity measurements, that the humic acid was tetrabasic. He added increasing amounts of alkalis to humic acid suspensions and after each addition determined the viscosity of the suspension with an Ostwald viscosimeter. He found that after the addition of a quantity of alkali corresponding to  $\frac{1}{4}$  of the number of equivalents of humic acid, the viscosity fell rapidly to a constant value, indicating the formation of a salt  $\text{NaH}_3$  (Hum) of a tetrabasic acid.

By the mild oxidation of humic acid with 5N nitric acid and other oxidizing agents Fuchs (5) was able to obtain oxidation products soluble in acetone whose molecular weights amounted to about 1300. It is believed that a mild treatment of this kind should act only on the outer parts of the humic acid molecule and should not change its internal structure and molecular magnitude. By the aid of group reagents and elementary analysis



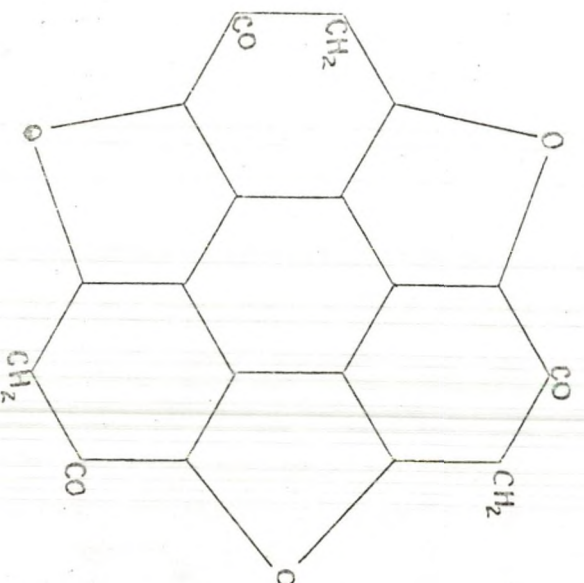
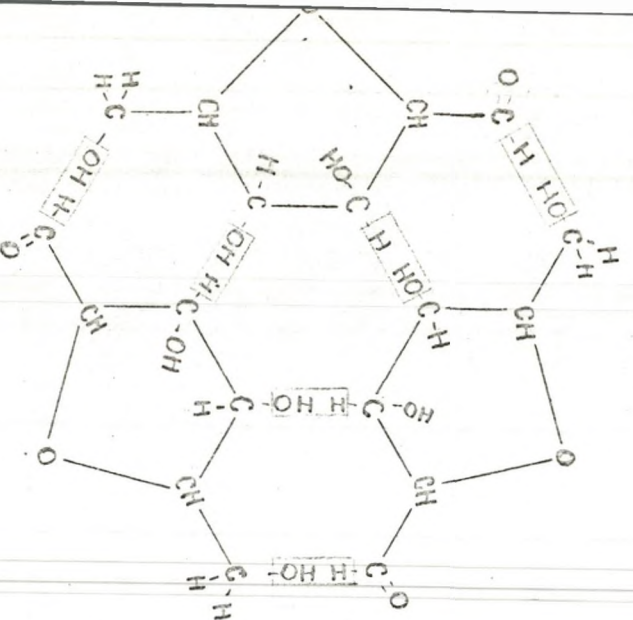
Fuchs concluded that a humic acid molecule with an empirical formula of  $C_{69}H_{52}O_{30}$  and molecular weight of 1350 would contain 4 COOH-, 5 acid OH-, one  $CH_2CO$ -, and one CO- group.

The aromatic character of the nucleus of the humic acid molecule has been well demonstrated by the results of oxidation studies. By treating humic acid with 1:1 nitric acid for about 1½ hours at about 90° C. Fuchs and Stengel (6) obtained products from which they were able to separate and identify a number of benzocarboxylic acids, including mellitic acid ( $C_6(COOH)_6$ ), benzo penta-carboxylic acid, pyromellitic acid (1,2,4,5 benzotetracarboxylic acid), trimelic acid (1,3,5 benzotri-carboxylic acid), and mellophanic acid (1,2,3,5 benzotetracarboxylic acid). Picric acid and small quantities of other unidentified nitrophenols were also formed. Fischer and Schrader (7) had before this obtained some of these benzocarboxylic acids by the pressure oxidation of coal, both high and low rank, and lignin. By this method the coal or lignin was treated for three hours with a 2½N sodium carbonate solution at a temperature of 200° C. and under a pressure of 45-50 atmospheres. Other investigators (8,9) have obtained mellitic acid and other aromatic compounds as well as formic, acetic, oxalic, and succinic acids from the oxidation of coal by various reagents. Thus the aromatic character of the lignin, humic acid, and coal molecule has been fairly well established.

Schrauth (10) has suggested a possible mechanism of the synthesis of coal according to the Fischer-Schrader lignin theory. By the condensation of three glucose molecules, linked through oxygen from the  $\alpha$  to the  $\delta$  carbon atoms, there could be formed the ketoderivative of a perhydrogenated 9-10 benzophenanthrene, which could be further reduced to the compound of Formula II. It would possess the aromatic and phenolic constitution required and the three oxygen bridges would give it the character of a furan derivative, which



Levassour, (14), who obtained furan compounds by the dry distillation of linnic acids, believed them to possess. This compound, whose empirical formula is  $C_{12}H_{12}O_6$ , could form molecules the size of lignin and linnic acid molecules by condensation between CO and  $CH_2$  groups, it could form phenolic hydroxy groups by a tautomeric shift of the  $-CH_2-CO-$  groups, and by splitting one of these groups under hydrating or oxidizing influences carboxyl groups could be formed.



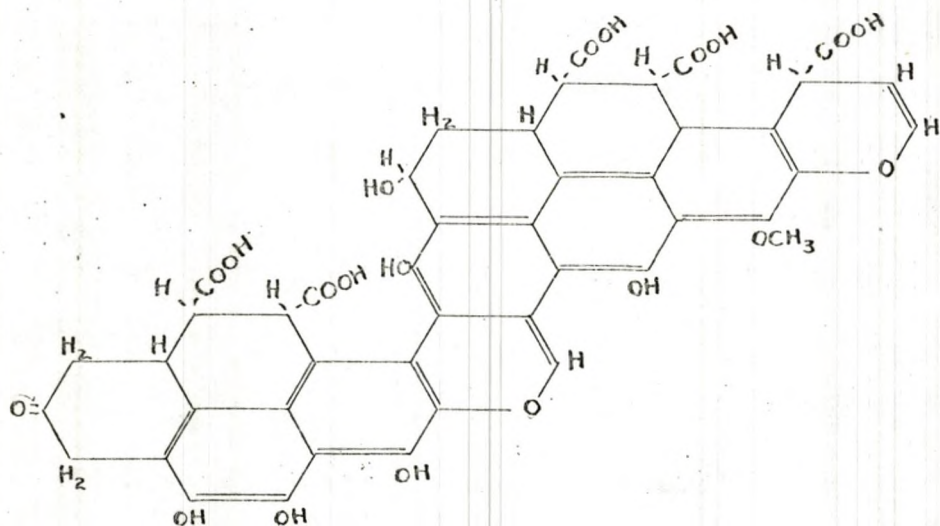
Formula I

Formula II

Other investigators (11, 12) have found direct evidence to lack or insufficiency of evidence to show that a furan grouping is an essential characteristic of the structure of linnic acid. Thus, Lucis and Lear (13), from their studies of the constitutional groups, molecular magnitude, and primary and other oxidation of lignin and linnic acid, have arrived at



Formula III as a structure at least similar to that of humic acid. It should be remembered that we cannot hope to obtain a single formula for the constitution of humic acids, since that term refers to a class of similar compounds rather than to a single compound.



Formula III

#### Properties.

A number of other properties of humic acid besides its reaction with methanolic HCl and diazomethane show its acid nature. Odin (17) found that on the addition of ammonium hydroxide to a suspension of humic acid in water its electrical conductivity increased to values above those to be expected of the ammonium hydroxide itself, indicating the formation of an ionized salt.

Humic acid also has the ability to liberate acetic acid from acetates. This property has been utilized in a method (18) for the determination of humic acids in lignite. A sample of the lignite is mixed with a few grams of CaCO<sub>3</sub> and refluxed with a 10% solution of calcium acetate, the CO<sub>2</sub> evolved being absorbed and determined.



The ability to liberate acetic acid from acetates is an example of the property of base exchange (19) which humic acid possesses. A suspension of undissolved humic acid can exchange its hydrogen ion for the basic constituent or cation of most metallic salts and bases and many organic bases, as substituted amines, pyridine, piperidine, nicotine, caffeine, quinine, quinine, morphine and others. The quantities of different bases absorbed are in stoichiometric proportion, indicating that the phenomenon is due to a chemical reaction.

Besides its chemical properties humic acid possesses colloidal character. Oden (20) describes the acidification of alkali humate solutions as follows: Some of the alkali humate is present as ions, so that with the increase in concentration of hydrogen ion caused by the addition of acid the solubility product of humic acid reaches its maximum and humic acid is thrown out of solution in the form of "primary particles" which are estimated to have a size of about 20  $\mu\mu$ . and to contain about 2000 molecules of humic acid. They are negatively charged, highly hydrated, and too large to pass through a dialyzing membrane. Thus the greater part of the alkali and acid ions and other electrolytes may be separated by dialysis and the humic acid obtained as a colloidal solution. Humic acid strongly adsorbs impurities, especially organic anions, so that it cannot be completely purified.

If the solution of humic acid contains a larger concentration of cations, especially hydrogen ions, the "primary particles" lose their electrical charge and form larger aggregates or "secondary particles". If the concentration of electrolytes is great enough the size of the particles increases until a brownish-black, slimy, voluminous precipitate, still containing much water of



dration, is thrown down. On filtering and washing sufficiently with water the humic acid is again peptized and begins to go through the filter, "secondary particles" about  $1\mu$  in diameter being formed. If the filtered precipitate is allowed to dry the humic acid is obtained as a glossy black substance which may be ground to a dark brown powder.

In a summary of the present (1930) knowledge of humic acids Fuchs (21) discusses many of the properties of humic acid. The work of a number of investigators on the solution and peptization of humic acids by alkalies is reviewed. According to Ostwald and Roediger the solubility of humic acid (erck (a product prepared from peat) in NaOH solution is due entirely to the production of alkali humate for low concentrations of NaOH (0.0005N to 0.001N) and for concentrations above 0.025N, but that peptization also occurs at concentrations between 0.0005N and 0.025N. Buzagh finds that NaOH peptizes humic acid, the reaction being of the autocatalytic type.

According to Buzagh humic acid itself is a peptizing agent. Clays can be more easily peptized in alkaline solution in the presence of humic acids than otherwise. This fact is not without importance in soil science.



EXPERIMENTALMaterials.

## (a) Lignite.

Velva lignite from the Truax-Traer mine at Velva, North Dakota, was the only lignite used in this study. The proximate and elementary analysis of the coal was as follows:

## Proximate analysis as received:

Moisture .....	37.3
Volatile matter.....	29.0
Ash.....	3.4
Fixed carbon.....	30.4
B.T.U. ....	6833.

## Elementary analysis, ash and moisture free basis:

C -----	69.6
H -----	4.57
Remainder-----	25.8

The lignite was shipped from the mine to the School of Mines in a sealed steel drum. As much of the coal as thought necessary was transferred to sealed two-quart glass jars and kept until needed.

The coal was dried at 35° in a Hyvac oven under a current of nitrogen at atmospheric pressure. The nitrogen was circulated through the oven, a pump, a solution of pyrogallol to remove oxygen, and a drying tower. A slow constant stream of nitrogen was added from a tank in order to prevent dilution of the circulating gas by air. The moisture content of the coal was lowered to about 20% by this process. From time to time, as needed, portions were ground to pass a 40 and be retained by a 60 mesh sieve.



(b) Subbituminous Coal.

Subbituminous coal was obtained from the Coalstrip mine near Forsyth, Montana, and was prepared in the same manner as the lignite. Its proximate analysis was as follows:

Moisture-----	19.9%
Volatile Matter----	31.1%
Ash-----	11.6%
Fixed Carbon-----	37.4%
B.T.U.-----	8715.

(c) Peat.

A sample of airdried peat from the Lake Forest deposit in Madison, Wisconsin, was obtained from the Department of Mining and Metallurgy of the University of Wisconsin. It was ground to 40-60 mesh before use.

Reagents for extraction.

(d) Sodium Hydroxide.

A commercial grade of sodium hydroxide was used. Solutions were made up by weight, generally fresh for each extraction.

(e) Sodium Carbonate.

A technical grade of anhydrous Sodium Carbonate from Central Scientific Co. was used. Solutions were made up in the same manner as the sodium hydroxide solutions.

Methylation with methanolic HCl.

(f) Methyl Alcohol.

Merck's reagent grade of absolute methyl alcohol.



Methylation with diazomethane.

(g) Hydrazine Hydrate.

Hydrazine hydrate 85% in water from Eastman Kodak Co.

(h) Chloroform.

U. S. P. Merck.

(i) Potassium Hydroxide.

U. S. P.

(j) Ethyl Alcohol.

Absolute ethyl alcohol was prepared by refluxing 95% alcohol for about 5 hours with quicklime and distilling.

(k) Ether.

Absolute ether was prepared by allowing U. S. P. ether to stand first over Calcium Chloride and then over metallic sodium, and distilling.

Methoxy determination.

(l) Hydriodic Acid.

Hydriodic acid, density 1.7, Merck.

(m) Pyridine.

Merck Medicinal and Bakers C. P.

(n) Silver Nitrate Solution.

.1060N.

(o) Ammonium Thiocyanate Solution.

Approximately 0.1N, standardized against the silver nitrate solution.

(p) Ferric-Ammonium Alum Indicator Solution.

A saturated ferric-ammonium sulfate solution to which nitric acid is added until the disappearance of brown color.



## APPARATUS AND PROCEDURE

Extractions.

Two cast iron autoclaves of about 200 cc. capacity were prepared for use in extractions. The covers of the autoclaves were fitted with thermometer wells, and then all the inside surfaces were thoroughly cleaned and electroplated with alternate layers of copper and nickel until a good thickness of metal had been deposited when a last coat of nickel was applied. They were then polished with emery cloth in order to cover pin holes and provide a smooth surface. A photograph of the autoclaves, including covers and clamps, is shown. (Fig. 1)

In making extractions 10 grams of coal and 180 cc. of solution were used each time. The autoclave was charged and then heated until the solution had boiled a minute or so before the covers were clamped on in order to expel dissolved oxygen and air from the free space. The autoclaves were heated by Bunsen burners.

After the desired time of extraction, usually four hours, had elapsed the autoclaves were cooled under a tap, opened, and the black liquid containing the extracted humic acid siphoned off without disturbing the coal residue on the bottom. Water was added to and stirred with the coal residue; after settling a few minutes the liquid was again siphoned off. The coal residue was then washed onto a Buchner funnel fitted with a Schleicher and Schull #575 hardened filter paper, and washed with about 200 cc. of water. The residue was discarded. The filtrate and liquid siphoned from the autoclaves were combined, giving a volume of about 500 cc. and centrifuged for about 12 minutes. After having poured off the liquid, the sediment was transferred to an ordinary filter, washed, and the filtrate added to the main body of liquid.





Figure 1



Concentrated hydrochloric acid was then added to the solution until the appearance of a precipitate of humic acids. When the extraction had been carried out with concentrated NaOH solutions the odor of  $H_2S$  could be detected at this point.

The humic acids were filtered on a Büchner funnel fitted with a weighed Schleicher and Schull #575 hardened filter paper, and washed with distilled water, usually until the humic acid began to peptize and pass through the filter. Since the precipitate could not be washed any longer after it had once dried sufficiently to check or crack, it was not always washed this much. However, since the weight of humic acid was obtained by difference in weight on drying and on ignition, a small amount of sodium chloride not washed out would make no difference.

The filter paper containing the humic acid was transferred to a crucible and dried for 24 hours at  $105^{\circ}C.$ , and after weighing was ignited at about  $700^{\circ}C.$  with a stream of air passing over it, and again weighed. The filter papers used were found to lose between 0.0305 grams and 0.315 grams on drying at  $105^{\circ}$  and to give an insignificant amount of ash on ignition.

#### Preparation of humic acid for methylation studies.

An autoclave of the same type as the small ones already described but of about 2 liters capacity was used in extracting humic acid for methylation studies. In general the same procedure as described above was followed, except that the humic acid was dried for about 5 hours in a Hyvac oven at  $105^{\circ}C.$  in an atmosphere of nitrogen at a reduced pressure.



### Methylation with methanolic HCl.

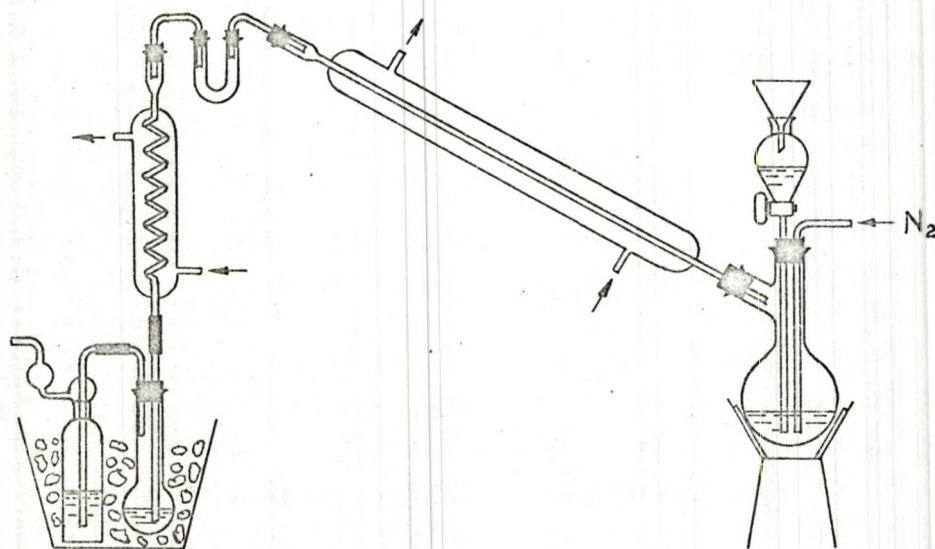
Methylation with methanolic HCl was carried out as described by Fuchs and Tongel (27). Three to five grams of material to be methylated were suspended in 25 cc. of absolute methyl alcohol, and hydrogen chloride, generated by the reaction of concentrated sulfuric acid upon sodium chloride, was lead into the suspension until the alcohol was saturated. After standing in tightly stoppered flasks for several days, the suspension was washed into 200 cc. of water, filtered, washed with distilled water until free of chloride and dried in the manner as described above for the preparation of humic acids.

### Preparation of and methylation with diazomethane.

Diazomethane was prepared according to the method given in Gatterman's "Die Praxis des Organischen Chemikers" (23). It is a greenish-yellow, poisonous gas produced by the reaction of hydrazine with potassium hydroxide and chloroform.



The apparatus for its preparation is represented in Figure 2.





In the flask a solution of 75 g. of KOH in 180 cc. of absolute ethyl alcohol to which has been added a solution of 15 g. of hydrazine hydrate in 50 cc. of absolute alcohol is heated while a solution of 40 g. of chloroform in 50 cc. of absolute alcohol is slowly added through the thistle tube. A slow current of nitrogen gas is led into the solution. The diazomethane gas generated passes through a condenser and calcium chloride tube in order to remove alcohol vapor, through a spiral condenser to cool it, and is absorbed in three flasks containing absolute ether cooled by ice and salt. A solution of diazomethane in ether is thus obtained.

Methylation with diazomethane is effected by adding the etheric solution to an etheric suspension of the material to be methylated until nitrogen is no longer given off and diazomethane remains present after standing several days.

#### Methoxy determination.

Methoxy determinations were made by the method of Kirpal and Bühl as modified by Hewitt and Jones (24). According to this method the material to be analyzed for methoxy group is decomposed by hot concentrated hydriodic acid, the methyl iodide formed is carried off by a stream of carbon dioxide and absorbed in pyridine, and the iodide determined by the Volhard method. The apparatus includes a carbon dioxide generator, a decomposition flask heated in a glycerol bath, and a rectifying column.

In making a determination 20 cc. of hydriodic acid, density 1.7, is placed in the flask and heated to  $120^{\circ}$  C. for a few minutes while a slow current of dry carbon dioxide is passed through it, in order to drive off impurities. After cooling, a sample of the material to be analyzed is introduced



into the flask, which is then heated for one hour at  $130^{\circ}$  C. with the current of carbon dioxide passing through, while the vapor from the rectifying column is lead through two test tubes each containing 10 cc. of pyridine. After an hour the pyridine is washed into a flask with much water and titrated with silver nitrate and ammonium thiocyanate, using ferric ammonium sulfate as the indicator according to the Volhard method (25).



DATA FROM EXTRACTION STUDY

Effect of concentration of NaOH upon extraction 10 g. coal  
extracted for four hours at 110° C.

TABLE I

Conc. NaOH %	Amount of humic acid extracted g.	% Combustible in coal %	% Combustible extracted
0.3	0.299	78.1	3.8
0.5	0.864	78.1	11.1
1	1.18	66.3	17.8
5	1.19	66.3	17.9
10	.879	66.3	13.3
15	.920	78.1	11.8
20	.976	78.1	12.5
25	.634	78.1	8.1
30	.786	78.1	10.1
35	.601	72.6	8.3

Effect of concentration of Na<sub>2</sub>CO<sub>3</sub> upon extraction with Na<sub>2</sub>CO<sub>3</sub>  
10 g. coal extracted for 4 hours at 110° C.

TABLE 2

Conc. Na <sub>2</sub> CO <sub>3</sub> %	G. extracted	% Combustible in coal	% Combustible extracted
0.5	0.100	78.1	1.3
1	0.366	78.1	4.7
5	0.531	78.1	6.2
10	0.381	78.1	4.9
14	0.360	78.1	4.6
20	0.243	78.1	3.1



## RATE OF EXTRACTION

10 g. coal extracted at 100° C.  
with 1% NaOH

TABLE 3

No. hours extracted	G. extracted	% combustible in coal	% combustible extracted
1	1.04	66.3	15.7
2	1.13	66.3	17.1
4	1.18	66.3	17.8
6	1.53	66.3	20.0
Extracted with 10% NaOH			
1	.726	66.3	11.0
2	.730	66.3	11.8
4	.879	66.3	13.3
6	1.06	66.3	16.1

## EFFECT OF TEMPERATURE UPON EXTRACTION

10 g. coal extracted for 4 hours with 10% NaOH

TABLE 4

Temperature of extraction	Amount extracted	% combustible in coal	% combustible extracted
85	.672	78.1	8.6
95	.738	78.1	9.7
110	.879	66.3	13.3
125	1.53	78.1	20.3
140	2.90	78.1	37.2



## Elementary analysis of humic acids, coal and coal residue.

TABLE 6

Material	: Elem. Anal.				
	: Ash	: Moisture	: Ash and moisture		
	: :	: :	: H	: C	: O
1. Coal	: 0.4:	2.8	: 4.57	: 69.7	: 25.8
2. Humic acid, NaOH extraction	: 0.2:	2.0	: 3.86	: 66.8	: 29.3
3. Humic acid, $\text{Na}_2\text{CO}_3$ "	: 0.14:	2.85	: 4.08	: 66.7	: 29.2
4. Coal residue, NaOH "	: 13.6:	2.4	: 4.96	: 65.1	: 50.0

## Methylation results

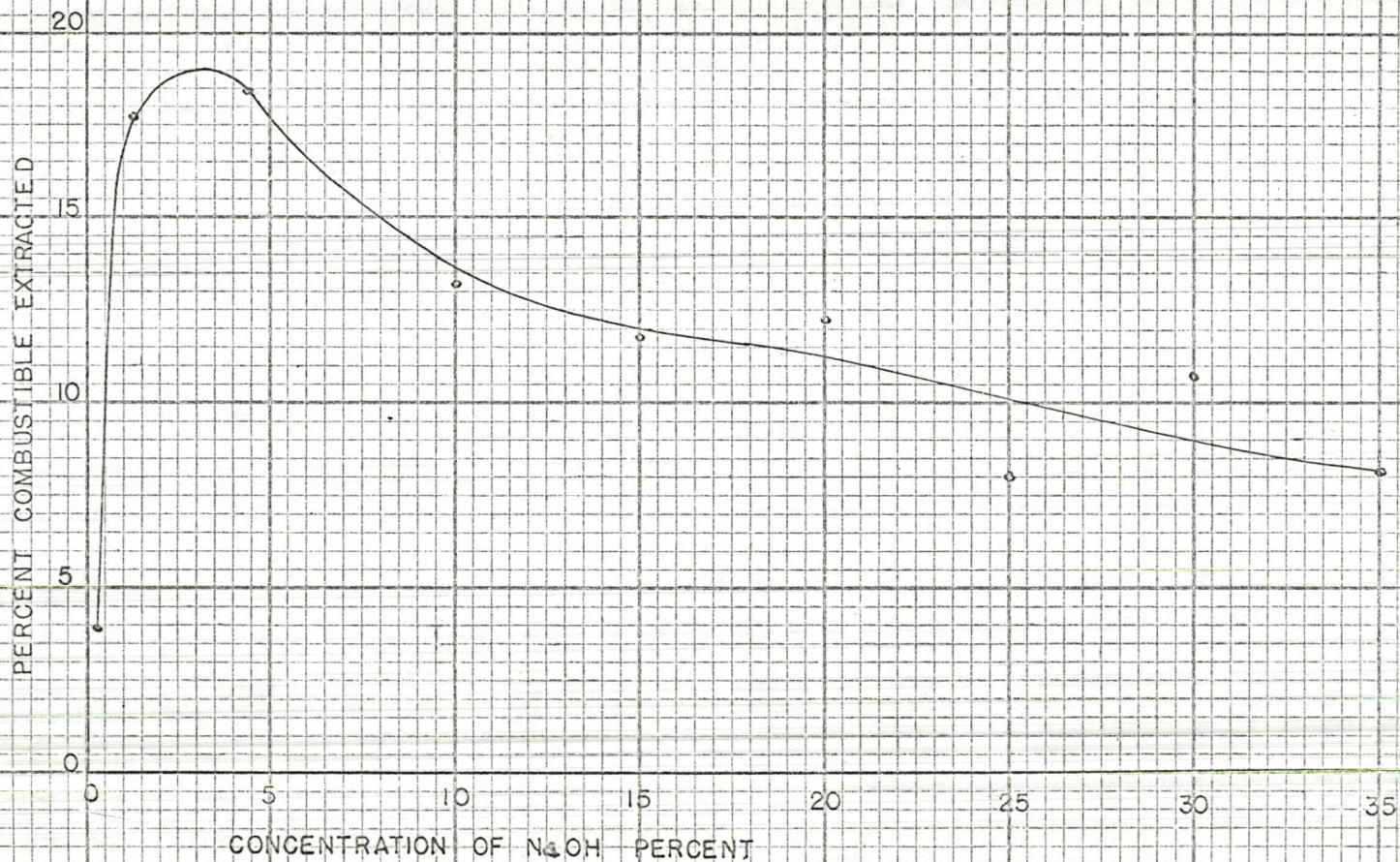
TABLE 7

	: Methoxy content		
	: 1st methylation	: 2nd methylation	: methylation
	: with meth.HCl	: with meth.HCl	: with $\text{CH}_2\text{N}_2$
1. Coal	: 5.4	: 6.4	: 4.5
2. Humic acid, NaOH extraction	: 5.9	: 6.2	: 16.6
3. Humic acid, $\text{Na}_2\text{CO}_3$ "	: 6.8	: 8.0	: 14.8
4. Coal residue, NaOH "	: 7.4	:	:
5. Coal residue, NaOH "	: 8.4	:	:
6. Coal residue NaOH "	: 6.3	:	:
7. Coal residue $\text{Na}_2\text{CO}_3$ "	: 5.9	:	:



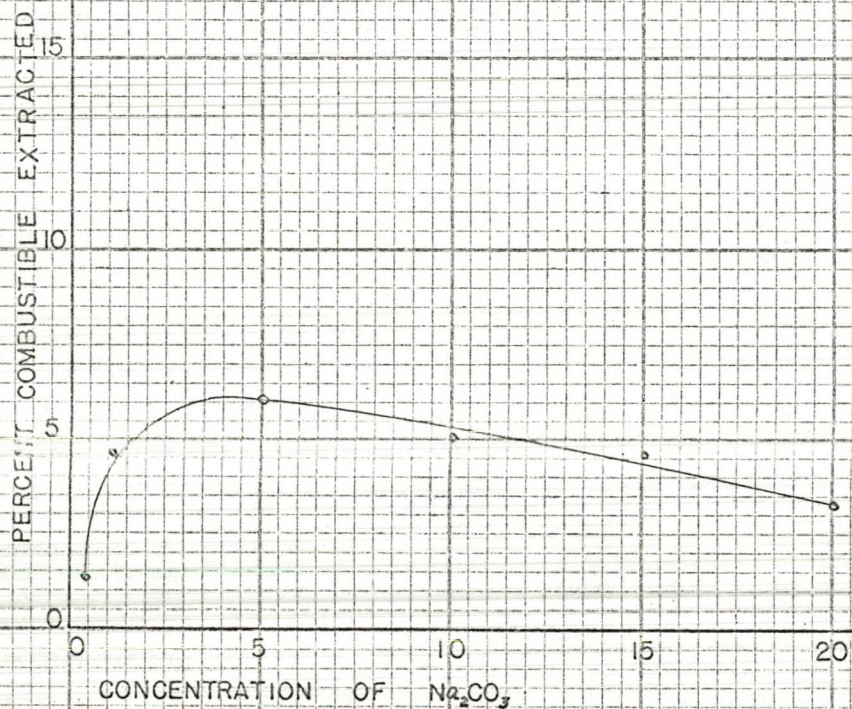
GRAPH NO. 1

EFFECT OF CONCENTRATION OF  $\text{NaOH}$   
UPON EXTRACTION





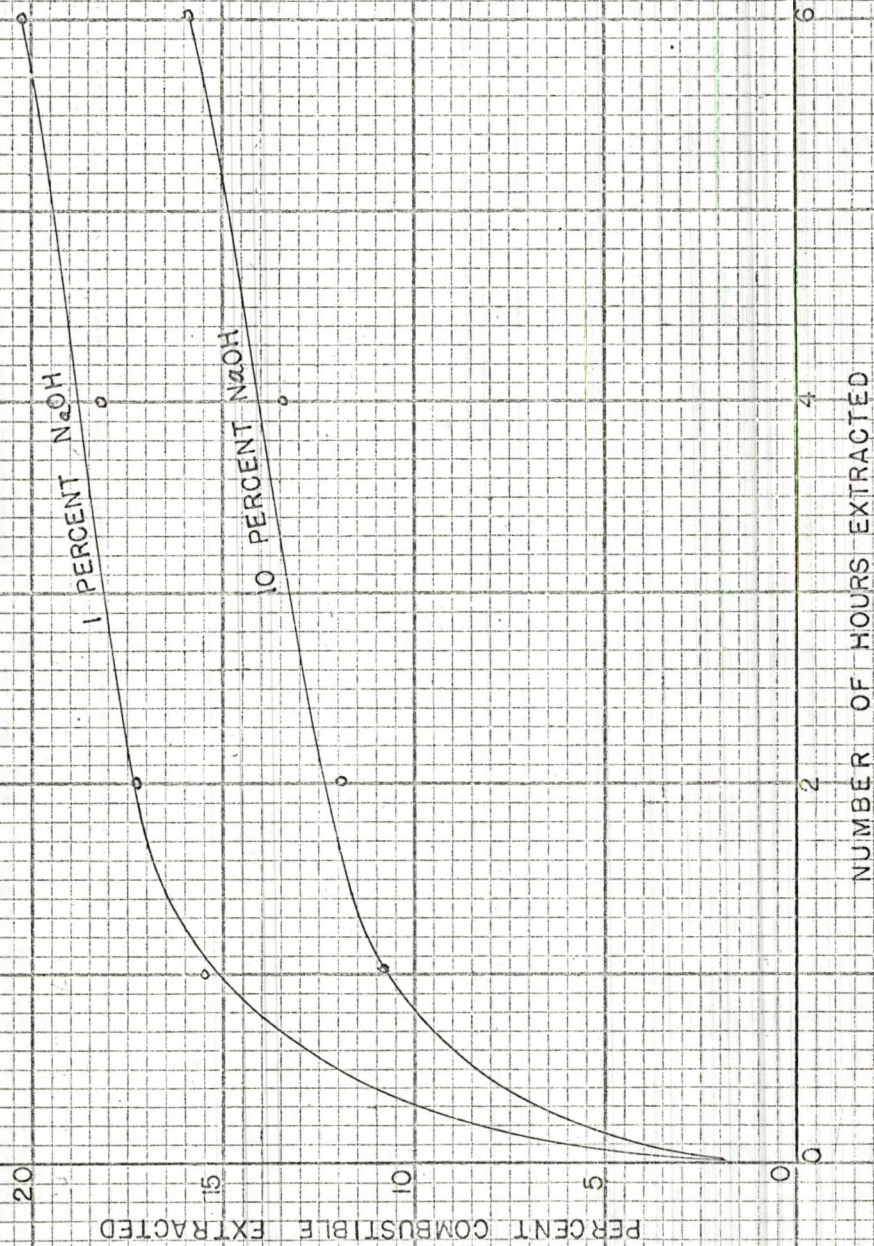
GRAPH NO. 2  
EFFECT OF CONCENTRATION OF  
 $\text{Na}_2\text{CO}_3$  UPON EXTRACTION





University of North Dakota  
College of Engineering

GRAPH NO. 3

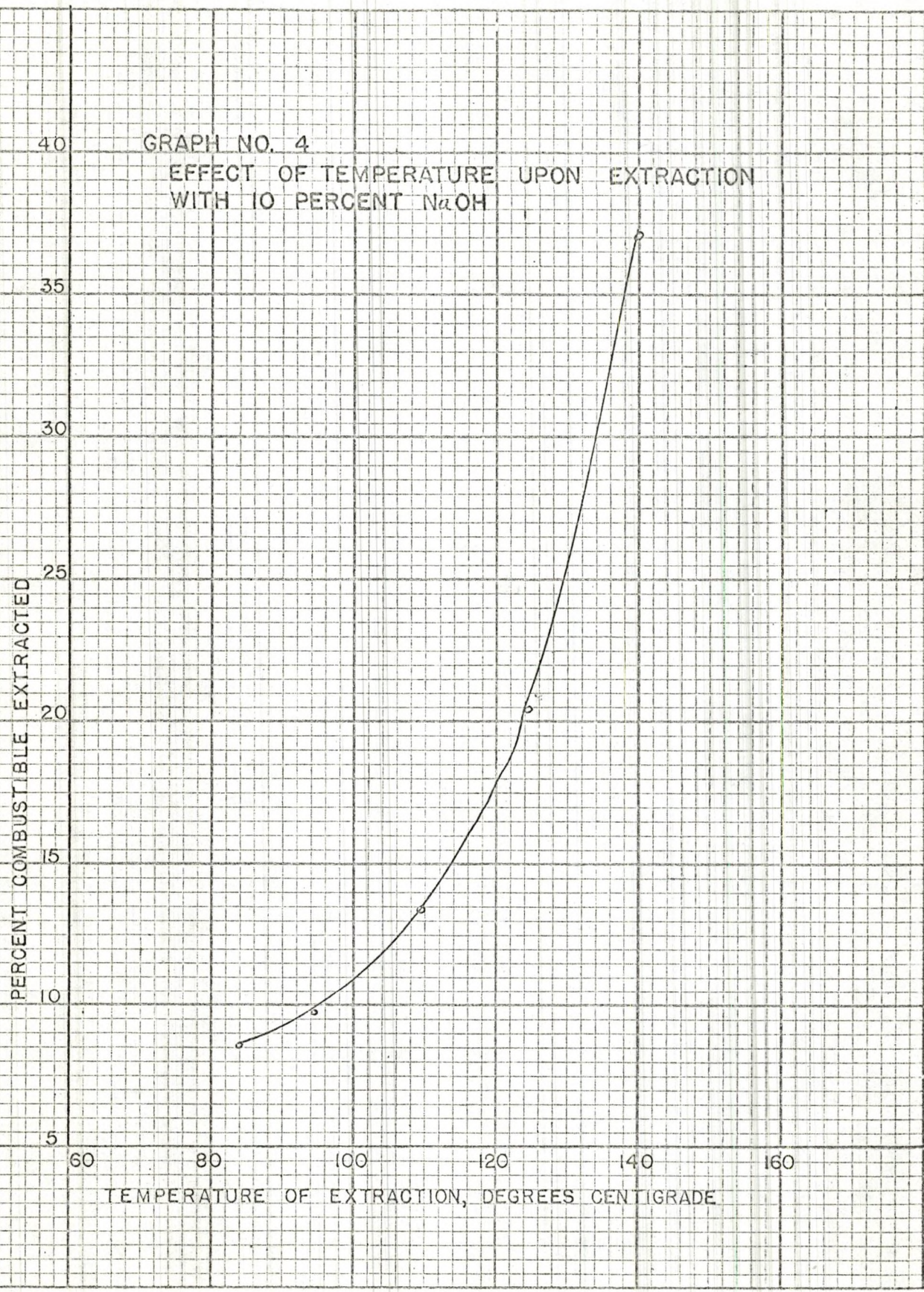
RATE OF EXTRACTION WITH  $\text{NaOH}$ 



University of North Dakota  
College of Engineering

GRAPH NO. 4

EFFECT OF TEMPERATURE UPON EXTRACTION  
WITH 10 PERCENT NaOH





## DISCUSSION OF EXTRACTION STUDIES

Effect of Rank.

In order to show the effect of rank upon the extraction of humic acid extractions were made of the peat and subbituminous coal described above. The results are given below.

TABLE 5.

Effect of Rank on Extraction  
10 g. of material extracted for 4 hours at 110° with 1% NaOH

Material	Amount extracted grams	% Combustible in material	% Combustible extracted.
Subbituminous Coal	0.28	73.8	3.5
Lignite	1.18	66.3	17.8
Peat	4.08	77.7	53.5

Effect of Concentration of extraction medium.

The extraction-concentration curve for sodium hydroxide rises steeply for concentrations under 1%, passes through a maximum between 1 and 5% and then gradually falls with increase in concentration. The curve for sodium carbonate is of the same general shape but lower on the graph, representing considerably smaller yields.

Three possible reactions may be proceeding during the extraction:

1. Saponification of the acid groups of humic acid, that is, formation of sodium humate.
2. Oxidation of the humus material with formation of -COOH and other groups.
3. Peptization of humic acid, or formation of hydrated and electrically charged colloidal particles.

The extractions were guarded against oxidation by excluding oxygen as completely as possible, but small amounts, probably not exceeding 0.005 grams, may have been present and taken part in the reaction. The question of



oxidation will be further discussed later.

As far as the writer knows there is no reason why a saponification or oxidation reaction should produce the maximum point exhibited by the curves described above. On the other hand it seems very possible that a high concentration of electrolyte might hinder the peptization of humic acid, since it is well known that an increase in electrolyte concentration will precipitate most colloids. It would also appear possible that the lower yields obtained with sodium carbonate are due to its lesser peptizing power.

#### Rate of Reaction.

The curve obtained by plotting yield of humic acid against time of extraction rises sharply during the interval representing the first hour and then becomes almost straight with a small positive slope. Two curves, one for 1% sodium hydroxide extractions and the other for 10%, are shown. The two curves are similar, apparently the only difference being that the curve for 10% sodium hydroxide is lower than the other, representing the smaller yield obtained with the more concentrated extraction medium.

Probably the sharp initial rise in the curve is due to the extraction of the more easily dissolved humic acids, while the straight portion represents a slow peptization and saponification of humic constituents.

#### Effect of Temperature.

The curve obtained by plotting yield of extraction with 10% sodium hydroxide against temperature rises steeply with the temperature, the slope increasing continuously. According to the shape of the curve, nearly 100% extraction or conversion of lignite to humic acid would be expected on raising the temperature of extraction a few more degrees. It may be that at these



temperatures larger molecules are split to form soluble humic acids. It may be mentioned here that by repeated extraction with 1.5% sodium hydroxide at  $140^{\circ}\text{C}$ . 6% of the coal, calculated to the moisture-and ash-free basis, has been recovered as humic acid. It is likely that some oxidation took place here, since the solution was changed and the coal exposed to the atmosphere several times.

#### Methylation Studies.

The various substances investigated in this study were as follows:

1. Coal, washed with warm dilute hydrochloric acid for several hours, in order to leach out iron, calcium, and aluminum oxides, which, by forming humates, block off hydroxyl groups from methylation.
2. Humic acid, extracted with 15% sodium hydroxide at  $110^{\circ}\text{C}$ .
3. Humic acid, extracted with 6% sodium carbonate solution at  $125^{\circ}\text{C}$ .
4. Coal residue, obtained as the residue from two extractions of three hours each at  $110^{\circ}\text{C}$ . with 1% sodium hydroxide.

Elementary analyses were made of these and all were methylated with methanolic HCl. Some of the methylated products of the first three was re-methylated with methanolic HCl in order to see if the methylation had been complete. Also samples of the first three materials were methylated with diazomethane, though not completely, since insufficient diazomethane hydrate was available.

5. Coal residue, obtained as the residue from the repeated extraction with 1.5% sodium hydroxide described earlier.
6. Coal residue, obtained as the residue from a single 4 hour extraction with 1% NaOH at  $110^{\circ}\text{C}$ .
7. Coal residue, obtained as the residue from a single 4 hour extraction with 6%  $\text{Na}_2\text{CO}_3$  at  $110^{\circ}\text{C}$ .

These three materials were methylated with methanolic HCl.



Discussion of Methylation Studies.

Several conclusions may be drawn from the methylation studies. It is apparent that the ester hydroxy content of the coal, humic acids, and coal residues are all of the same order of magnitude, since the methoxy values from methylation with methanolic HCl are all within a few percent of each other.

Although the elementary analyses of the two humic acids show no appreciable differences, the methoxy content of humic acid extracted with  $\text{Na}_2\text{CO}_3$  appears to be higher than that of the humic acid extracted with NaOH. It might therefore be concluded that the sodium carbonate extracts the more easily soluble humic acids richer in hydroxy groups.

By comparing the elementary analysis of the coal residue #4, and the methoxy content of this and the coal residue #5 with the analysis and methoxy content of the original coal, it may be seen that these coal residues, both of which were obtained by repeated extractions with sodium hydroxide, have been oxidized. The oxygen content of the original coal is 25.8%, and that of the coal residue #4 is 30.0%, while the methoxy values of these residues are higher than any others in the same column. This oxidation has probably taken place between or after extractions, while the residue was in contact with air and an alkaline medium.

Probably no conclusions should be drawn as to differences in hydroxy content of coal, humic acids, and residues from single extractions until further work has been done on the subject.



No comparisons between coal, humic acids, and coal residues may be made from results of methylation with diazomethane, since the methylations were not complete. However, it has been shown that humic acid may be methylated by this method to at least 16% methoxy. If we assume an ester methoxy content of 7%, the ether methoxy content, by difference, will be 9%. From the total methoxy content, 16%, an equivalent weight may be calculated:

$\frac{100.31}{16} - 31 + 17 = 189$ . The percentage of hydroxy oxygen in this  $\frac{16}{189} = 8.45\%$ , or, taking 29.2% as the total oxygen content of the humic acid,

$\frac{8.45}{29.2} = 29\%$  of the total oxygen of humic acid is found to be hydroxy oxygen.



## SUMMARY OF RESULTS

The results attained show that in the extraction of humic acids by

alkalies:

1. The yield of humic acid decreases with increasing rank of the coal.
2. Sodium hydroxide solutions give much larger yields than sodium carbonate solutions.
3. Maximum yield is obtained when the concentration of extracting medium is between 1 and 5 percent.
4. Extraction is very rapid during the first hour, and then becomes slower and continues uniformly.
5. The yield of humic acid increases as the temperature of extraction is raised, the effect being very pronounced as the temperature rises above 130° C.
6. Alkalies probably act as peptizing agents as well as saponifiers in dissolving humic acids.
7. Oxidation takes place on repeated extraction with sodium hydroxide, but plays an insignificant role in single extractions.
8. Humic acid from sodium carbonate extractions has a higher content of hydroxy group than humic acid from sodium hydroxide extractions, the reason probably being that sodium carbonate extracts the more easily soluble humic acids richer in hydroxy groups.
9. Methylation results show an ester methoxy content of methylated humic acids of about 7%, and of ether methoxy, 9%.
10. Humic acid, coal, and coal residue all have roughly the same carboxy group content.



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