A STUDY OF THE THERMAL DECOMPOSITION PRODUCTS OF LIGNITE

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A STUDY OF THE THERMAL DECOMPOSITION
PRODUCTS OF LIGNITE

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CHAPTER I

LIGNITE AND ITS UTILIZATION

CRACKING OF LIGNITE

Lignite and Its Origin

Lignite is a low grade of coal widely distributed throughout the world. It is distinguished from anthracite and bituminous coals by its lower density, higher moisture content, and woody structure. It is thought to have originated from partial "coalification" of vegetable matter. The isolation from lignite of wood-substances such as lignocericin acid, humic acid, and humates supports this theory. The occurrence in lignites, near Cothen, Germany, of bunches of hair-like yellowish-brown fibres which gave the chemical tests for rubber also serves to support the theory. Marcussen and Wisbar contend, from their investigations of lignite, that cellulose also enters into the formation of lignite and that lignite is merely "mummified wood."\(^1\)

The Analysis of Lignite

A complete analysis of lignite has not been made, due to the difficulty encountered in the separation of the complex organic compounds bonded therein. However, through the use of selective solvents, most of the more important constituents of

lignite have been isolated and analyzed by various investigators.

From a Guben (Germany) lignite, Schneider and Jantsch extracted 14 \% crude montan wax (bitumen A) by Soxhlet extraction with benzene; further extractions under pressure gave 9 \% of bitumen B.\(^2\)

Ciusa and Gallazzi isolated and analyzed compounds found to have the following formulas: (1) \(\text{C}_{15}\text{H}_{28}\) (b.p. 240-4\(^\circ\)), (2) \(\text{C}_{15}\text{H}_{26}\) (b.p. 265\(^\circ\)), (3) \(\text{C}_{20}\text{H}_{24}\) (m.p. 74-5\(^\circ\), having characteristics resembling those of hydrodocamphene), and (4) \(\text{C}_{24}\text{H}_{48}\text{O}_{2}\) (m.p. 78-9\(^\circ\), and having characteristics of and giving the lead and silver salts of lignoceric acid).\(^3\)

In further investigations, Ciusa and Galazzi detected two more compounds. By ether extraction, they obtained an oil which had the formula \(\text{C}_{22}\text{H}_{34}\) and boiling point 209-211\(^\circ\). On steam distillation of lignite, they obtained a thick, greenish oil, with a pinene odor, which gave a compound \(\text{C}_{14}\text{H}_{24}\) (b.p. 140-1\(^\circ\)) on fractional distillation.\(^4\)

Marcusson and Wisbar obtained humus acids by extraction with ammonia, free humus and lignitic acids by extraction with 10 \% sodium hydroxide, and cellulose on their analysis of German lignites.\(^5\)

\(^2\)W. Schneider and O. Jantsch, "Lignite Soluble in Alkali From the Hiederslansitz District", Chemical Abstracts, XIV (1920), 2069.

\(^3\)R. Ciusa and A. Galazzi, "The Constituents of Lignite", Chemical Abstracts, XV (1921), 2708.

\(^4\)R. Ciusa and A. Galazzi, "Researches on Some Constituents of Lignite", Chemical Abstracts, XIX (1925), 884.

\(^5\)L. Marcusson and G. Wisbar, "The Composition of Lignite"
Zechmeister and Frehden conducted a chromatographic study of Hungarian lignite, finding a water-soluble potassium salt belonging to the ascorbic-reducing acid reductose group, and a well crystallized compound belonging to the triterpene class. The latter compound had a molecular weight close to 400 (m.p. 244-7°).⁶

Utilization of Lignite

Lignite has a variety of uses; the principal use is as a fuel. However, the large moisture content decreases its heating capacity, and it is a poor fuel in comparison with anthracite or bituminous coal. It is also utilized to produce coke by the "water gas" method; tar, methane, acetylene, ammonia, and other gases being produced as by-products.

Lignite has been used in Germany as a pigment and as a fertilizer.⁷

Rosario used the ashes from lignite for the production of straw pulp in South America, and has suggested its commercial application in the pulp and paper industry.⁸

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⁷W. Schneider and O. Jantsch, "Lignite Soluble in Alkali from the Niederlansitz District", Chemical Abstracts, XIV (1920), 2069.

A patent issued to I. G. Farbenindustrie A.-G. in Great Britain covers the use of a dried, chlorinated product of degraded lignite as a tanning agent.\(^9\)

Cracking Lignite Under Atmospheric Pressure

Current investigation of lignite has been directed, primarily, at obtaining motor fuels and lubricating oils by its destructive distillation or by its hydrogenation.

Barlot obtained a patent covering the formation of lighter oils and gasoline obtainable by heating lignite very rapidly, electrically or by gas, in a fixed multitubular furnace under partial vacuum in an atmosphere of active reducing gases.\(^10\)

Egloff, Morrell, Timmerman, and Lemen cracked a mixture of lignite tars to produce gasoline and fuel oil residues. Greater corrosion was encountered, and lower plant capacities were obtained in comparison to petroleum cracking. The finished gasoline had a greater heating value per unit volume than that obtained from petroleum cracking. The gasoline also had good anti-knock qualities. The gas obtained was lower in molecular weight and heating value than that from petroleum cracking.\(^11\)

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\(^11\) Gustav Egloff and Others, "Cracking Tars and Distillates from Coal", Chemical Abstracts, XXXIV (1940), 1153.
Léopold obtained a patent covering the distillation of lignite by treating it in a powder or fine-grain form in a uniform layer of three millimeters thickness or less in a non-oxidizing atmosphere. The material was caused to progress by continuous or discontinuous movements over a heated surface approaching the area of highest temperature.\(^\text{12}\)

**Cracking Lignite Under Pressure**

The effect of various pressures on the cracking of lignite has been under investigation to increase the yield of oil fractions, improve the qualities as a motor fuel, and decrease the amount of harmful impurities difficult to remove.

Sustmann and Ziesecke studied the cracking of a Saxon brown coal (lignite) at 600\(^\circ\) at one, twenty-five, and fifty atmospheres of pressure. The light oil fractions were examined in detail and found to show an increase in aromatic compounds, identified as \(m\)- and \(p\)-xylene. A decrease in olefins was found with the use of pressure. Experiments at fifty atmospheres gas pressure and temperatures of 400\(^\circ\), 500\(^\circ\), and 600\(^\circ\) showed an increase of gas and a decrease of coke yields with increase in the cracking temperature. The tar yield remained constant, but its specific gravity and viscosity increased with increase in temperature. The content of aromatic compounds increased

\(^{12}\text{André Léopold, "Low Temperature Distillations of Carbonaceous Materials", Chemical Abstracts, XXXII (1938), 753.}\)
strongly, the content of paraffins decreased, while olefins and naphthenes remained unchanged. At 400°C, light oil containing 0.32% of aromatic compounds was obtained. This was 1% based on a moisture-free and ash-free coal as compared to 0.74% aromatic compounds obtained at 600°C and atmospheric pressure.\textsuperscript{13}

In the Blumner process, used commercially in Germany, low quality lignite tars are pumped and injected through a pipe lowered into molten lead contained in an externally heated autoclave. By this process the charged oil bubbles are brought to the surface of the melted lead without touching the walls of the heated zone. The process is conducted under a pressure of 35–40 atmospheres and a temperature of 450°C, the cracking temperature of the oil, which prevents overheating and coking. A larger yield of benzine of better quality, continuous operation, and greater safety to handle the crude and distillate simultaneously are said to be the main advantages of the Blumner process.\textsuperscript{14}

The Use of Catalysts in Cracking Lignite

The use of various catalysts in the cracking of lignite has been another approach toward obtaining larger quantities of high grade motor spirit. In conjunction with the catalyst

\textsuperscript{13}H. Sustmann and K. H. Ziesecke, "The Effect of Pressure and Temperature Upon the Characteristics of Tars Obtained In the Low-temperature Carbonization of Brown Coal Under Gas Pressure", \textit{Chemical Abstracts}, XXXIV (1940), 7577.

\textsuperscript{14}A. Karsten, "Cracking, Especially of Lignite Tars and Shale Oils, By the Blumner Process", \textit{Chemical Abstracts}, XXII (1928), 2050.
to increase the yield of petroleum spirit, various substances may be added to remove objectionable impurities, such as phenols and sulfur compounds.

In a process covered by the patent of Gabriel E. Salek, materials containing colloidally dispersed carbonaceous material, as constituents of lignite, are mixed with finely divided absorbent or adsorbent carbonaceous material, (preferably in amount substantially equal in quantity to that of fixed carbon in the hydrocarbon mixture treated) and the resulting mixture is heated and subjected to distillation. Hydrocarbon fractions and a residue of coke are obtained. "Activated" or "absorptive" carbons prove to be the most effective of various carbons used to facilitate the "unlocking" of volatile products from the initial materials. The process is further facilitated by the use of a small proportion of "nitrate alkali salt" or "alkali nitrates". 15

A German patent covers a process for catalysis in the vapor phase of gas mixtures from low-temperature distillations of bituminous fuels treated with desulfurizing metals or metallic oxides, preferably precipitated on porous carriers, and then with non-metallic contact catalysts such as active carbon or silica gel, without intermediate condensation. The resulting product contains a high proportion of light oils. As an example, gases from a low-temperature distillation of

of bituminous lignite were, without condensation, passed over nickel and bismuth to eliminate sulfur, and then over active carbon at 350-450° to increase the benzine yield.¹⁶

Michot-Dupont used a low-temperature, methylating carbonization process on lignite in obtaining a fuel for combustion engines. He used a mixture of 1000 parts of the fuel, 20 parts of calcium acetate, one part of iron oxide, and 20-40 parts of sodium carbonate in a horizontal rotating oven at 500°. Phenolic compounds were eliminated by conversion into methylated aromatic compounds. There was an increase in the yield of the oil and its volatility and a decrease in the sulfur content over other methods of low-temperature carbonization. Methylation modified the odor of the oil obtainable. The heavy oil was crackable by usual methods, particularly in vapor phase.¹⁷

De Gray carried out destructive distillations of French lignites using varied amounts of calcium carbide up to 5 % to study its effect on oil and gasoline yield. In proportions up to 2 % improvement in yield was observed. A 57 % increase was obtained in oil boiling below 220°, with 100 % increase in gasoline cut after removal of phenols and refining.¹⁸


The Physical Chemistry Research Company obtained a French patent covering the distillation of solid and liquid fuels such as lignite and petroleum distilled in the presence of alkali or alkaline earth salts. These salts are of acids capable of furnishing directly or by mutual reaction, either in the presence of a catalyst or not, molecules containing hydrocarbon groups of the treated material.

Lighter hydrocarbons are thus obtained. A metallic oxide may be used as a catalyst, and a base such as sodium carbonate may be added if a high content of sulfur is present.19

A French patent covers a process for the distillation of lignites carried out in the presence of a certain amount of sawdust impregnated with salts of iron and milk of lime.20

A United States patent by Karl Winkler covers the distillation of carbonaceous materials, such as middle oils from brown coal, to produce hydrocarbons suitable for use as an automotive fuel. The material is decomposed into lower hydrocarbons by heating in the presence of catalysts as graphitic acid or graphitic sulfide.21

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20 Soc. d'etude and d'exploitation de Breuets, "Distilling Lignites", Chemical Abstracts, XXXII (1938), 1077.

21 K. Winkler, "Hydrocarbons from Materials Such as Middle Oils from Brown Coal Distillation", Chemical Abstracts, XXXII (1938), 8127.
The Use of Both Pressure and Catalysts in Cracking Lignite

The use of both pressure and catalysts in the cracking of lignite seems to offer the solution to obtaining the highest yield of hydrocarbons suitable for consumption as a motor fuel. Most of the better processes use various pressures with appropriate catalysts.

In a French patent by Arthur F. Fabre, coal, lignite, peat, or like material is heated at about 100° in air, and then under pressure with a solution of potassium or sodium hydroxide. The products obtained are sprayed into a reaction zone kept at 1200°, and then mixed with steam and subjected in turn to the action of an electric discharge and the action of chlorine. Light hydrocarbon oils are thus obtained when the products are condensed. 22

In another French patent, Friedrich Uhde produces valuable hydrocarbons by using pressure and finely divided metals, preferably iron and water, as the catalyst. Petroleum, coal tars, lignite, and their distillation products are substances to which the process may be applied. If iron is used as the catalyst, it is regenerated by the hydrogen produced. 23

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23 F. Uhde, "Liquid Hydrocarbons", Chemical Abstracts, XXIV (1930), 3897.
Extraction of Diesel Fuel from Lignite

A number of diesel fuels are obtained from lignite by extraction with various selective solvents. The extraction is often accelerated by heating the mixture under pressure.

Through the use of selective solvents, Marder obtained oils of excellent quality by the treatment of lignite tars. Solvents discussed were benzene, nitrobenzene, and chlorox.24

A French patent to I. G. Farbenindustrie covers a process where oily products are obtained from lignite. A lignite which has a moisture content of 8-15 \% was treated with hydrogenated aromatic hydrocarbon solvents at a temperature ranging from 340\° to 430\° advantageously under a pressure of 50 to 200 atmospheres. The water was eliminated from the resulting oily products, which were easily separated from the solid substances.25

Bartholomaeis and Magaldi studied the action of solvents on Italian coal. They extracted six Italian coals with tetralin under pressure. Semiliquid products were obtained, which contained practically all of the original combustible material. Hydrogenation of the extracts led to products

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24 M. Marder, "The Use of Selective Solvents for Improving the Quality of Lignite Motor Fuels for Use in Diesel Motors", Chemical Abstracts, XXXIV (1940), 2564.

which were comparable in regard to nature and yield with those products produced by direct hydrogenation of the original coal.  

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CHAPTER II

ANALYTICAL PROCEDURE AND TESTS

The Problem

The major problem in the study of the thermal decomposition products of lignite centers itself around the analysis of the distillation tar in an attempt to identify the constituents of the complex mixture of organic compounds thus obtained. As it is practically impossible to identify the constituents of a mixture without separating them, some systematic method of analysis and attempt at separation of the mixture into its components, and the isolation of each component in its pure state, will be followed.

The Analysis Scheme

There are a number of excellent and accepted methods of approach to the analysis of an organic mixture, but the method of Clarke as outlined below was used.

TABLE 1

SCHEME FOR SEPARATION OF A MIXTURE OF ORGANIC COMPOUNDS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Distilled on</th>
<th>Water-bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Volatile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treated with Ether</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insoluble in Ether</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soluble in Ether</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treated with dilute H₂SO₄</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The various fractions, denominated I, II, etc., may contain the following types of compounds:

I. Hydrocarbons, ethers, alcohols, ketones, esters, aliphatic halogen compounds; and conceivably aldehydes, acetals, nitriles, aliphatic amines, mercaptans, sulphides, and alkyl nitrates and nitriles whose boiling points lie below 100°.

II. Metallic salts, salts of organic bases with mineral acids, carbohydrates and other polyhydroxylic compounds, amino acids, sulphonlic acids of all types.

III. Aliphatic and aromatic primary, secondary, and tertiary amino compounds; possibly some amides.

IV. Aldehydic and ketonic compounds, containing no groups which would have placed them in another fraction.

V. Hydrocarbons, ethers, alcohols, higher ketones, esters, and aliphatic or aromatic halogen compounds, not included in other fractions. Also nitriles; nitro-
hydrocarbons, ethers, alcohols; simple azoxy, azo hydrazo compounds; sulphides, disulphides, sul- phoxides, sulphones, sulphonamides and a few non-reactive anhydrides, ketones, and esters of mineral acids.

VI. Simple and substituted phenols, ketoenolic substances, mercaptans, some thioamides.

VII. Carboxylic acids; nitrophenols in which the nitro groups are present in either ortho or para position.¹

The low boiling volatile solvents of fraction I were removed by heating the substance in a distilling flask on a water bath. An efficient condenser was attached to the distilling flask, and heating was continued until no more liquid passed over. The liquid was then redistilled; a thermometer was used to see whether it was homogeneous or not. If not homogeneous, the mixture was further investigated with a view to separation by chemical means as fractional distillation in the ordinary way is not generally well adapted to the separation of mixtures in small amounts.

The residue of fraction II was washed with ether, the washings were added to the filtrate, and the residue itself was examined independently. Since most of the compounds in the group were oxygenated compounds, extraction with methyl

alcohol was carried out as a preliminary step towards further separation.

The solution of ether-soluble compounds was shaken with dilute sulfuric acid to remove the basic compounds. By means of a separatory funnel, the aqueous layer was then separated from the ether layer. The basic compounds were recovered by making the solution alkaline and extracting with ether.

The ethereal solution after this treatment was washed with water to remove the acid, the washings were discarded. It was then shaken with dilute sodium hydroxide solution to remove all compounds of an acidic character.

The ether layer then contained only neutral substances. All aldehydic and many ketonic compounds were removed by shaking with a concentrated sodium bisulphite solution. Acidification of the resulting precipitate with dilute sulfuric acid served to regenerate the aldehydes and ketones, and they were recovered by distillation, extraction, or filtration.

The alkaline solution of acidic substances was saturated with carbon dioxide and extracted with ether to remove all phenolic compounds containing no carboxyl or nitro groups, oximes and similar weak acids. After this extraction, acidification of the alkaline solution remaining served to liberate carboxylic acids and nitro compounds. They were recovered by extraction, filtration, or distillation.

When the mixture had been separated into the preceding groups, all ethereal solutions were evaporated. The ether, for safety, was efficiently condensed and recovered.
General Analytical Procedures

The further separation of the individual substances found in the different fractions followed no definite scheme, but a few general alternate suggestions were followed.

The treatment of the fractions with different liquids which exert selective solvent effects could in many cases be employed in the separation. Various liquids, such as water, ethyl alcohol, ligroin, benzene, acetone, chloroform, or glacial or dilute acetic acid might be used for this purpose. The mixture might be dissolved in one solvent and the components precipitated by the addition of another liquid in which it was insoluble.

Alternate steam distillations from acidic and alkaline solutions often constituted an excellent means of separation in place of extraction with ether. The tendency of certain compounds, such as esters and amides, to decompose or hydrolyze in acidic or alkaline solutions prevented this scheme from being used unless such compounds were known to be absent. However, they retain their identity when treated in ethereal solution with these reagents.

Fractional crystallization and fractional distillation under atmospheric or reduced pressure might be employed as a last resort when all other methods have failed. The extreme tediousness of the processes made them less favorable when other methods were available.
Separate Group Tests

Various tests may be performed before the compounds are isolated and individually analyzed. In fact much about the constituents of a mixture may be discovered by various tests employed. Many of the mixtures encountered in the groups often were so complex that isolation of individual compounds was difficult, and a study of the mixture itself offered the only knowledge of its nature.

Much about the nature and type of the phenolic compounds can be learned by the ferric chloride phenol test.

The Ferric Chloride Phenol Test—Many phenols give typical blue, green, purple, or red colors when a drop of ferric chloride is added to a dilute aqueous solution of the unknown. A number of phenols which do not give this test readily are found to respond when tested in alcoholic solution. Among the carboxy derivatives of phenol, those having the carboxyl group ortho to the phenolic hydroxyl, as in salicylic acid, respond with a typical deep purple color, but many compounds with the carboxyl group in the meta or para position fail to respond to the test.

Much about a hydrocarbon mixture might be learned by a study of its reaction toward a mixture of cold, concentrated nitric and sulfuric acids. Clarke has the following to say about hydrocarbons:

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2 Oliver Kamm, Qualitative Organic Analysis, p. 56.
Hydrocarbons, unless saturated or aromatic, do not exhibit a wide scope of reactions. Saturated hydrocarbons may be distinguished from unsaturated and aromatic hydrocarbons by their failure to rise in temperature when treated with a cold mixture of concentrated nitric and sulfuric acids. They are also completely insoluble in concentrated sulfuric acid, while unsaturated hydrocarbons are as a rule either dissolved or polymerised to higher-boiling products.  

Analysis of Individual Compounds

The ultimate analysis of individual compounds after purification can be even more systematically applied than can the separation of a mixture. One of the best outlined methods of attack is that of Oliver Kamm: (1) physical examination, (2) determination of physical constants, (3) elementary analysis, (4) solubility tests, (5) homologous tests, (6) consultation of literature, and (7) preparation of derivatives.  

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4 Oliver Kamm, *Qualitative Organic Analysis*, p. 108.
CHAPTER III

PROCEDURE AND RESULTS OF THE ANALYSIS

Dehydration of the Lignite: First Attempt

Several large lumps of the lignite were ground to pellet size and pulverized in a pulverizer. The pulverized lignite was then placed in containers to a depth of about 2-3 centimeters. Some of the lignite was placed in a weighed evaporating dish, and the dish reweighed. The containers were placed in an oven and heated to 120° C. At the end of each hour the evaporating dish containing the lignite was removed from the oven, cooled in a desiccator, and weighed. The process was continued until constant weight was obtained.

The lignite was weighed after one hour of heating and found to have lost approximately 10 °/o of its weight.

TABLE 2

DATA ON FIRST ATTEMPT AT DEHYDRATION OF LIGNITE

<table>
<thead>
<tr>
<th>Description</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of evaporating dish empty</td>
<td>47.0834 g</td>
</tr>
<tr>
<td>Weight of evaporating dish + lignite</td>
<td>90.2107 g</td>
</tr>
<tr>
<td>Weight of lignite</td>
<td>43.1273 g</td>
</tr>
<tr>
<td>Weight of evaporating dish + lignite</td>
<td>85.9690 g</td>
</tr>
<tr>
<td>Weight of water vapor lost</td>
<td>4.2417 g</td>
</tr>
</tbody>
</table>
The lignite was allowed to remain in the oven until the next morning when it was examined and found to consist of ashes. Several reasons might be advanced for its combustion. Firstly, the natural tendency of lignite to ignite spontaneously should be increased with a rise in the temperature. Secondly, the regulation of the oven was probably out of order. It was noticed on observations of the oven next night that the temperature rose as high as 145°, and did not stay at 120° first supposed to be its regulation. Lignite was being heated when the temperature reached 145°. Upon its removal, the odor of gases given off was noted. Although no flames or smoke was noted, the evolution of these gases apparently constitute a slow oxidation which leads to final combustion.

Dehydration of Lignite: Second Attempt

To present a better opportunity for observation of the dehydration of the lignite, the lignite was heated at a time convenient for frequent examination. The evaporating dish full of lignite was removed from the oven after each successive hour, cooled in the desiccator and weighed.

Difficulties in obtaining constant weight in the lignite were observed. The chain of the chainmatic balance was lowered so as to make the weights exceed the weight of lignite

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and container. In twenty or thirty seconds the lignite and container did displace the balance to the other side. The chain could be lowered to displace the balance again, by an excess of 20-30 milligrams. Within a minute or two enough moisture would be absorbed by the lignite to displace the balance again to the right. This was undoubtedly due to adsorption of atmospheric moisture.

**TABLE 3**

DATA ON SECOND ATTEMPT AT DEHYDRATION OF LIGNITE

<table>
<thead>
<tr>
<th>Hours Heating</th>
<th>Weight of Lignite + Evaporating Dish</th>
<th>Weight of Moisture Lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>82.8730 g.</td>
<td>........................</td>
</tr>
<tr>
<td>1</td>
<td>80.0330 g.</td>
<td>2.8400 g.</td>
</tr>
<tr>
<td>2</td>
<td>78.7952 g.</td>
<td>4.0778 g.</td>
</tr>
<tr>
<td>3</td>
<td>78.7700 g.</td>
<td>4.1030 g.</td>
</tr>
<tr>
<td>4</td>
<td>78.6764 g.</td>
<td>4.1966 g.</td>
</tr>
<tr>
<td>5</td>
<td>78.2151 g.</td>
<td>4.6579 g.</td>
</tr>
<tr>
<td>6</td>
<td>78.3246 g.</td>
<td>4.5484 g.</td>
</tr>
<tr>
<td>8</td>
<td>78.2104 g.</td>
<td>4.6626 g.</td>
</tr>
<tr>
<td>12</td>
<td>78.2228 g.</td>
<td>4.6502 g.</td>
</tr>
<tr>
<td>16</td>
<td>78.2225 g.</td>
<td>4.6505 g.</td>
</tr>
</tbody>
</table>

**Preliminary Attempts at Cracking Lignite**

Some of the powdered anhydrous lignite was mixed with U. O. P. Type B catalyst and heated with the flame of a Bunsen burner, then with the oxygen-gas (methane) torch to red heat. The gases from the cracking were condensed in a test tube.
cooled in a beaker of water. A few drops of greenish-colored oil over a clear liquid (presumably water) were obtained. The oil clung tenaciously to the sides of the test tube. It had a cresol like odor. A combustible gas, burning with a smoky, luminous flame was given off during most of the time the cracking took place.

Some of the lignite was cracked without catalyst by Bunsen flame. A larger proportion of combustible gases seemed to be given off when the catalyst was used. A small, almost invisible flame was produced by the combustion of the gas during the latter part of the cracking. A larger proportion of tar was yielded than was obtained in cracking by the use of the catalyst. The tar was of a greater density, as some of it was below the layer of clear liquid obtained. The product obtained, like that in the first cracking, had a creosote odor.

Sodium acetate and iron wire were employed as the catalyst in another cracking attempt. A larger proportion of gas was given off than was obtained in the second cracking. The distillate consisted of a layer of tar-oil on top, and a light orange colored solution below. There appeared to be less tar than previously, and more of the other liquid.

A mixture of calcium acetate, iron oxide, and sodium carbonate was used as a catalyst in another cracking to study its effect on reducing the phenolic odor of the distillate
obtained. The components were mixed in approximately the proportions advocated by Michot-Dupont.\textsuperscript{2} About the same amount of gases was obtained as in the foregoing attempts, but the tar obtained was more oily and had a less characteristic phenolic odor.

Phosphorus pentoxide was employed in another cracking of the lignite. The amount of gases, tar, and light liquid given off seemed to be approximately the same as that obtained in previous crackings. The tar had a very foul odor, much more objectionable than any previously noted.

Cracking of the Lignite

It was finally decided to crack the lignite under atmospheric pressure without the use of a catalyst. The distillation product was then studied with an attempt at isolation and analysis of the individual compounds it contained, when possible. The cracking was carried out in Pyrex test tubes, employing the Bunsen burner as the source of heat.

The test tube was inclined in a horizontal position during the cracking process. The tube was filled with lignite to a depth of about one-fourth of its diameter in this position. The lignite was cracked by heating the tube vigorously and moving the flame from the closed end of the tube toward the end with the delivery tube to drive all

distillation products from the tube. Uniform heating was insured by using a very loose-fitting cork stopper around the delivery tube, thus allowing the tube to be rotated by turning the stopper and tube at the cool end.

The temperature at which the cracking took place was not determined. However, it was about the temperature at which Pyrex glass begins to soften, 650° C. "Blisters" formed on two of the large Pyrex tubes used during the cracking, causing them to "blow out". Three (medium-sized) heavy-wall Pyrex test tubes, also "blistered", became distorted under heating during the cracking process.

The distillation products were condensed by passing them through a water condenser and catching the distillate in a test tube cooled in a beaker of water. Some of the distillation products collected in the cool part of the tube, but were driven out by heating that portion of the tube vigorously with the Bunsen burner. Copious quantities of white to yellow smoke were yielded at times with decreasing amounts at the end of the cracking. The tar which condensed in the receiver was of a light-yellow color and low viscosity. The tar became viscous and darker near the end of the distillation.

The final distillate settled into three layers—a black tar on the bottom of the receiver, a yellow or brown liquid in the middle, and a dark, viscous tar on top. The top tar was presumably closely identified with the smoke yielded, as condensation of the smoke aided in its formation. The
condensation of the smoke seemed to further facilitate condensation of the colloidal distillation products.

Preliminary Separation Attempts on the Lignite Tar

A one cubic centimeter sample of the tar was taken (after being thoroughly shaken up to insure a uniform sample) and subjected to the following investigations:

1. The mixture was heated on the water bath in a distilling flask attached to a condenser and found to contain no volatile solvent.

2. The residue in the flask was then treated with an excess of dry ether and found to be soluble leaving no visible residue. (Thus salts, carbohydrates and other polyhydroxylic compounds, sulphonics acids and similar substances insoluble in ether were eliminated from consideration in the analysis).

3. The ethereal solution was extracted with dilute sulfuric acid. The sulfuric acid layer was neutralized with sodium hydroxide and extracted with ether. Evaporation of the ether left no liquid or residue, indicating absence of basic compounds.

4. The ethereal solution from the sulfuric acid treatment was extracted with dilute sodium hydroxide solution to remove compounds of an acidic character.

5. The alkaline solution was saturated with carbon dioxide and extracted with ether to remove all
phenolic compounds containing no carboxyl or nitro groups, oximes and similar weak acids. Evaporation of the ether layer left a brownish-crystalline mass in the bottom of the flask, indicating a considerable proportion of phenols in the lignite tar.

6. Dilute sulfuric acid was added to the solution from the carbon dioxide saturation until carbon dioxide was no longer evolved. Carboxylic acids and nitrophenols were thus liberated and removed by extraction with ether. On evaporation of the ether, a brown stain was left, indicating the possibility of some strongly acidic compounds.

Separation and Study of the Constituents of Lignite Tar

As the preceding method of separation seemed satisfactory for the separation of the constituents of the tar into major groups, a like procedure was carried out on 15 cc. of the tar, but with the elimination of steps previously shown not to be necessary.

The tar was treated with ether and extracted with dilute sulfuric acid. The ether layer, containing the neutral and acidic constituents, was set aside for further analysis, and the acidic layer was neutralized with sodium hydroxide solution and cooled under the tap. A sweet, nauseating odor was noted when the acidic solution was neutralized. After cooling, the solution was made basic and extracted with ether.
A dark-brown extract was obtained in the ether, with the nauseating odor persisting. The ether containing the basic compounds was evaporated until all the ether was removed. A drop of brown liquid was obtained, with a few small, muddy crystals present.

The ether layer from the acidic extraction was made basic with dilute sodium hydroxide solution, and the neutral compounds were extracted with ether. The ether layer was removed by use of the separatory funnel and was set aside for further analysis. The alkaline layer was next saturated with carbon dioxide. The carbon dioxide was generated by allowing dilute sulfuric acid to drop from a separatory funnel slowly into a saturated sodium carbonate solution. A large area of absorption and saturation under pressure was obtained by passing the carbon dioxide into the solution through a large funnel lowered deep into the solution. The carbon dioxide was passed into the solution until two layers separated. It was extracted with ether to remove the weakly acidic constituents. The other layer (strongly acidic compounds) was drained from the separatory funnel and set aside for further analysis. The ether layer was dried over calcium chloride, and the ether was evaporated. A phenolic odor was noted in the remaining liquid which crystallized into muddy looking crystals on cooling. The crystals were treated with ethyl alcohol and benzene, ethyl alcohol, benzene, and acetone, but no solvent was found which would dissolve the impurities and
not the crystals. The crystals did not give the ferric chloride test for phenols, either in the aqueous or alcoholic solution. Formation of nitration and bromination derivatives was attempted, but the small amount of material limited further investigation.

The ether solution containing the neutral substances was shaken with a concentrated solution of sodium bisulphite, but no precipitate was formed, indicating the absence of aldehydic and ketonic compounds. The ether was evaporated, and the mixture was fractionated, fractions 45-90°, 105-120°, 120-220°, 220-240°, 240°-up being collected. A complex mixture was indicated by the fact that no stable boiling point was reached during any part of the fractionation process. The fractions were not redistilled because of the limited amounts.

**TABLE 4**

INVESTIGATION OF NEUTRAL FRACTIONS

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Amount</th>
<th>Boiling Point Range ° C.</th>
<th>Unsaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20 cc.</td>
<td>45-90</td>
<td>high</td>
</tr>
<tr>
<td>2</td>
<td>0.10 cc.</td>
<td>90-105</td>
<td>high</td>
</tr>
<tr>
<td>3</td>
<td>0.05 cc.</td>
<td>105-120</td>
<td>fair</td>
</tr>
<tr>
<td>4</td>
<td>0.35 cc.</td>
<td>120-220</td>
<td>fair</td>
</tr>
<tr>
<td>5</td>
<td>0.30 cc.</td>
<td>220-240</td>
<td>high</td>
</tr>
<tr>
<td>6</td>
<td>0.60 cc.</td>
<td>240 up</td>
<td>fair</td>
</tr>
</tbody>
</table>

The test for unsaturation was made with a mixture of cold concentrated nitric and sulfuric acids. All fractions showed
varying amounts of unsaturation, the first two fractions evolving the most heat. Fractions 4 and 6 gave the least amounts. All fractions after standing overnight contained two layers: (1) a bottom layer of clean, yellow liquid (acid mixture) and (2) top layer of brown reaction product. An equal volume of water was added to each mixture and shaken, then filtered. Yellow, oily stains were left on the filter paper in each case. Fractions 5 and 6 showed a few well-defined crystals, but not enough was left to offer an amount sufficient for running of a melting point determination in an attempt at identification. The fractions were noted to be of a light, yellow color, increasing in color to dark brown as the boiling point of the fraction increased. Evidently the darkening of the fractions was due to cracking as higher temperature was reached—some smoke and other evidences of cracking was noted during the distillation of the higher fractions.

The alkaline solution containing the strongly acidic compounds was acidified with sulfuric acid and extracted with ether. The ether was evaporated and a brown residue was left in the bottom of the beaker. It had the odor of valeric acid—probably n-valeric or some other aliphatic acid above propionic. The residue was tested with water and found to be insoluble for the larger part. The residue was "oily" to the water and did not emulsify or mix with it. In the water solution, the odor akin to valeric acid was even more noticeable than before.
CHAPTER IV

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

It is concluded that the lignite used did not have a great tendency to ignite spontaneously. However, the fact that it burned on one dehydration attempt gives credulence that it does have some tendency toward spontaneous combustion. The lignite used had been in storage in a dry place for several months, and it is to be concluded that it would not have the water content of fresh lignite. The lignite tar consisted principally of neutral components and phenolic compounds. No aldehydes or ketones were obtainable. The residue obtained from the basic fraction can probably be more closely associated with pyrolytic decomposition impurities than any basic components, and the absence of basic compounds be concluded.

In pursuit of further work, a larger amount of tar seems to offer the only solution to obtaining fractions in large enough quantities for isolation and identification of the individual compounds. It is suggested that a speedier method of obtaining larger quantities of tar be obtained. Also a method of controlling and observing the temperature is suggested as a method to insure obtaining the tar under regulated conditions. A more extensive study of cracking
with different catalysts and various pressures might also be suggested as an extension of the study.
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