

CARBONIZATION PRODUCTS
FROM SCHOLLER LIGNIN

by

ROBERT LOUIS KROLL

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APPROVED:

Professor of Chemistry

In Charge of Major

Head of Department of Chemistry

Chairman of School Graduate Committee

Associate Dean, Graduate Division

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CARBONIZATION PRODUCTS FROM SCHOLLER LIGNIN

INTRODUCTION

Present economic estimates (10) of the modified Scholler process for saccharification of wood, in particular, Douglas Fir, for the production of ethyl alcohol, indicate that the economic feasibility of the process in this country will depend to some extent upon the value that can be assessed from the by-products. Perhaps the most important of these, as regards the quantity of production, is the lignin residue from the wood hydrolysis. This quantity amounts to about 29 per cent of the wood used, as 13 pounds are produced for every gallon of alcohol (10). This lignin has been produced by dilute acid hydrolysis of the wood under pressure. This process involves a continuous extraction of the wood with dilute sulfuric acid for a period of hours. The lignin residue has been found (17) to contain some cellulose and has a fuel value of about 10,750 B.T.U. per pound, which puts it intermediate between wood, with a value of about 8,500 B.T.U. per pound, and bituminous coal, which varies from 11,000 to 14,000 B.T.U. per pound. Present economic calculations are based on this utilization of the material. However, this attaches but a small value to the material; and it has been estimated that, for each cent per pound increase that can be assessed the lignin over the value it may have as a fuel will reduce alcohol costs by approximately ten cents per gallon. Thus, it is desirable that an attempt be made to develop means of better utilization of this material.

Considering, then, the aromatic character of lignin, it was thought that through dry distillation of the material, the tars produced

therefrom might be of value as a source of phenolic materials, together with a carbon residue which may have some value as an activated charcoal (26).

It was the object of this research to determine the products obtainable upon atmospheric distillation of this lignin.

HISTORICAL

The origin of destructive distillation of wood and the use of the products is somewhat obscure. Klar and Rule (21) report the Egyptians made use of fluid tars and the pyroligneous acid products, whereas writings of Theophrastus (21) mentioned that the Macedonians burned charcoal in pits for the purpose of obtaining tar.

The examination of the distillation products from wood is mentioned in writings as far back as 1658, when Glauber identified the pyroligneous acid with the acid in vinegar. Boyle, in 1661, mentioned the separation of a spiritous liquid from the volatile products of wood distillation, which was not identified until 1812, when Taylor (33) found a resemblance of the material to ordinary alcohol. This was confirmed in 1835 by Dumas and Peligot (8) who gave the material the name of methyl alcohol. It was during this period also that Reichenbach, 1835, ascertained the components of wood tar and Lebon and Pellenkofer determined the composition of Wood-gas.

The industrial distillation of wood is said (9) to date from 1798, with the experiments of Lebon. Lebon was interested primarily in the distillation gas and the charcoal as a source of light, heat, and power; and the industry as developed was concerned with the recovery of the chemical products only to a minor extent. Acetic acid and methanol were of greatest interest, and by 1870 acetic acid was being prepared from the pyroligneous acid fraction with a degree of purity acceptable for use as a food. The wood spirit was being used as a denaturant.

The development of the dye industry following Perkin's discovery of Mauve, and Verguiss preparation of Fuchsin, gave stimulus to the utilization of the tars; but, it was not until the manufacture of smokeless powder that acetone assumed economic importance. This substance

had been recognized with the wood-spirit; but, because of its high price, it did not find technical application.

With the work of Payen (24) who first showed wood to be a heterogeneous mixture, the lignin problem developed. In his work on the isolation of cellulose, he removed a substance of higher carbon content than the cellulose which he designated as the "incrusting materials". This began the question of the composition of wood, and the manner in which the cellulose is associated with the lignin. Schulze (30) treated wood with nitric acid and potassium chlorate and obtained an insoluble material that he considered to be pure cellulose. Fremy (13) considered that the residue, remaining after treatment of wood with 72 per cent sulfuric acid, consisted principally of "ligneux" which he claimed had been chemically combined with the cellulose.

Thus, we see that lignin originated from a separation of wood into two components, a soluble and an insoluble material, by treatment of the wood with certain chemical reagents. With 72 per cent sulfuric acid the insoluble substance is in the lignin.

Chemical analysis of the composition of lignin and cellulose show that lignin is composed of a higher percentage of carbon, approximately 60 per cent to 70 per cent, as compared with 44 per cent in cellulose. The oxygen percentage, on the other hand, is lower in lignin than in cellulose. Lignin is composed of 25 per cent to 35 per cent oxygen, while cellulose contains approximately 50 per cent oxygen.

The isolation of lignin from wood, by dissolving the cellulose, is accomplished by several methods which are sometimes associated with the name of the man who developed the method. Klason lignin is produced by the treatment of wood with 72 per cent sulfuric acid, as previously mentioned. Willstätter and Zechmeister (36) employed fuming

hydrochloric acid, 40 to 42 per cent, which readily dissolves cellulose. Lignin from this process is usually termed Willstätter lignin. In addition to these two methods of lignin isolation numerous other reagents have been used; but these are of minor importance.

The chemical analysis of lignin differs but slightly with the method of isolation. Table No. 1 shows a comparison of carbon, hydrogen, and methoxyl analysis of spruce lignin isolated by various methods. From this it is seen that the methoxyl content is most changed by the method of isolation. However, agreement between different investigators using similar procedures is not much better than the differences in values expressed in the table.

TABLE NO. 1

Lignin Analysis from Various Preparations of
Spruce Wood (37)

<u>Procedure</u>	<u>% Carbon</u>	<u>% Hydrogen</u>	<u>% Methoxyl</u>
Sulfuric Acid	63.9	5.3	14.47 & 17.3
Fuming HCl	64.0	5.3	14.39
Fuming HCl	62.4	6.4	15.5
HCl & H ₃ PO ₄	63.9	6.0	-
Aqueous NaOH	64.0	5.5	-
Alcoholic Extract.	63.6	6.2	12.1
Cuprammonium Method	63.6	5.7	16.0

The saccharification of wood as accomplished by the Scholler process has been described by Collins (7). Wood waste, consisting of sawdust and chips, was compressed in brick-lined percolators to approximately 11 pounds per cubic foot by low-pressure steam (30-45 pounds per square inch) and then preheated with live steam to 265° F. to effect hydrolysis. Successive batches of 0.5 per cent sulfuric acid

were forced through the wood waste beginning at 165 and reaching 180 pounds per square inch in the final batch. Each batch remained in the percolator approximately 45 minutes. At the end of this time a dilute sugar solution was removed from the percolator, cooled in heat exchangers, neutralized, and otherwise prepared for fermentation.

The Bergius process of wood saccharification involves the use of dry wood and 40 per cent hydrochloric acid. The acid is contacted with the wood at room temperature in a battery of iron diffusers, the acid moving counter-current to the wood. A ratio of 7 parts acid to 1 part wood is used. With this process, practically complete hydrolysis of the wood is accomplished.

A modification of the Scholler process has been adopted in this country. This process is continuous as regards the dilute sulfuric acid extraction. Wood wastes from Douglas Fir are continuously extracted with 0.5 to 0.8 per cent sulfuric acid for a period of $3\frac{1}{2}$ hours at temperatures ranging from 145-185°C and at pressures of about 105 pounds per square inch. The lignin residue from this hydrolysis with from 70 per cent to 45 per cent moisture content is compressed to remove additional sugars.

There appear to be no publications on the destructive distillation of lignin, as such, until the work of Håggglund (16) in 1918 and that of Heuser and Skiölddebrand (19) in 1919.

Håggglund (16) destructively distilled Willstätter lignin from pine wood at atmospheric pressures with the following yield of products: charcoal 45 percent, oil 9.6 per cent, acetone 0.10 per cent, methanol 0.67 per cent, and acetic acid 0.64 per cent. There is no record of any attempt to separate the oil fraction into acidic and phenolic constituents.

Heuser and Skiöldebrand (19) distilled a Willstätter lignin from spruce under atmospheric pressure and obtained a charcoal residue of 50.6 per cent, and 13.0 per cent tars. The acetone, methyl alcohol and acid fraction, calculated as acetic acid, were 0.19 per cent, 0.90 per cent and 1.09 per cent, respectively, based on ash free lignin.

Working with Willstätter lignin from coniferous wood, Fischer and Schrader (11) found 57.2 per cent charcoal, 12.5 per cent tar, 13.2 per cent aqueous fraction and 17.0 per cent gas and loss upon atmospheric distillation. The tar was separated into 33.9 per cent phenolic material and 16.4 per cent acidic material.

Phillips (26) compared the atmospheric distilled products from 72 per cent sulfuric acid lignin, Willstätter lignin and alkali lignin. This lignin was all isolated from corn cobs. The alkali lignin gave a charcoal residue of 52.2 per cent, tar 17.7 per cent, aqueous fraction 15.5 per cent, and 13.5 per cent gas and loss. The tar was separated into 84 per cent phenols, 7.2 per cent neutral material, and 8.6 per cent acids. The Willstätter and 72 per cent sulfuric acid lignins gave a considerably higher per cent of charcoal residue, about the same amount of aqueous material and only about one-half as great a tar fraction as did the alkali lignin. The higher per cent of methanol from the alkali lignin than from the Willstätter and 72 per cent sulfuric acid lignins was explained as due in part to a higher methoxyl content of the alkali lignin.

Nasokin, Grog and Kaminskü (23) distilled a "commercial" lignin from pine pulp obtaining 57 per cent charcoal, 6.5 per cent tar and 1.2 per cent acids. They reported a methanol content of 0.45 per cent, acetone, 0.2 per cent, and 23.0 per cent gas and loss.

Katzen, Muller and Othmer (20) in a study of destructive

distillation of "lignocellulose" at atmospheric pressures, carbonized a "soluble" lignin prepared by a dilute sulfuric acid hydrolysis of maple wood. The lignin from this hydrolysis was extracted further with methanol. This extract was then precipitated by dilution with water. The material was termed soluble lignin, carbonization of which produced 55.8 per cent charcoal, 7.15 per cent tar, 11.7 per cent aqueous fraction, 9.3 per cent gas and loss. The products were found to contain 0.92 per cent methanol, 0.48 per cent acetic acid. It was found that 45 per cent of the tar was a neutral material. This may be compared with their carbonization of a "lignocellulose" containing 62 per cent lignin and 38 per cent cellulose. Such a material produced 45.8 per cent charcoal, 21.1 per cent aqueous distillate, 12.3 per cent tars and 18.5 per cent gas, by difference. The acetic acid amounted to 0.96 per cent and methanol 4.18 per cent of the original dry material. The neutral fraction of the tar amounted to 48 per cent. They concluded that the acetic acid was produced chiefly from the cellulose, while methanol came from the lignin. The aqueous distillate decreased with decreasing the cellulose content in the lignocellulose, while the charcoal increased.

Heuser and Brötze (18) compared the products of destructively distilling Willstätter lignin from spruce and aspen. They obtained 45.6 and 44.3 per cent charcoal residues, 13.1 and 14.2 per cent tars and 11.7 and 12.4 per cent aqueous distillate respectively. The acetone, methanol and acetic acid contents were about the same. They obtained 0.18 per cent and 0.21 per cent acetone, 0.82 per cent and 0.86 per cent methanol and 1.26 and 1.28 per cent acetic acid, respectively, from the spruce and aspen.

Szelenyi and Gromory (32) compared the products obtained from

destructive distillation of hard wood lignin with those obtained by Heuser and Brötz from soft wood lignin. They distilled lignin from oak at atmospheric pressures and obtained 53.0 per cent charcoal, 2.98 per cent tar, 1.29 per cent acetic acid, 1.47 per cent methanol, and 0.21 per cent acetone.

The distillation of lignin under reduced pressure was studied by Tropsch (34) and Fischer and Tropsch (12) with similar results. Fischer and Tropsch used pressures of 1 mm. which raised to 15 mm. They obtained a charcoal residue of 55.4 per cent, tar 11.6 per cent, aqueous distillate 22.9 per cent, and gas and loss 10.1 per cent. The tars were found to contain 31.5 per cent phenolic material, 7.5 per cent neutrals, and 53.1 per cent acids.

Pictet and Gaulis (28) distilled Willstätter lignin from fir under pressures of 5-25 mm and obtained the following yields: carbon 52.0 per cent, tar 15.0 per cent, aqueous distillate 21.0 per cent. The tars contained 11 per cent materials which were classified as neutral.

Using reduced pressures in an inert atmosphere (25 mm. of CO_2) Phillips and Goss (27) distilled an alkali lignin from corn cobs and obtained 50.5 per cent charcoal, 28.3 per cent tar, 11.7 per cent aqueous material, 9.3 per cent gas, 0.1 per cent acetone, 0.65 per cent methanol and 0.3 per cent acetic acid. An examination of the tar through separation with 5 per cent NaOH and NaHCO_3 extractions, steam distillations, and finally fractionation, resulted in the identification of acetic acid, catechol, phenol, o-cresol, quaiacol, creosol, 1-vinyl-3-methoxy-4-hydroxy benzene, and 1-n-propyl-3-methoxy-4-hydroxy benzene. Oxidation of the steam volatile neutral oil with potassium permanganate yielded anisic acid, while n-nonacosanane was identified in the non volatile oil.

A comparison of atmospheric and vacuum distillation was made by Bridger (5) using an alkali lignin from corn stalks. He found that reduced pressures favored the production of a tar which contained a larger per cent of phenolic materials. At atmospheric pressures he obtained the following products: charcoal, 59.2 per cent; tar, 11.6 per cent; aqueous distillate, 15 per cent, and gas, 14.2 per cent. The tar contained 49.2 per cent phenols, 37.9 per cent neutrals, and 12.9 per cent acids. At reduced pressures of 5.5 in. the carbon residue amounted to 57.5 per cent, wet tar, 17.7 per cent, aqueous distillate, 11.1 per cent, and 13.7 per cent gas. The tar was composed of 60.0 per cent phenols, 35.4 per cent neutrals, and 4.6 per cent acids. The phenolic materials from the tar were fractionated at atmospheric pressure with the identification of phenol, o-cresol, p-cresol, guaiacol, 3,5-xyleneol and creosol.

Bridger concluded from his studies that the rate of heating of the lignin during distillation was inconsequential and that the phenolic fraction of the tar was increased by low pressure distillation. Maximum tar formation was found, however, at 5.5 in. of Hg., while maximum phenol content of the tar was obtained at 2.2 in. of Hg., and it was estimated that lower pressures would further increase this fraction. The carbon residue was found to reach a minimum at pressures of 5.5 in. of Hg. and then to increase markedly as the pressures were lowered.

Freudenburg and Adam (14) distilled lignin from spruce wood which was mixed with nickel and nickel compounds in an atmosphere of hydrogen. They report obtaining an ether soluble distillate of from 20 to 48 per cent depending upon the substance mixed with the lignin. A phenolic content of 35 per cent of the inserted lignin is reported with a neutral fraction amounting to 7 per cent. The phenolic fraction was composed of 5.5 per cent phenol, 1.1 per cent p-ethyl phenol, 3.9 per cent guaiacol,

7.1 per cent p-cresol, 1.6 per cent p-ethyl guaiacol, 0.5 per cent o-ethyl guaiacol, 1.3 per cent isoeugenol.

The results of the various investigators are shown in tables, Nos. 2 and 3. (Table No. 2 is located on Page 12; Table No. 3, directly below.)

TABLE NO. 3

Summary of Composition of Tar from
Carbonization of Lignin

Investigator	Lignin	Source	Carboniza- tion Press.	Tar Analysis		
				% Phenols	% Neutrals	% Acids
Fischer & Schroder	Willstätter	Conif. Wood	Atmospheric	33.9	-	16.4
Phillips	Alkali	Corn Cobs	Atmospheric	84.0	7.2	8.6
Katzen & Muller	Methanol					
Othmer	Soluble	Maple	Atmospheric	-	45.0	-
Bridger	Alkali	Corn- stalks	Atmospheric	49.2	37.9	12.9
Bridger	Alkali	Corn- stalks	5.5 in.Hg	60.0	35.4	4.6
Bridger	Alkali	Corn- stalks	2.2 in.Hg	86.9	7.6	5.5
Fischer & Tropsch	Willstätter	-	1-15 mm.Hg	37.5	7.5	53.1

TABLE NO. 2

Summary of Carbonization Work in Literature

<u>Investigator</u>	<u>Lignin</u>	<u>Source</u>	<u>Pressure</u>
1- Heuser and Skioldebrand	Will.	Spruce	Atmospheric
2- Hägglund	Will.	Pine	Atmospheric
3- Fischer and Schrader	Will.	Conif. Wood	Atmospheric
4- Phillips	Alkali	Corn Cobs	Atmospheric
5- Grog, Nasokin and Kamenslů	-	Pine	Atmospheric
6- Heuser and Brötz	Will.	Spruce	Atmospheric
7- Heuser and Brötz	Will.	Aspen	Atmospheric
8- Szelenyi and Gromory	Will.	Oak	Atmospheric
9- Katzen, Muller and Othmer	Methanol Soluble	Maple	Atmospheric
10-Bridger	Alkali	Corn Stalks	Atmospheric
11-Bridger	Alkali	Corn Stalks	5.5 in. Hg.
12-Bridger	Alkali	Corn Stalks	2.2 in. Hg.
13-Tropsch	Will.	-	1-2 mm. Hg.
14-Fischer and Tropsch	Will.	-	1-15 mm. Hg.
15-Pictet and Gaulis	Will.	Fir	5-25 mm. Hg.
16-Phillips and Goss	Alkali	Corn Cobs	25 mm. Hg. in CO ₂

TABLE NO. 2 (Continued)

<u>Investigator</u>	<u>% Char.</u>	<u>% Tar</u>	<u>% Pyro- ligneous Acid</u>	<u>% Gas & Loss</u>	<u>% Acetone</u>	<u>% Methanol</u>	<u>% Acetic Acid</u>
1	50.6	13.0	-	-	0.19	0.90	1.09
2	45.0	9.6	-	-	0.10	0.67	0.64
3	57.2	12.5	13.2	17.0	-	-	-
4	52.2	17.7	15.5	13.5	0.13	1.90	0.05
5	57.0	6.5	-	23.0	0.20	0.45	1.20
6	45.6	13.3	29.7	-	0.18	0.82	1.26
7	44.3	14.2	30.5	-	0.21	0.86	1.28
8	53.0	2.98	-	-	0.21	1.47	1.29
9	55.8	7.15	12.4	24.7	-	1.92	0.48
10	59.2	11.6	15.0	14.2	-	-	-
11	57.5	17.7	22.9	10.1	-	-	-
12	56.0	15.5	14.7	13.8	-	-	-
13	53.8	10.2	14.2	-	-	-	-
14	55.4	11.6	22.9	10.1	-	-	-
15	52.0	15.0	21.0	-	-	-	-
16	50.5	28.3	11.7	9.3	0.10	0.65	0.30

Fischer and Tropsch (12) have reported the distillation of cellulose, wood, and lignin, under the same conditions. These distillations were made under reduced pressures. However, the cellulose is described only as a bleached commercial pulp, without analysis. The results of these distillations are shown in Table No. 4.

TABLE NO. 4

Vacuum Distillation of Wood, Cellulose and Lignin					
	% Charcoal	% Total Distillate	% Gas and Loss	% Alkali Soluble	% Acetic Acid
Cellulose	16.0	71.9	12.1	1.7	2.8
Cellulose	13.8	75.4	10.8	--	--
Cellulose	14.8	76.9	8.3	--	--
Extracted pine wood	20.4	59.6	20.0	5.5	6.1
Extracted beech wood	26.2	63.7	10.1	5.0	8.2
Lignin (commercial)	51.5	29.6	18.9	10.3	0.9
Pine lignin (lab)	46.7	43.7	9.6	8.8	--

EXPERIMENTAL PROCEDURE

Carbonization: The lignin used in this work was prepared in a pilot plant at the Forest Products Laboratory in Madison, Wisconsin. The lignin has been found, by analysis at Madison, (17) to have 17.7 per cent cellulose associated with the lignin. This material, air dried to a moisture content of approximately ten per cent, was used as the raw material in the present work.

For the carbonization experiments an iron, rotary retort, which held a charge of about 15 lbs. of lignin, was used. This retort was heated by a direct gas flame, as shown in figure No. 1, and rotated at a rate of 0.5 r.p.m. The lignin was entered at the free end of the retort, which was sealed by a cover held in place by a series of bolts around the periphery of the end of the retort. An asbestos gasket was used with this. The retort was also fitted with a chromel-alumel thermocouple which extended into the mass of the material undergoing carbonization. The vapor line through which the distillate passed led directly to the trap A, figure 1, which was cooled by a water spray. Above this trap was another trap B, through which the vapors were passed. This trap was packed with wood shavings to effect further condensation of the distillate. The vapors were then metered through a wet test meter and burned. Analysis from a previous work indicated that this gas could be assumed to have a mass of 0.07 lbs. per cubic foot

The lignin that was charged in any run was sampled for moisture content analysis by the standard A.S.T.M. toluene distillation procedure. All calculations are based on moisture free lignin.

The lignin undergoing carbonization was heated, while being rotated, to a temperature between 400° and 500° C. This normally required about

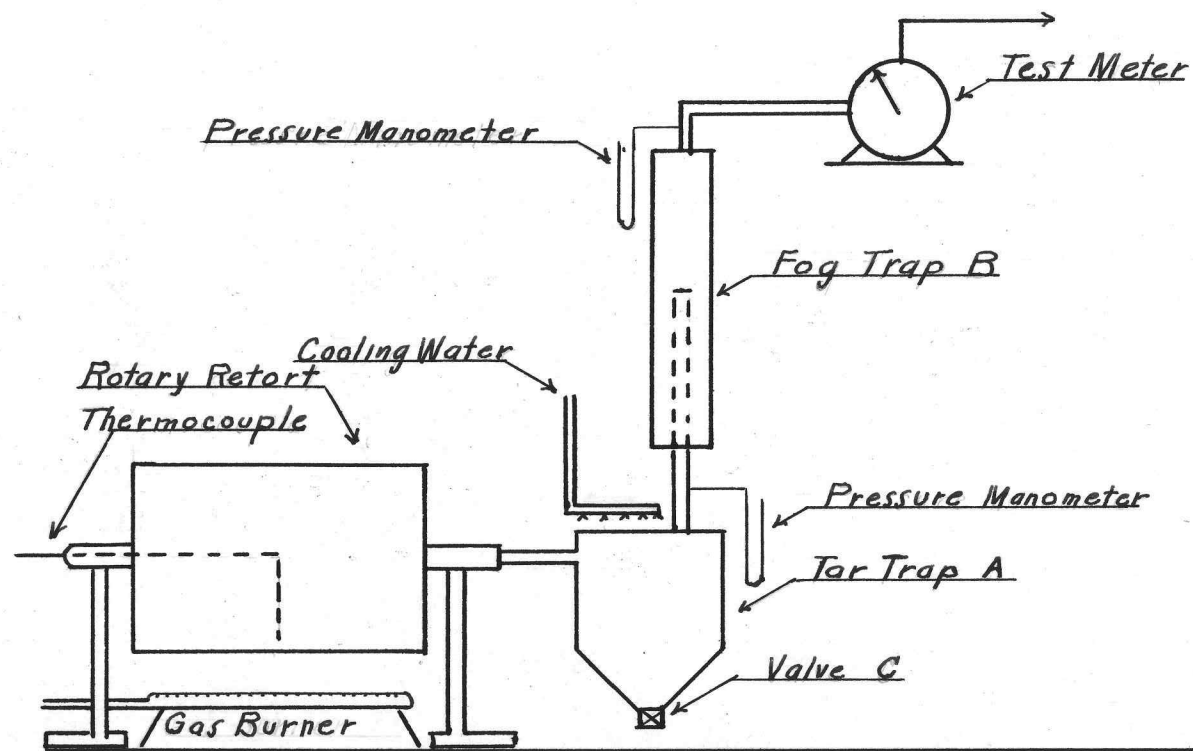


Figure 1, Carbonization Apparatus

4 $\frac{1}{2}$ hours.

At the completion of a run, the distillate, pyroligneous acid and tar, ^{were} removed from the water cooled trap A, through valve C, by heating the trap with steam. The material was not collected from trap B; instead the gain in weight of this trap was noted from weighing it before and after the carbonization experiment. The tar was removed from the pyroligneous acid by decantation and filtration.

Analytical procedures: The pyroligneous acid was analysed for acetic acid, acetone, methanol, and dissolved tar. The water content was assumed by difference. The acetic acid was determined by direct titration of a sample of the pyroligneous acid with standard base, using a Beckman glass electrode to determine the end point. The acetone content was determined by the Messinger method (15). This was applied to a weighed fraction of distillate of the pyroligneous acid, which distilled below 100° C. The methanol was estimated from specific gravity measurements on a weighed distillate from a known amount of the pyroligneous acid. This distillate was composed of material boiling up to 100° C. The dissolved tar was determined by distilling the water from a sample of the pyroligneous acid at atmospheric pressure, and weighing the residue in the distillation flask after the distillation had been carried to 150° C.

The charcoal from two different runs was analysed for volatile matter and ash content. These procedures were standard A.S.T.M. procedures (1).

Separation of Settled Tar: The tar from the various runs was combined and dried by vacuum distillation of the water from the tar. This was carried out on a water bath heated to 90° C and at pressures obtained by a water aspirator. A portion of this tar was taken up in ether, in

which to all appearances it was soluble, and separated into acidic, phenolic, and neutral fractions as characterized by solubility in 10 per cent aqueous sodium bicarbonate, solubility in 10 per cent aqueous sodium hydroxide and insolubility in either of these reagents respectively. A schematic representation of these separations is shown in figure 2.

All extractions made in this work were made with successive batches of fresh extracting solution until these solutions showed no coloration when shaken in a separatory funnel with the material undergoing extraction.

The ether solution of the tar was first extracted with the NaHCO_3 solution. This extraction was followed by extraction with 10 per cent NaOH . Upon addition of the NaHCO_3 solution, three layers were formed: the ether layer, the aqueous layer, and a solid precipitate which was soluble in neither the ether nor the aqueous layer. This third layer was separated by filtration, and upon acidification was found to be soluble in ether, leaving a small residue which was partially soluble in acetone. The remainder appeared to be charcoal.

Distillation of Settled Tar: A second fraction of the anhydrous tar was subjected to distillation at atmospheric pressure in a regular laboratory distilling flask. The tar was heated in the flask until a frothing of the residue occurred. This took place at a temperature between 275° and 300° C. At this temperature the distillation was stopped. The distillation resulted in a light oil distillate and a non-distillable residue. The distillate was separated into an acid fraction, as characterized by solubility in cold 10 per cent NaOH , and a neutral fraction. A portion of the material extracted by the NaOH was acidified and extracted with NaHCO_3 . Since there appeared to be only a slight

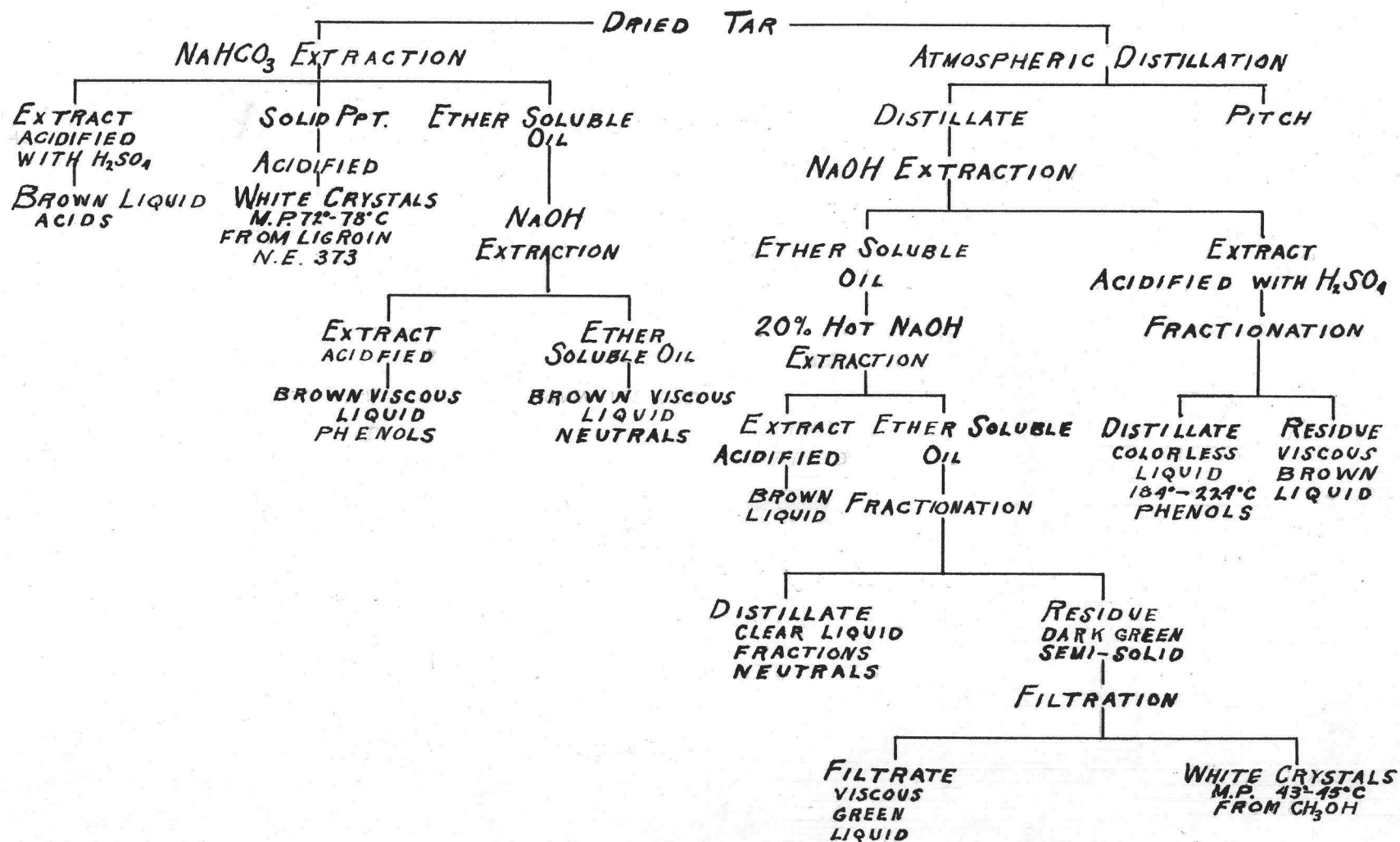


FIGURE 2, SEPARATIONS OF THE DRIED TAR

amount of material removed by this extraction, the NaOH extract was assumed phenolic and no effort was made to remove any acids therefrom.

Upon treating the neutral fraction from this distillation with 20 per cent NaOH at a temperature of 80° C a further separation was obtained which yielded an additional NaOH soluble fraction.

Fractionation of the products from the secondary distillation of the anhydrous tar: The distilled phenols and neutral materials were subjected to atmospheric fractionation in a Stedman-type, packed column (31). This column is diagramed in figure No. 3. It was constructed of pyrex glass, 12 mm. i.d. tubing packed to a height of 40 inches with a conical type packing made of 40 x 50 mesh monel metal screen. This was jacketed by a glass tube 25 mm. o.d. heated in two sections by a nichrome wire heating element coiled around the length of this jacket, and controlled by two 110 volt voltrons. The temperatures of the column were measured by two chromel-alumel thermocouples placed at the top and bottom of the heated zone respectively, between the heated jacket and the packed column.

The heated jacket was again jacketed by a 45 mm. o.d. glass pyrex tube which was insulated with 85 per cent magnesia pipe insulation. A slot in this insulation enabled the column packing to be observed over the length of the column. The column was attached by means of a standard tapered joint to a 500 ml. pot. This was fitted with a 360° C thermometer to indicate pot temperatures. The pot was heated by a fiber glass mantel heater.

The column head was cooled by a finger type condenser with the take-off from a side arm just above the thermometer bulb.

Refractive indices were taken of all the fractionation cuts, using an Abbe refractrometer.

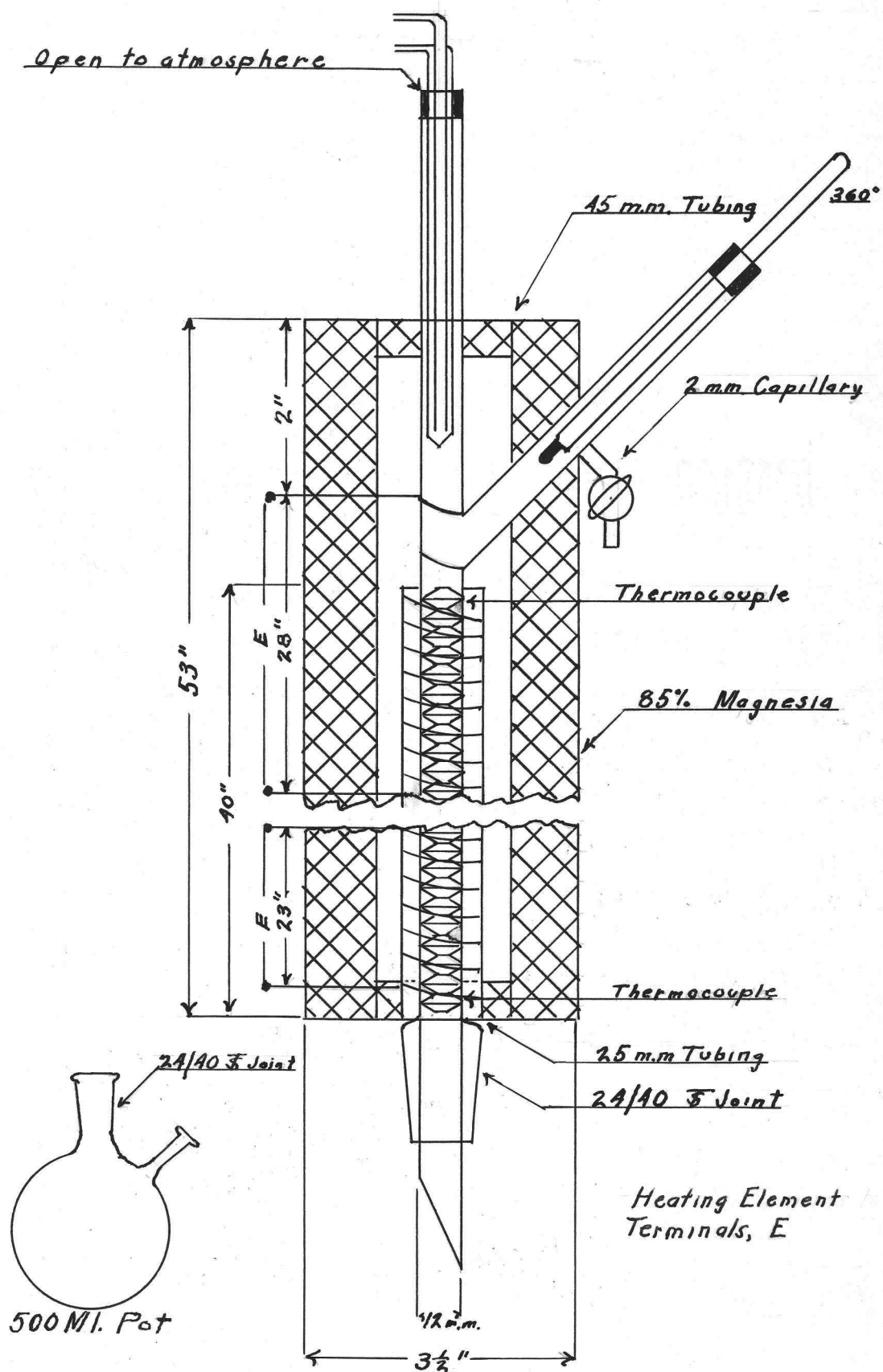


FIGURE 3, FRACTIONATING COLUMN

Further characterization of the cuts from the phenolic material was attempted by the preparation of various derivatives from the cuts. These consisted of 2,4-dinitrophenyl ethers, aryloxyacetic acids and 3,5-dinitrobenzoates. These derivatives were prepared by standard methods described in McElvain, Characterization of Organic Compounds (22) on fractions boiling below 225° C.

No derivatives were prepared from the neutral fractionation cuts. This material appeared to consist chiefly of a hydrocarbon mixture.

Methoxyl group (35) and hydroxyl group (25) analyses were run on the total, unfractionated, neutral sample. This sample was also tested for unsaturation by treatment with alkaline KMnO_4 and bromine in CCl_4 .

Steam distillation: Steam distillation procedures were applied to the phenolic fraction from the vacuum dried tar, and to the material which precipitated from the NaHCO_3 extraction of this tar. The acidic and neutral fractions of the material from the distilled tar were also steam distilled.

PRESENTATION OF DATA

Carbonization: A summary of the time-temperature, carbonization data for all the carbonization experiments is listed in Table No. 5. This table shows the time required to reach the various temperatures, the temperature at the end of each experiment, and the duration of the heating.

TABLE NO. 5

Time-Temperature Data							Final
Time in hrs.	1	2	3	4	5	6	
Run No.	°C	°C	°C	°C	°C	°C	
L-35	210	304	338	349	360	-	360 at 5 3/4 hrs.
L-36	132	360	382	407	410	438	438 at 7 1/2 hrs.
L-37	210	327	349	355	382	394	394 at 6 hrs.
L-38	188	310	388	418	441	443	432 at 7 1/2 hrs.
L-39	218	332	421	449	-	-	460 at 4 1/2 hrs.
L-40a	238	399	440	-	-	-	446 at 3 1/2 hrs.
L-40b	232	427	443	-	-	-	443 at 3 hrs.
L-41a	177	388	427	435	-	-	435 at 4 hrs.
L-41b	291	438	-	485	-	-	485 at 4 hrs.

The products recovered and weight balance data for the individual experiments are presented in Table No. 6. The averages of the product distribution on a percentage basis of moisture free lignin is presented in Table No. 7.

TABLE NO. 6

Product Recovery from Runs L-35 to L-41b

Run	Pounds Lignin Charged	% Water	Pounds Charcoal	Pounds Tar	Pounds Pyroligneous Acid	Cu. Ft. Gas
L-35	13.51	-	7.76	0.67	2.94	10.59
L-36	17.38	11.4	8.45	1.72	4.43	17.33
L-37	16.96	11.4	8.99	1.75	4.53	14.72
L-38	18.99	10.5	8.94	2.08	4.66	27.15
L-39	15.74	7.8	7.63	2.43	3.42	23.88
L-40a	18.39	8.2	-	-	-	20.39
L-40b	17.45	22.4	-	-	-	-
L-41a*	18.81	22.7	8.08	2.90	14.09	25.65
L-41b	18.36	-	7.48			27.68

* Products from L-41a and L-41b were combined.

TABLE NO. 7

Average Product Distribution
(L-36, L-37, L-38, L-39, L-41a & b)
Weight % Moisture Free Lignin

Charcoal	55.2
Settled Tar	12.3
Pyroligneous Acid	17.7
Gas and Loss (by difference)	<u>14.8</u>
Total	100.0

A sample calculation of a material balance is shown for run L-39 in Table No. 8. This run is taken as an example, as a better material balance was obtained from this run than from the others, from which material was lost through leaks in the rotary retort.

TABLE NO. 8

Material Balance from L-39

Lignin added	15.74 lbs.
% Water	7.8 %
Weight of Moisture Free Lignin	14.51 lbs.
Material Recovered	
Pyroligneous Acid	3.42 lbs.
Settled Tar (30.9 % Water)	2.43 lbs.
Charcoal	7.63 lbs.
Gas (23.88 cu. ft.)*	<u>1.67 lbs.</u>
Total	15.15 lbs.
-Water from Lignin	<u>1.23</u>
	13.92 lbs.
% Loss	4.06 %

* The gas is assumed to have a specific gravity of 0.07 lbs. per cu. ft.

Analysis of the pyroligneous: Analysis of the pyroligneous acid fraction by methods previously described resulted in the per cent composition listed in Table No. 9. The percentages listed here are on a weight per cent basis of the pyroligneous acid.

TABLE NO. 9

Composition of Pyroligneous Acid

	Weight % pyroligneous acid
Acetic Acid	2.53
Acetone	0.31
Methanol	1.95
Dissolved Tar	5.95
Water, by Difference	89.26

Separation of vacuum dried tar: The separation of a composite sample, from the combined vacuum-dried tars from all the runs, into phenolic, acidic and neutral fractions is summarized in Table No. 10. The

designation of solid acid is applied to the material previously mentioned, which was insoluble in a NaHCO_3 solution, but was ether soluble upon acidification. This material was solid when the ether solvent was removed. The liquid acids are those which were soluble in NaHCO_3 solution. When this material was acidified and removed from the ether solvent, the resulting material was liquid.

TABLE NO. 10

Composition of Vacuum Dried Tar

	Weight Per Cent of Dried Tar			Average
	1.	2.	3.	
Neutrals	24.9	24.6	21.0	23.5
Phenols	43.5	29.0	31.0	34.5
Solid Acids	15.8	23.4	26.4	21.6
Liquid Acids	7.2	5.6	5.4	6.1
Residue	6.9	9.5	7.5	7.9
Loss	1.8	7.8	8.7	

The product distribution of run L-39 may then be summarized as in Table No. 11. The percentages are calculated as per cent of moisture free lignin.

TABLE NO. 11

Summary of Product Distribution from L-39

	Weight % Moisture Free Lignin
Charcoal	52.60
Neutral Tar	2.72
Phenolic Tar	4.00
Acidic Tar, Solid	2.50
Acidic Tar, Liquid	0.70
Residue in Tar	0.91
Acetic Acid	0.60
Methanol	0.46
Acetone	0.07
Dissolved Tar	1.40
Water (from Pyroligneous Acid)	12.52
Water (from Settled Tar)	5.16
Gas	11.50
Losses	<u>4.80</u>
Total	99.95

Secondary distillation of dried tar:

The dried tar, which was subjected to a secondary distillation before separation into the phenolic and neutral components, is divided into the components listed in Table No. 12. These distillations were carried out in a laboratory distilling flask and heated until a frothing took place in the flask residue. This temperature was between 275° and 300° C.

TABLE NO. 12

Secondary Distillation of Dried Tar

	Weight % Tar 1.	Weight % Tar 2.	Average
Distillate	53.3	55.9	55.1
Residue (pitch)	39.5	41.3	40.4
Loss	6.2	2.8	4.5

It was found that, by carefully controlled heating of the residue material from this distillation, a further distillation was possible. This was accomplished by carefully heating the residue until the frothing reached the neck of the distilling flask. The heat was then withdrawn until the frothing subsided, whereupon, the process was repeated. Following this procedure with Sample No. 1 listed in Table No. 9, a temperature of 325° C was reached and the following analysis was obtained from the vacuum dried tar.

Distillate	71.7 %
Residue	19.2 %
Gas & Loss	9.0 %

The distillates were separated into acidic and neutral fractions by extracting the material with NaOH. Since the material extracted exhibited but a small solubility in NaHCO₃, after acidification, the mixture was considered essentially phenolic.

Separation data of this distillate are presented in Table No. 13.

TABLE NO. 13

Composition of Distillate from Secondary Distillation of Dried Tar

	Weight % Dried Tar		Average
	1.	2.	
Phenols	41.8	40.7	41.3
Neutrals	57.4	58.7	58.0
Loss	0.9	0.6	0.7

It was found that further separation of the neutral fraction from the separation listed in Table No. 13 could be brought about by treating this neutral fraction with 20 per cent NaOH at a temperature of 80° C. The results from this treatment are presented in Table No. 14.

TABLE NO. 14

Extraction of Neutrals with 20 per cent Hot NaOH

	Weight % Neutrals		Average
Insoluble in Hot NaOH	69.2	68.8	69.3
Soluble in Hot NaOH	26.1	28.0	27.1
Loss	4.1	3.2	3.9

Methoxyl determinations were run by the modified Zeisel method (35) on the material which was neutral to 20 per cent hot NaOH. A sample of 0.5096 grams was found to require less than 0.10 cc of 0.0160 N. $\text{Na}_2\text{S}_2\text{O}_3$, an amount which could be attributed to the reagents, as a blank was found to require 0.10 cc of the $\text{Na}_2\text{S}_2\text{O}_3$. Therefore, the presence of ethers in this fraction was not indicated.

Hydroxyl group analyses were run on the material, neutral to 10 per cent cold NaOH, and neutral to 20 per cent hot NaOH. These were carried out by acetylation of the mixture with acetic anhydride using potassium acetate as a catalyst. The sample was refluxed with the reagents for a period of 3 hours. This resulting product was then neutralized with NaHCO_3 , 10 per cent, and extracted with ether. The acetyl groups were then determined by the method developed by E. P. Clark (6) which consists of saponification of the acetyl groups with alcoholic KOH. The saponified material is then acidified and distilled at constant volume and the first 50 cc of distillate are titrated with

standard base to determine the acetic acid content. The analysis resulted in a hydroxyl percentage of 1.132 per cent for the fraction neutral to 10 per cent cold NaOH and 1.127 per cent for the material neutral to 20 per cent hot NaOH.

This method was checked by a procedure similar to that of Peterson, Hedberg and Christensen (25), applied to a macro scale. This analysis gave a hydroxyl percentage of 1.866 per cent for the material neutral to 20 per cent hot NaOH and 1.747 per cent for the material neutral to 10 per cent cold NaOH.

Steam distillation: In an attempt at further purification of the phenolic, acidic and neutral mixtures obtained in various parts of this work, they were subjected to steam distillation to separate the more volatile components. The phenols from the vacuum dried tar and from the distilled tar were steam distilled. The secondary distilled tar proved to be more steam volatile. The solid acid fraction was steam distilled in an attempt to remove the more volatile acids as an aid to further purification. During these distillations, which were carried out on samples weighing less than 100 grams, it was noted that the greater quantity of material distilled with the first 1000 cc of condensate, and thereafter the distillation appeared to proceed at a very slow rate. The results of these distillations are shown in Table No. 15.

TABLE NO. 15

Steam Distillation of Phenolic and Neutral Material

	Phenols from Tar Wt. %	Solid Acids Wt. %	Distilled Neutrals Wt. %	Distilled Phenolics Wt. %
Steam Volatile	41.8	17.3	72.3	88.6
Residue	56.6	78.6	22.5	11.3

Identifications of solid acids: In an attempt to further identify the material which precipitated from the NaHCO_3 extraction of the dried tar, the material was recrystallized from ligroin and from acetone. The ligroin proved to be the better medium. These recrystallizations resulted in white crystals that melted from 73° to 78° C. These were soluble in ether, petroleum ether, ligroin and acetone. This material gave no evidence of unsaturation with KMnO_4 or bromine in carbon tetrachloride. Neutral equivalents were run on different recrystallizations which gave an average value of 373. The preparation of the amide from this material resulted in products which gave melting points of $94-96^\circ$ C, $102-105^\circ$ C and $85-89^\circ$ C. A definite sharp melting point was never obtained from these derivatives. A list of neutral equivalent determinations from various melting fractions of the acid is presented in Table No. 16.

TABLE NO. 16

Melting Point and Neutral Equivalents of
Material Precipitated from NaHCO_3 Extraction

Mp C	N.E.
76-78	373
76-78	370
76	376
72	383

Fractionation of phenols: The phenolic fraction from the distilled tar was divided into two parts and fractionated in the 40 inch column previously described.

This column was constructed in an attempt to obtain a better fractionation of the complex phenolic mixture than that obtained by previous investigators (5). From a comparison of this column with columns of similar type packings tested by Bragg (4), this column should have approximately 70 theoretical plates.

To test the efficiency of the column in separating a phenolic mixture, a fractionation was run on a known mixture containing 25 ml of o-cresol, 20 ml of p-cresol, 25 ml of m-cresol, and 25 ml of guaiacol. The data from the fractionation of this sample are presented in Table No. 17.

TABLE NO. 17

Fraction of a Known Phenolic Mixture
 Mixture Composed of 25 ml o-cresol, 20 ml p-cresol,
 25 ml m-cresol, 25 ml guaiacol.

Cut No.	CC.	Temp° C	N 20
1	1	184-191	1.5430
2	3	184-191	1.5430
3	2	191	1.5441
4	3.2	190	1.5450
5	2.8	191	1.5455
6	4.4	191	1.5457
7	7.6	191-197	1.5420
8	5.0	197-198	1.5440
9	10.0	198-201	1.5425
10	10.0	201	1.5430
11	14.4	202	1.5435
12	5.0	202 $\frac{1}{2}$	1.5432
13	16.6	203	1.5438

The first fraction of the phenolic material was fractionated without further treatment, and the fractionation curve is shown in Figure 4a with the data in Table No. 18. Above 217° C decomposition of the material in the pot prevented further fractionation. So Sample II was distilled again in an ordinary laboratory distillation flask, and only that material boiling below 250° C was entered into the column pot for fractionation. This fractionation was carried to 225° C and the product distribution above 217° C is shown in Figure 4b. The data are given in Table No. 19.

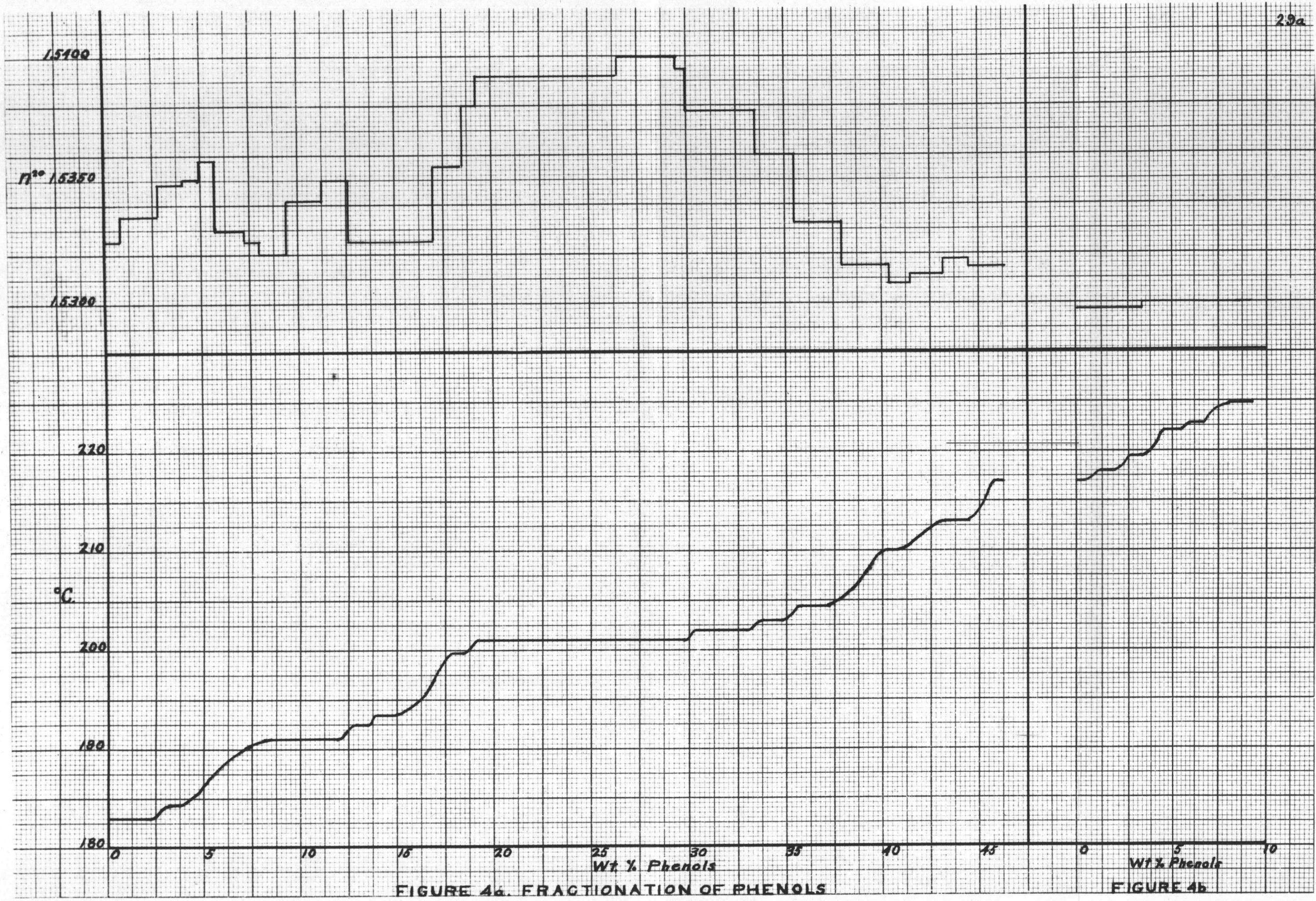


FIGURE 4a. FRACTIONATION OF PHENOLS

FIGURE 4b

TABLE NO. 18

Fractionation of Phenolic Tar
Sample I (248.5 grams)

Cut No.	CC.	Temp. °C	N ²⁰	Weight %
	15.0	Below 183	-	6.80
1	8.8	183-186 $\frac{1}{2}$	1.5335	4.04
2	6.9	186 $\frac{1}{2}$ -188 $\frac{1}{2}$	1.5358	3.16
3	5.4	188 $\frac{1}{2}$ -190	1.5320	2.48
4	5.0	190-191	1.5320	2.29
5	7.0	191-193	1.5350	3.21
6	4.0	193-198	1.5325	1.84
7	4.9	198-201	1.5355	2.25
8	15.6	201-201 $\frac{1}{2}$	1.5392	7.16
9	7.6	201 $\frac{1}{2}$	1.5400	3.48
10	8.1	201 $\frac{1}{2}$ -203	1.5378	3.72
11	4.4	203-204 $\frac{1}{2}$	1.5360	2.02
12	5.3	204 $\frac{1}{2}$ -206	1.5330	2.43
13	5.0	206-210	1.5315	2.29
14	2.7	210-211	1.5308	1.24
15	3.5	211-213	1.5312	1.61
16	2.8	213-216	1.5318	1.28
17	3.0	216-217	1.5315	1.38
18	44.4	200-210	-	20.40
Pot Residue	67.1 grams			27.0

TABLE NO. 19

Fractionation of Phenolic Tar, Sample II (169.8 grams)

Cut No.	CC.	Temp.	N ²⁰	Weight %
	3.3	Below 184	-	1.78
1	2	184-186	-	1.07
2	2	186-192	-	1.07
3	3	192-195	1.5291	1.61
4	3	195-196	1.5325	1.61
5	6.4	184-195	1.5320	3.44
6	5.0	195-199	1.5355	2.69
7	5.0	199-202	1.5369	2.69
8	5.6	197-202	1.5370	3.02
9	5.0	193-200	1.5361	2.69
10	4.0	200-202	1.5368	2.15
11	3.0	202-203	1.5368	1.61
12	2.8	203-204	1.5365	1.51
13	6.2	201-202	1.5365	3.34
14	3.0	202-204	1.5370	1.61
15	3.0	204-205	1.5361	1.61
16	3.0	205-206	1.5361	1.61
17	9.0	201-206	1.5361	4.84
18	2.4	206-209	1.5328	1.29
19	4.6	209-212	1.5300	2.48
20	4.6	212-214	1.5295	2.48
21	5.4	214-216	1.5298	2.90
22	5.0	216-218	1.5300	2.69
23	7.0	218-220	1.5300	3.77
24	3.0	220	1.5300	1.61
Pot Residue	48.9 grams			23.1
Residue Above 250°	42.0 grams			19.8

The residue material left in the pot after fractionation was a dark brown viscous liquid.

Attempts were made to further characterize the various cuts of fractionation I by the preparations of the derivatives (1) 2,4-dinitrophenyl ethers, (2) the aryloxyacetic acids and (3) 3,5-dinitrobenzoates. Attempts to prepare the N-phenyl carbamates were unsuccessful. The fractionated cuts and the derivatives prepared therefrom are presented in Table No. 20.

TABLE NO. 20

Cut No.	Wt. %	Derivatives from Phenolic Fractionation			
		N ²⁰	Derivative M.P. °C*	Lit. Value °C	Phenol
1	4.0	1.5348	(1) 66 $\frac{1}{2}$ -67° (2) 95°	(1) 69° (2) 99°	Phenol
2	3.2	1.5329	(2) 150-152	(2) 152°	o-cresol
3	2.5	1.5320	(2) 150 $\frac{1}{2}$ -151 $\frac{1}{2}$	(2) 152°	o-cresol
4	2.3	1.5320	(2) 153	(2) 152°	o-cresol
5	3.2	1.5350	(2) 152-153	(2) 152°	o-cresol
6	1.8	1.5325	(2) 153	(2) 152°	o-cresol
7	2.2	1.5380	(2) 132 $\frac{1}{2}$ -134 $\frac{1}{2}$	(2) 136°	p-cresol
8	7.2	1.5393	(2) 130-134	(2) 136°	p-cresol
9	3.5	1.5395	(1) oil (2) oil		
10	3.7	1.5378	(2) 136-139		
11	2.0	1.5360	(2) 139-140		
12	2.4	1.5333	(2) 141-142		
13	2.3	1.5315	(2) 135-136		
14	1.2	1.5388	(2) 139-140		
15	1.6	1.5312	(2) 138-140 (3) 157-159		
16	1.3	1.5318	(2) 138-140 (3) 162-163		
17	1.4	1.5315	(2) 106		

* (1) 2,4-dinitrophenyl ether

(2) aryloxyacetic acid

(3) dinitrobenzoates

The derivatives from fractions 10 to 17 formed constant melting compounds only after numerous recrystallizations. The melting points of these derivatives are not indicative of any particular phenol.

From the boiling points as shown in the fractionation curve, the phenolic distillate is estimated to have the composition listed in Table No. 21.

TABLE NO. 21

Composition of Fractionated Phenols

	Wt. % Total Phenols
Phenol	0.5 %
O-Cresol	10.0
M & P-Cresols	17.5
Guaiacol	2.5
Xylenols (205-220)	
2,4 & 2,5 xyleneol	3.0
2,6 xyleneol	4.0
2,3 xyleneol	3.0
3,5 xyleneol	2.0
	12.0
Creosol	2.5
3,4 Xyleneol	1.5

Fractionation of neutrals: The fractionation of the neutral fraction was carried out at atmospheric pressure to a temperature of 275°C. At this temperature, as recorded at the column head, pot temperatures were near 350° C. Therefore, the fractionation was discontinued. The fractionation curve is shown in Figure 5 and the data are listed in Table No. 22.

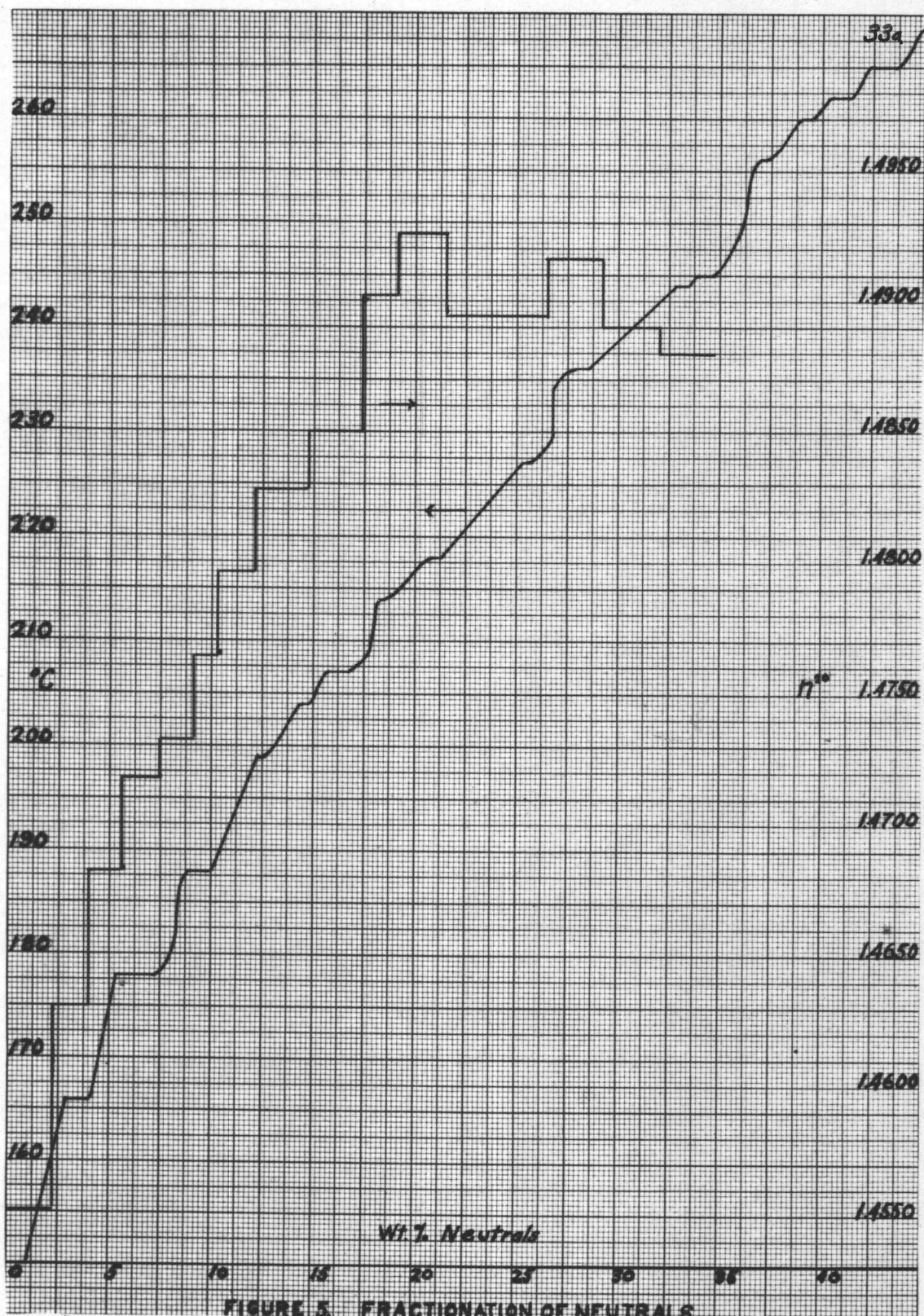


FIGURE 5. FRACTIONATION OF NEUTRALS

TABLE NO. 22

Fractionation of Neutrals

		119.5 Gram Sample		Wt. %	N ²⁰
Cut	Temp.	CC.	Neutrals		
Below	144°	8.2	7.1	-	
1	144-160	2.5	2.16	1.4552	
2	160-166	2.0	1.72	1.4630	
3	166-178	2.0	1.72	1.4682	
4	178-178½	2.0	1.72	1.4718	
5	178½-188	2.0	1.72	1.4732	
6	188-189	1.5	1.29	1.4625	
7	189-199	2.0	1.72	1.4796	
8	199-204	3.0	2.59	1.4828	
9	204-210	2.8	2.42	1.4850	
10	210-215	2.2	1.90	1.4902	
11	215-219	3.0	2.59	1.4926	
12	219-224	3.0	2.59	1.4894	
13	224-230	2.5	2.16	1.4894	
14	230-237	3.5	3.02	1.4906	
15	237-243	3.0	2.59	1.4890	
16	243-246	3.0	2.59	1.4880	
17	246-258	4.0	3.45	-	
18	258-263	4.0	3.45	-	
19	263-275	6.0	5.17	-	

Residue above 275° 55.5 grams 46.4 %

There was no evidence of decomposition having taken place during the fractionation. The pot residue was a viscous grease-like material from which white crystals were separated by filtration. These crystals

were recrystallized from methanol and from acetone with a resulting melting point range of 43° - 45° C.

The refractive indices of the material above 237° C could not be taken with the Abbe refractometer, since the material did not give a sharp line that could be read.

Analysis of Charcoal: Ash content and per cent volatile matter analyses were run on the charcoal from runs L-41b and L-36. The charcoal from L-41b had been heated to 485° C and that from L-36 had been heated to 438° C. These determinations were run according to standard A.S.T.M. procedures (1). The results are shown in Table No. 23.

TABLE NO. 23

Analysis of Charcoal		
	L-41B	L-36
Volatile Matter	20.3 %	32.5 %
Ash Content	1.88	8.74

DISCUSSION

The products from the destructive distillation of this Scholler lignin are in line with the values reported in the literature from the atmospheric distillation of the various lignins. The charcoal content is slightly higher than most reported values from Willstätter lignins, and slightly lower than the content of charcoal Bridger (5) found from alkali lignin from corn stalks. The reduced pressure carbonization of Willstätter lignin by Fischer and Tropsch (12) gives values in agreement with these obtained at atmospheric pressure.

The value which is attributed to the tar in evaluating product distribution may be misleading. Values reported as settled tar may contain varying amounts of occluded water, and consequently show a higher value than is shown when the tar is calculated as dry tar. In making comparisons with data in the literature this must be considered. Often the material is listed only as tar with no mention of the water content. Considering this possibility of error, the values found in this work compare favorably with most reported, and definitely higher than the yields from pine lignin.

A direct comparison of this work with most reported in the literature is not strictly valid, due to the variation of product distribution with the lignin source, and the fact that this lignin contains some cellulose which Katzen, Muller and Othmer (20) have shown to have some effect. Their work with "lignocellulose" materials with varying percentage composition of lignin and cellulose led to a correlation from which one might predict the product distribution from the carbonization of a given cellulose lignin composition. It is interesting to compare these values with the values found from this lignin. The comparison is shown in Table No. 24.

TABLE NO. 24

Comparison of Product Distribution with Predicted Values

	Predicted	Found
Charcoal	50%	52.6 %
Tar	10	11.6
Pyroligneous Acid	20	14.3
Gas	20	15.5

The methanol, acetone and acetic acid content of the pyroligneous acid fraction are not high enough to be of importance economically. On a basis of per cent dry lignin, the values are slightly lower than most reported in the literature. Closest agreement is with the values obtained from the carbonization of Willstätter pine lignin. The acetic acid content compares favorably with predicted values from Katzen, Muller and Othmer.

The separation of the dried tar into acidic, phenolic and neutral components indicates that this tar is a bit unusual in that the acid content is higher than all reported values except for that of Fischer and Tropsch (12) obtained from reduced pressure carbonization. In fact, the values for this tar are high by about the amount of material that is precipitated from the NaHCO_3 extraction of the tar, and which has been classed as solid acids. This material seems to be unique to this work, as there is no literature mention of obtaining such a material in the quantities obtained here.

The material apparently is a mixture of long chain fatty acids. The neutral equivalent determinations indicate this, and the melting point of the material behaves in a manner quite similar to long chain fatty acids. These acids are difficult to separate from a natural source in a degree of purity sufficient to give the melting point of

the same acid which has been synthetically prepared. The behavior of the amide prepared as a derivative from this material also indicates a mixture. The highest melting fraction obtained, after numerous recrystallizations, melted from 102-105° C, while the melting point of the amide of cerotic acid is 109° C (2).

The phenolic content of the tar is about the same as is obtained from various Willstätter lignins, but considerably lower than the yields obtained from alkali lignins. This is in agreement with the work of Phillips (23)

The resulting products from the separation of the dried tar into its constituents differed, physically, chiefly in odor. They all were dark brown in color, and all were liquid with the exception of the solid acids. The liquid acids had a very sharp odor characteristic of organic acids, while the phenols possessed an odor resembling creosote. The solid acids, when recrystallized from ligroin, were white crystals, soluble in petroleum ether, ether, and acetone.

A comparison of product distribution on the dried tar, and in the tar after subjection to atmospheric distillation, indicates a decrease in the phenolic and acidic concentration, with increasing neutral content in the tar which had been distilled. This may be due to pyrolytic decarboxylation of the acids to the hydrocarbon material. This comparison is listed in Table No. 25.

TABLE NO. 25

Product Distribution in Dried and Distilled Tars

	% of total dried tar	
	Dried tar	Distilled tar
Phenols	34.5	22.7
Neutrals	23.5	31.9
Acids	27.7	----
Residue	7.9	40.4

The fractionation of the phenolic material was not what was hoped for from the column. This column had been built to take advantage of a superior theoretical plate-per-inch value over columns previously described in the fractionation of phenolic mixtures. However, when used with a known phenolic mixture, the results were disappointing. While 24 ml. of a known 25 ml. of o-cresol in the mixture were made to crystallize when cooled below the melting point of the compound and seeded with a crystal of o-cresol, it was found that the meta- and para-cresols were not separated, nor was there a sharp break up to the guaiacol boiling range. This material apparently distilled with the meta- and para-cresols to an extent. This difficulty may have been due, in part, to the small sample that was used, which made column equilibrium difficult to obtain, for in the fractionation of the phenolic material from the dried tar it was possible to form crystalline derivatives of p-cresol from cuts which gave the boiling point and refractive index of this compound. Above p-cresol, definite melting derivatives of the different phenols could not be prepared, and only the boiling point flats of these cuts can be used for an approximation of this mixture. These flats do correspond to the boiling points of the xlenols.

All of the fractionated cuts were clear, and these, after standing,

had a tendency to take on a yellow orange tint. The still residue from this fractionation was a very viscous brown material which looked as if some charring had taken place.

The further separation of the material neutral to 10 per cent cold NaOH, shown in Table No. 14 by treatment with hot 20 per cent NaOH indicates the presence of esters in this material which are saponified by the more drastic action of the hot NaOH.

Not a great deal can be said from the fractionation of the neutrals. The curve is characteristic of that obtained from a mixture of hydrocarbons, and the stability of this material at high temperatures, combined with the low melting points of material crystallized from the residue, bear out this conclusion. No decomposition was observed to have taken place even when pot temperatures had risen above 300° C. The pot residue was a green, grease-like material. However, the crystals obtained from it were white, and soluble in alcohol, ether, acetone and petroleum ether. The fractionated cuts were clear but possessed a slight greenish tint.

The charcoal analysis indicates that the volatile matter is high for the best grades of activated charcoal, but they indicate that by carrying the carbonization to higher temperatures, temperatures above 500° C, that this value would be lowered considerably. This is shown by the lower value of volatile matter found in the charcoal which had been heated to the higher temperature, shown in Table No. 23.

SUMMARY

Several pyrolysis experiments were carried out on a Scholler lignin residue obtained from the saccharification of Douglas fir wood. The crude products from these runs, the pyroligneous acid, 17.7 per cent, tar, 12.3 per cent, and charcoal, 55.2 per cent, were subjected to analysis. The volume of gas given off was measured and burned.

The pyroligneous acid fraction was found to be composed of 2.53 per cent acetic acid, 0.31 per cent acetone, 1.95 per cent methanol, and 5.95 per cent dissolved tar. These values are in general agreement with published data.

The settled tar was vacuum dried and divided into two portions. The first fraction was separated into acidic, phenolic and neutral fractions, which were 27.7, 34.5, and 23.5 per cent of the dry settled tar respectively. The second fraction was subjected to an atmospheric distillation before separation into phenolic and neutral fractions. Results from this treatment gave 22.7 per cent phenols, 31.9 per cent neutrals, and 40.4 per cent nondistillable residue.

The phenolic and neutral fractions of the distilled tar were fractionated in a Stedman type packed column at atmospheric pressure. The fractionation of the phenols indicates a mixture composed chiefly of ortho-, meta- and para-cresols and the xlenols (Tables 18, 19, 20) with the guaiacol concentration too low for economic utilization.

The neutral fraction of the distilled tar consists of a mixture of hydrocarbons, alcohols and esters.

The greater portion of the acidic fraction of the dried tar is composed of a mixture of long chain fatty acids with a neutral of 373 and a melting point range of 73-78°C which might correspond to a mixture of

C_{24} and C_{26} carbon acids.

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