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DESTRUCTIVE DISTILLATION OF THE LIGNIN
RESIDUE FROM ETHANOL MANUFACTURE*

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Present estimates of the modified Scholler process for the saccharification of wood 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 obtained from the by-products. The most important of these, in regard to the quantity of production, is the lignin residue from the wood hydrolysis. This quantity amounts to about 29 per cent of the wood used or 13 pounds for every gallon of alcohol produced (5).

This lignin is produced by dilute acid hydrolysis of the wood under pressure by a process which involves a continuous extraction of the carbohydrates in wood with dilute sulfuric acid for a period of approximately four hours.

The lignin residue may contain about 15 per cent of cellulose and has a fuel value of approximately 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 fuel as the major utilization of the material. However, this attaches but a small value to the lignin, and it has been estimated that each cent per pound increase that can be assessed the lignin over the fuel value will reduce alcohol cost by approximately ten cents per gallon (5). Chemically, this lignin is the most inert of all present sources of industrial lignins.

Considering that lignin is of an aromatic character and that around 85 per cent of the methoxyl groups in wood are combined as ethers with the lignin, the charcoal, tars, and methanol produced therefrom through destructive distillation would indicate a better means of utilization. Aromatic compounds reported as obtained by the dry distillation of lignin are catechol, cresols, creosol, guaiacol, ethyl guaiacols, n-propyl guaiacol, xylenols, p-ethyl phenol, isoeugenol, and high boiling phenols (3, 6, 11). An investigation made by the senior author in 1940 on tars produced by the Goodell process from kraft black liquor (9), revealed a possible recovery of phenols (distilling range 184 to 255° C.) of 30.4 to 36.2 per cent and of neutral oil of 9.2 to 16.8 per cent. Katzen, Muller, and Othmer (8) reported a yield of 1.92 per cent of methanol from the dry distillation of maplewood

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lignin and concluded that the destructive distillation of hydrolyzed lignocelluloses had a possibility of being profitable when their phenolic and acidic tars are considered. Bridges previously concluded that alkali lignin could be considered as an important source of phenols (3). Therefore, it appeared desirable to explore further the destructive distillation products obtained from the lignin residue produced by the saccharification of Douglas fir wood which is the raw material used in the wood sugar alcohol plant at Springfield, Oregon.

Materials Used

The lignin used in this work was produced by the acid hydrolysis of Douglas fir wood waste in the pilot plant at the Forest Products Laboratory, Madison, Wisconsin, and had a reported residual cellulose content of 17.7 per cent (7). Analyses made on the lignin in this laboratory revealed the presence of about 3 per cent of water-soluble matter, consisting largely of sulfates and sugar, 1 per cent of ash, and nitrogen present in traces only. It was slightly acidic, having about 225 parts per million titratable acid, which undoubtedly was absorbed sulfuric acid.

Extraction of the lignin with ether gave on the average 7.1 per cent of a soluble, hard wax, the chief constituent of which is a solid fatty acid, M.P. 73° - 78° C., described later in this report.

Analytical Procedures

Acid content: Total acid content of the pyroligneous acid was determined as acetic acid by direct titration with standard base using a Beckman glass electrode for measuring the end point. Volatile acid was determined on a redistilled sample.

Acetone and Methanol: The acetone and methanol contents were determined by the customary Messinger and specific gravity methods, respectively, applied to redistilled samples.

Methoxyl: Methoxyl determinations were made by the method of Vieback and Schwappach (13).

Dissolved tar: The dissolved tar in the pyroligneous acid was determined by evaporation to dryness in vacuo on a water bath.

Dry settled tar: The occluded moisture in the settled tar was removed in vacuo on a water bath.

Carbonization

The carbonization runs were made in an iron, rotary retort, which held a charge of about 15 pounds of lignin. This retort was heated by a direct gas flame and was rotated at a rate of 0.5 rpm. The lignin was charged at the free end of the retort, which was sealed by a cover and an asbestos gasket held in place by a series of bolts around the periphery. The retort was 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 Trap B, through which the noncondensable gases passed. Trap B was packed with wood shavings to remove fog and effect further condensation of the distillate. The vapors were then metered through a wet test meter and burned.

The lignin undergoing carbonization was heated to a temperature between 400 and 500° C. This normally required about 4 1/2 hours. At the completion of a run, the condensate (pyroligneous acid and tar) was 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 by weighing it before and after the carbonization run. The settled tar was removed from the pyroligneous acid by decantation and filtration.

A summary of the time - temperature carbonization data is listed in Table 1. This table shows the time required to reach the various temperatures, the temperature at the end of each experiment, and the duration of heating.

Table 1. Carbonization of lignin.

Temperature at various hours in degrees C.

Run No.	Hours						Final
	1	2	3	4	5	6	
L- 23	-	-	-	-	-	-	415 at 4.75 hrs.
L- 24	-	-	-	-	-	-	415 at 10.5 hrs.
L- 25	296	392	421	427	427	-	427 at 5 hrs.
L- 26	238	371	396	396	-	-	396 at 4 hrs.
L- 30 (a)	102	243	390	393	-	-	393 at 4.5 hrs.
L- 31 (b)	121	348	382	390	-	-	350 at 4.5 hrs.
L- 36	132	360	382	407	410	438	438 at 7.5 hrs.
L- 37	210	327	349	355	382	394	394 at 6 hrs.
L- 38	188	310	388	418	441	443	432 at 7.5 hrs.
L- 39	218	332	421	449	-	-	460 at 4.5 hrs.
L- 41- 1	177	388	427	435	-	-	435 at 4 hrs.
L- 41- 2	291	438	-	485	-	-	485 at 4 hrs.

(a) 28 inches absolute pressure

(b) 27 inches absolute pressure

The products recovered, calculated on the weight of the moisture-free lignin, are presented in Table 2. This table shows the yields of charcoal, condensate, dry settled tar, gas, and losses for ten runs with various rates of heating at atmospheric pressures and from two runs made with pressures 2 to 3 inches below atmospheric.

Table 2 - Products from the Carbonization of Lignin

(Based on Weight of Moisture-free lignin)

Run No.	Lignin Charge Lbs.	H ₂ O in lignin %	Dry wt. of lignin %	Rate of Heating	Lbs.	Charcoal %	Aq. condensate (less H ₂ O in lignin)		Dry settled tar		Gas*		Loss %
							lbs.	%	Lbs.	%	Lbs.	%	
L - 23	12.45	10.6	11.13	Rapid	6.51	58.9	1.70	15.2	0.86	7.6	1.17	10.3	8.0
L - 24	11.46	11.9	10.10	slow	5.82	57.7	1.57	15.5	0.86	8.5	1.10	10.9	7.4
L - 25	14.96	12.8	13.04	slow	7.61	58.4	2.09	16.0	0.94	7.2	1.35	10.3	9.1
L - 26	14.85	19.7	11.93	rapid	6.89	57.8	2.20	18.4	1.19	10.0	0.97	8.1	5.7
L - 30	21.69	28.9	15.42	rapid (a)	9.03	58.5	2.91	18.8	1.40	9.1	-	-	-
L - 31	15.21	22.4	12.48	rapid (a)	7.30	58.6	2.43	19.5	0.91	7.3	-	-	-
L - 36	17.38	11.4	15.44	moderate	8.45	54.8	2.97	19.3	1.20	7.8	1.21	7.9	10.3
L - 37	16.96	11.4	15.00	moderate	8.99	59.8	3.09	21.2	1.23	8.2	1.03	6.9	3.9
L - 38	18.99	10.5	17.00	moderate	8.94	52.6	3.20	18.8	1.45	8.6	1.90	11.2	8.9
L - 39	15.74	7.8	14.50	rapid	7.63	52.6	2.93	20.1	1.68	4.6	1.67	11.5	4.2
L - 41-1	18.81	22.7	14.55	rapid	8.08	55.4	(4.95	(17.2	(2.03	(7.1	1.79	12.2	8.1
L - 41-2	18.36	22.7	14.19	rapid	7.48	52.8	((b)	((b)	((b)	((b)	1.92	13.6	9.3

(a) Run No. L - 30 made at 28" absolute pressure and Run L - 31 at 27" absolute pressure

(b) Composite sample of 41-1 and 41-2

(*) 0.07 lbs. per cubic foot (assumed)

The average yield of lignin carbonization products from ten runs at atmospheric pressure and from two runs with 27 to 28 inches of pressure are shown in Table 3.

Table 3. Yield of Crude Products

	Atmospheric pressure - %	27 to 28 inches pressure
Charcoal	55.8	58.5
Settled tar	8.4	8.2
Pyroligneous acid	18.0	19.1
Gas	10.3	-
Losses	7.5	-

There is no conclusive evidence that the rate of heating within the limits of the experiments had a material effect on the yield of products. Further, carbonization with pressures 2 to 3 inches under atmospheric gave no difference in tar yield. Settled tar yields from lignin with high moisture content were somewhat lower because of the greater dilution of the pyroligneous acid, which in turn exerted a greater solubilizing action on the settled tar. This is shown by Runs 41-1 and 41-2.

The pyroligneous acids had a dissolved tar content ranging from 3.0 to 5.9 per cent; and an average acetone, methanol, volatile acid, and total acid content calculated as acetic, of 0.31, 1.95, 1.47, 2.53 per cent respectively. Calculated on the basis of moisture-free lignin, the yields of acetone, methanol, and acetic acid were 0.06, 0.35, and 0.27 per cent respectively and thus are of only minor importance.

Investigation on the Settled Tar

The settled tars from a representative number of runs were combined and the occluded moisture removed in a hot-water bath with a water aspirator. The occluded water averaged 20.5 per cent of the weight of the wet tar. The dry tars were black-colored, waxy solids which became fluid at temperatures around 70° C. They were investigated for acids, phenols, and neutral substances, and also subjected to a secondary distillation in the laboratory to effect further decomposition into simpler compounds (Figure 2).

Initially, a portion of the tar was taken up in ether, in which to all appearances it was soluble. This ether solution was next extracted with an aqueous sodium bicarbonate solution to remove acids, and this was followed by extraction with a 10 per cent sodium hydroxide solution to remove the phenols. Upon addition of the sodium bicarbonate solution, three layers formed: the ether layer, the aqueous layer, and a solid precipitate which was insoluble in both the ether and the aqueous layers. The nature of the three layer system made the separation difficult to carry out. The insoluble material was removed by filtration and upon acidification was

found to be soluble again in ether, leaving a small residue which appeared to be charcoal and partially carbonized lignin. This apparently was carried over as dust with the vapors during the carbonization operation. The insoluble material that redissolved in ether upon acidification was found to be a solid fatty acid whose sodium salt was insoluble in water. The properties of this material are more fully described later. All extractions were made in a separation funnel with successive batches of fresh extracting solutions until they remained free of discoloration.

Table 4 gives a summary of the acids, phenols, and neutrals content of 4 samples of crude settled tars.

Table 4. Composition of Settled Tar
(Weight per cent of dry tar)

	(1)	(2)	(3)	(4)	Av.
Solid fatty acids	15.8	23.4	26.4	27.2	23.2
Acids soluble in					
Na HCO ₃	7.2	5.6	5.4	5.6	6.0
Phenols	43.5	29.0	31.0	34.5	34.5
Neutrals	24.9	24.6	21.0	26.0	24.1
Residue	6.9	9.5	7.5	5.7	7.4
Loss	1.7	7.9	8.7	1.0	4.8

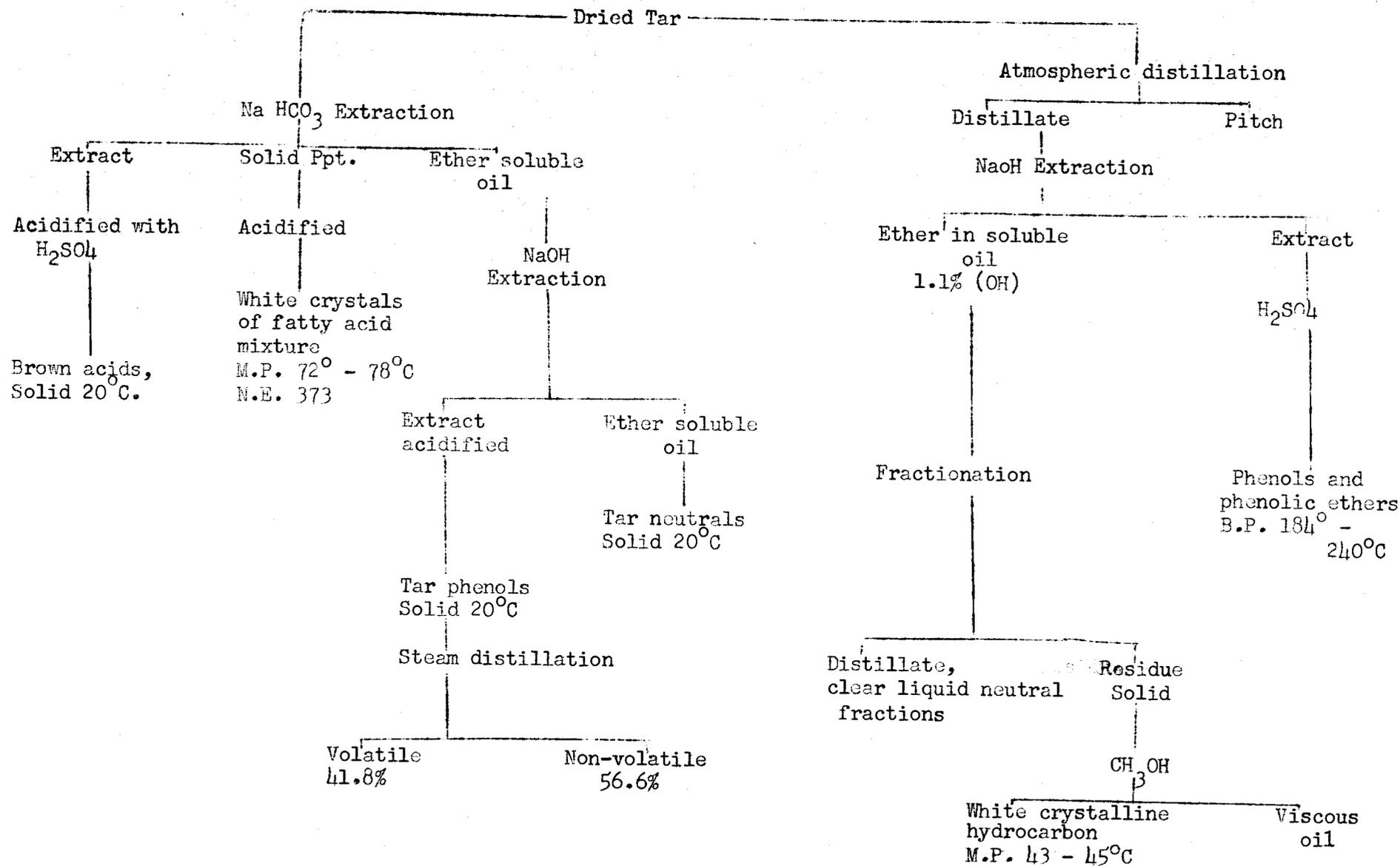
The products from the separation of the settled tar differed physically, chiefly in odor. They were dark brown solids below 20° C. and thick viscous oils at higher temperatures.

Solid fatty acid product. This acid fraction was soluble in ether, petroleum ether, ligroin, and acetone. Recrystallizations from ligroin and from acetone gave white crystals melting from 73 to 78° C. Tests with potassium permanganate and with bromine in carbon tetrachloride showed no evidence of unsaturation. The preparation of the amide derivative resulted in products which gave melting points of 94 - 96°, 102 - 105° C., and 85 - 89° C. A list of neutral equivalent determinations from various melting fractions is presented in Table 5. These indicate that the material is a mixture of long chain fatty acids corresponding to C₂₄ and C₂₅ carbon atoms. Fraction 3 showed a carbon content of 76.2 per cent and a hydrogen content of 12.4 per cent. The over-all properties correspond to those of lignoceric acid. This product undoubtedly is not a cleavage product of the lignin but results from the distillation of the fatty acid in the original lignin.

Table 5. Melting Point and Neutral Equivalents of Solid Fatty Acid Product.

Fraction	M.P. °C.	N.E.
1	76-78	373
2	76-78	370
3	76	376
4	72	383

Figure 2 - Separation of Tar Components



Tar Phenols

This fraction, amounts to roughly one-third of the crude tar, was a dark solid at 20° C., with an odor resembling creosote. It was soluble in petroleum ether. Attempts at distillation with reduced pressure were not successful because of a tendency to profuse frothing. The distillate obtained was a yellow colored solid, which darkened rapidly on standing. Steam distillation of the tar phenols indicated that 41.8% were volatile and 56.6 non-volatile.

Neutral fraction

The neutral fraction amounting to roughly one-fourth of the crude tar was dark colored and semi-solid at room temperature. Recrystallizations from hot methanol gave several crystalline fractions with melting points up to 65° C. with all of the characteristics of hydrocarbons. This material was concluded to be mainly a mixture of hydrocarbons.

Table 6. Summary of Carbonization Products

		% of moisture free lignin
Charcoal		55.8
Gas		10.3
Settled tar		8.4
Solid fatty acid	1.95	
N.P. 73-78° C.		
Other acids	0.34	
Phenols	2.90	
Neutrals	2.02	
Pyroligneous acid		18.0
Acetone	0.06	
Methanol	0.35	
Acetic acid	0.27	
Soluble tar, av.	0.80	
Losses		<u>7.5</u>
	Total	100.00

Redistillation of Dry Settled Tars

The dry settled tars were subjected to a secondary distillation in pyrex glass distilling flasks at atmospheric pressure and at reduced pressures obtainable with a water aspirator. The tars were heated with a precision type electric heater until approximately 60 per cent of their weight had distilled. At this point, with the temperature between 275 and 300° C., the tar residues had a tendency to froth. By carefully controlled heating of the tar residue, yields of distillate up to 72% were obtained. Only a slight increase in tar distillate could be obtained with reduced pressure over distillations at atmospheric pressure. The yield of distillate (Table 7) appeared to be more influenced by temperature than by reduced pressure.

The distillates were initially light yellow oils, which darkened on standing. All contained some water formed by a secondary decomposition of the tar. The residues in the distilling flasks were tough thermoplastic pitches, in contrast to the friable tar residues obtained from the distillation of tars from wood carbonization. They were found to be soluble in benzene or hot alcohol. The petroleum ether soluble extracts of the pitches were light colored crystalline waxes.

Table 7. Secondary Distillation of Dry Settled Tar

Tar Sample	<u>Distillate</u>	<u>Residue (pitch)</u>	<u>Gas & Loss</u>
	%	%	%
	(Distillation at atmospheric pressure)		
1	56.8	38.4	4.8
2	55.1	40.4	4.5
3	71.7	19.2	9.1
	(Distillation at reduced pressure)		
4	61.6	34.1	4.3

The distillates were separated into acidic and neutral fractions by extraction with caustic soda solutions. With these distillates a large variation in the yield of neutrals was observed depending upon the conditions of the separation. When the distillates were made strongly alkaline with solid caustic soda followed by extraction with ether the lowest yield of neutral oil was obtained. If the distillate was first taken up in ether and then extracted with cold 10% sodium hydroxide the yield of neutral oil was materially higher as is shown in Table 8.

It was found that further separation of the neutral fraction insoluble in cold 10% NaOH could be brought about by treating with 20 per cent sodium hydroxide at 80° C. Under these conditions an additional 27.1% dissolved in the caustic soda solution. A methoxyl determination on the oil neutral to 20 per cent hot caustic solution indicated a total absence of ethers in this fraction.

Table 8. Composition of Distillate From Secondary Distillation of Dried Tar

	Phenols - %	Neutrals - %
1a. Extraction of ether solution with cold 10% NaOH	41.3	58.0
1b. Hot 20% NaOH and ether extraction	57.0	42.3
2. Solid NaOH & ether extraction	79.9	18.1

Hydroxyl group determinations were made on the materials, neutral to 10 per cent cold sodium hydroxide, and neutral to 20 per cent hot sodium hydroxide by a procedure similar to that of Peterson, Hedberg, and Christensen (10), applied to a macro scale. This analysis gave a hydroxyl group content of 1.86 per cent for the

material neutral to 10 per cent cold sodium hydroxide. Acetylation with acetic anhydride and anhydrous acetate as a catalyst, followed by a determination of the acetyl groups by the method of Clark (4) gave an identical hydroxyl content of 1.13 per cent for the two neutral oils. The hydroxyl group analyses indicated the presence of only a small amount of alcohols in the neutral oils. It was found that 72.3 per cent of the neutral oils were readily distillable with steam.

Fractionation of the neutral oils in the Stedman type fractionation column (12) - Figure 3 - showed a distilling range from 144 to over 275° C as shown in Figure 4. The distillation curve is characteristic of that obtained from a mixture of hydrocarbons. No decomposition was observed to take place even when the pot temperature had risen above 300° C.

The fractionation cuts were water white or possessed a slight greenish tint. From the residue in the still, white crystals, m.p. 42 - 43° C. separated. These contained 85.7 per cent carbon and 14.3 per cent hydrogen, which correspond to a saturated hydrocarbon.

Description of the fractionation column

The fractionation column used in this work is shown in Figure 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. The heat input was controlled by two 110 volt voltrons. The temperatures between the heated jacket and the packed column were measured by two chromel-alumel thermocouples placed at the top and bottom of the heated zone. The heated jacket was again jacketed by a 45 mm. o.d. pyrex glass 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 to a 500 ml. pyrex glass pot by means of a 24/40 T joint. The pot, fitted with a 360° C. thermometer to indicate pot temperature, was heated by a fiber glass mantel heater.

The column head was cooled by a finger type condenser. Take-off was made from a side-arm just above the thermometer bulb. A reflex take-off ratio of at least 10 to 1 was maintained throughout the distillations.

This column was constructed in an attempt to obtain a better fractionation of the complex phenolic mixture than that obtained by previous investigators (3). From a comparison of this column with columns of similar type packings tested by Bragg (2), it should have approximately 70 theoretical plates.

The efficiency of the column was tested on a known phenolic mixture containing 26.4 per cent of each of o-cresol, m-cresol, and guaiacol, and 20.8 per cent of p-cresol. Although 96.5 per cent of the o-cresol was recovered in crystalline form, it was found that m- and p-cresols were not separated, nor was there a sharp break up to the guaiacol boiling range (Figure 5). This material apparently distilled with these two cresols to an extent. Difficulty in separating guaiacol from phenolic mixtures by distillation appears to be the general experience as is revealed by a review of the chemical literature.

Investigation of phenols from the secondary distillation of the dry settled tar

A preliminary distillation of a 200-gram sample of the phenolic oil from a pyrex distilling flask showed a final distillation temperature exceeding 240° C. Above this temperature, the phenols remaining in the flask were largely decomposed and were non-distillable at atmospheric pressure. The phenolic cuts as shown in Table 9 contained 8.5 to 10.8 per cent methoxyl, which indicated a high percentage of phenolic ethers.

Table 9. Methoxyl Content of Phenolic Oil

C	Percent of total phenols	OCH ₃ %	Phenolic ethers as guaiacol - %
105-180	3.0	---	---
180-203	11.0	8.5	34.0
203-210	26.5	8.5	34.0
210-225	31.0	10.8	43.2
225-240	19.0	9.8	39.2
Residue	9.5	---	---

The phenols soluble in cold 10 per cent caustic solution were distilled from the 40-inch column shown in Figure 3 without further treatment, and the fractionation curve is shown in Figure 5. Inasmuch as this oil had only a small solubility in aqueous sodium bicarbonate, it was considered to be essentially phenolic. A 242.5 gram sample was used for the fractionation. Above a distillate temperature of 217° C., decomposition of the material in the pot prevented further fractionation. Attempts were made to characterize the various cuts of this fractionation by the preparation of appropriate derivatives. The data taken on the cuts are presented in Table 10. All fractions were water white or had only a slight yellow tint, which darkened upon standing.

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. The methoxyl contents indicate that the fractions distilling in the range from 203 to 211° C. are high in phenolic ether content. When calculated as guaiacol, values from 45.2 to 65.6 per cent are obtained. Phillips found n-propyl - 3 methoxy-r hydroxybenzene in this phenol fraction from alkali lignin (11).

A second fractionation run of the phenolic oil, after a preliminary distillation to remove phenols distilling above 240° C., gave no better separation (Figure 5). The methoxyl contents of all fractions distilling above 200° C. were between 9.8 to 12.2 per cent, which indicates that these fractions contained a high percentage of phenolic ethers.

A summary estimation of the composition of the crude phenolic oil is given in Table 11.

Table 10. Fractionation of Crude Phenols.

Fraction Number	°C	N ²⁰	Wt. %	Derivatives* M.P. °C	OCH ₃ %	Material
Below 183° C	100-183	-	6.8	-	-	Oil
1	183-6.5	1.5348	4.0	(1) 66.5-67 (2) 95	-	Phenol
2 to 7	186.5-198	1.5325	13.0	(2) 152	-	o-cresol
7 to 9	198-201.5	1.5383	9.5	(2) 132-134	-	p-cresol
9	201.5	1.5400	3.4	(1) oil (2) oil	-	-
10	201.5-3	1.5378	3.7	(2) 136	0.87	p-cresol
11	203-4.5	1.5360	2.0	(2) 139-40	11.4	
12	204.5-6	1.5330	2.4	(2) 141-2	12.1	
13	206-10	1.5315	2.3	(2) 135-6 (3) 90-92°	11.3	
14	210-11	1.5308	1.2	(2) 139-40	16.4	
15	211-3	1.5312	1.6	(2) 138-40 (3) 157-9		
16	213-6	1.5318	1.3	(2) 138-40 (3) 162-3		
17	216-17	1.5315	1.4	(2) 106		
18	200-210	-	20.4	-		
Residue			27.0			
Total			100.0			

* (1) 2, 4 dinitrophenyl ether
 (2) Aryloxyacetic acid
 (3) 3, 5 dinitrobenzoyl ester

Table 11. Composition of Phenolic Oil

Material	Per cent
Below 183°	6.8
Phenol	4.0
o-cresol	13.0
p-cresol	16.6
203° - 10° C (guaiacol and etc.)	6.7
210° - 17° C.	25.9
over 217° C.	<u>27.0</u>
Total	100.0

Investigation of the Soluble Tar Fraction

The soluble tar was a dark, viscous material with a pungent odor. It was insoluble in petroleum ether and about one-half was soluble in ethyl ether. This portion was separated into phenols and acids with aqueous sodium bicarbonate solution. The acid fraction was a dark syrup which gave only water and coke when heated above 95° C.

The phenol fraction from the soluble tar was insoluble in petroleum ether as contrasted with the phenols in the settled tar, which were readily soluble in this solvent. This material differed further from the settled tar phenols in that no part could be distilled below 220° C. Inasmuch as the amounts obtainable was too small to be of practical significance it was not further investigated.

Analysis of Charcoal

Ash and volatile matter analyses were made on the charcoal from Carbonizations L-36 and L-41-2 in accordance with Standard A.S.T.M. procedures (1). The charcoal from L-36 had been heated to 438° C and that from L-41-2 had been heated to 485° C. The ash content of the charcoal from L-41-2 and L-36 were 1.8 per cent and 8.7 per cent respectively. The volatile matter was 20.3 per cent for charcoal L-41-2 and 32.5 per cent for charcoal L-36. These values indicate that the charcoal is inferior to the better grades of activated charcoal. The high ash content is associated with the high silica content of the bark present particularly in slab wood waste.

Summary

Several carbonizations were carried out on the lignin residue obtained from the saccharification of Douglas fir wood in a rotary retort at temperatures up to 485° C. The crude products from these carbonizations - charcoal 55.8 per cent, pyroligneous acid 18 per cent, and settle tar 8.4 per cent were subjected to analysis.

The charcoal analyses gave ash contents ranging from 1.8 to 8.5 per cent and volatile matter ranging from 20.3 to 32.5 per cent.

The pyroligneous acid liquor contained, on the average, approximately 4.5 per cent soluble tar and small amounts of acetone, methanol and acetic acid.

The settled tar contained 29.2 per cent acids, 34.5 per cent phenols, and 24.1 per cent neutrals. The major part of the tar acid fraction was a solid fatty acid mixture, M.P. 73-78 C, which resembled lignoceric acid. This material is initially present in the wood and in the lignin residue from the saccharification of the wood. Redistillation of the dried tar gave up to 71.7 per cent of a distillate consisting of hydrocarbons, phenols, and phenolic ethers and left a dark, waxy thermoplastic pitch as a residue. Phenol, o-cresol, and p-cresol were separated from the crude phenolic oil by fractionation in a 40-inch Stedman type column. The other phenol fractions had a methoxyl content ranging from 9.8 to 16.4 per cent which indicates a high content of phenolic ethers. The yield of tar and phenols produced by the carbonization of Scholler Douglas fir lignin was smaller than that reported in the literature from alkali lignins. This fact materially diminishes its consideration as a commercial source of phenols.

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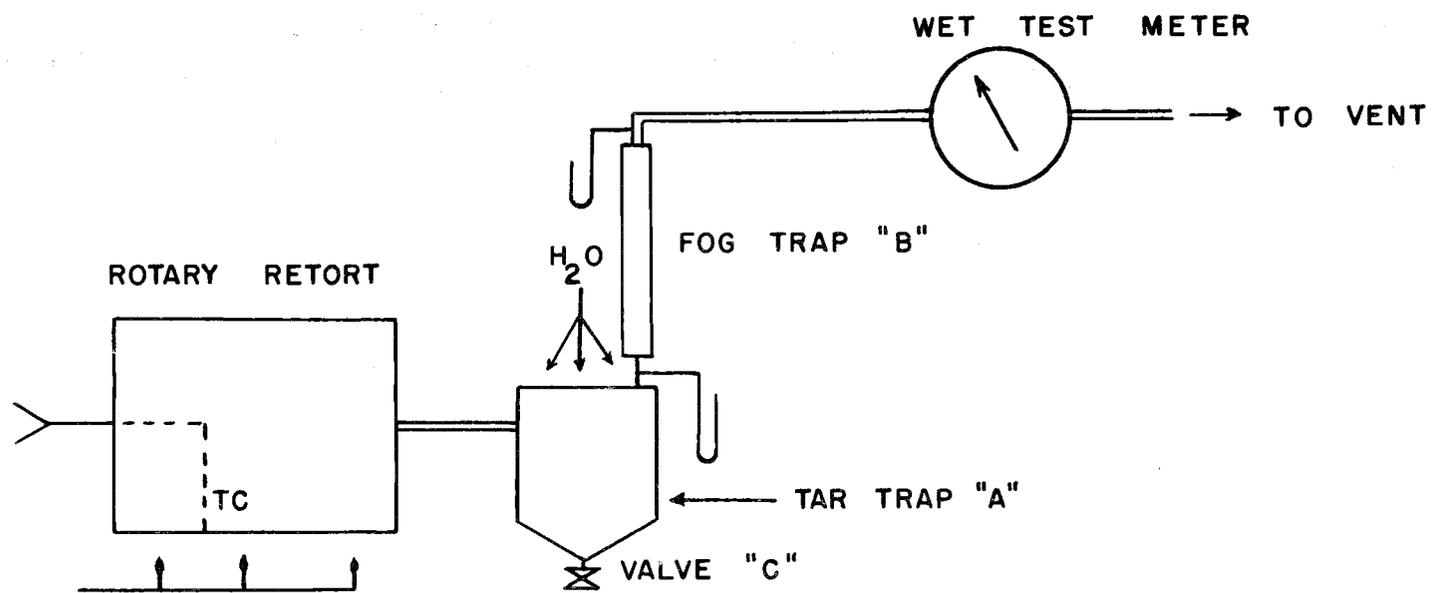


FIGURE I. CARBONIZATION APPARATUS

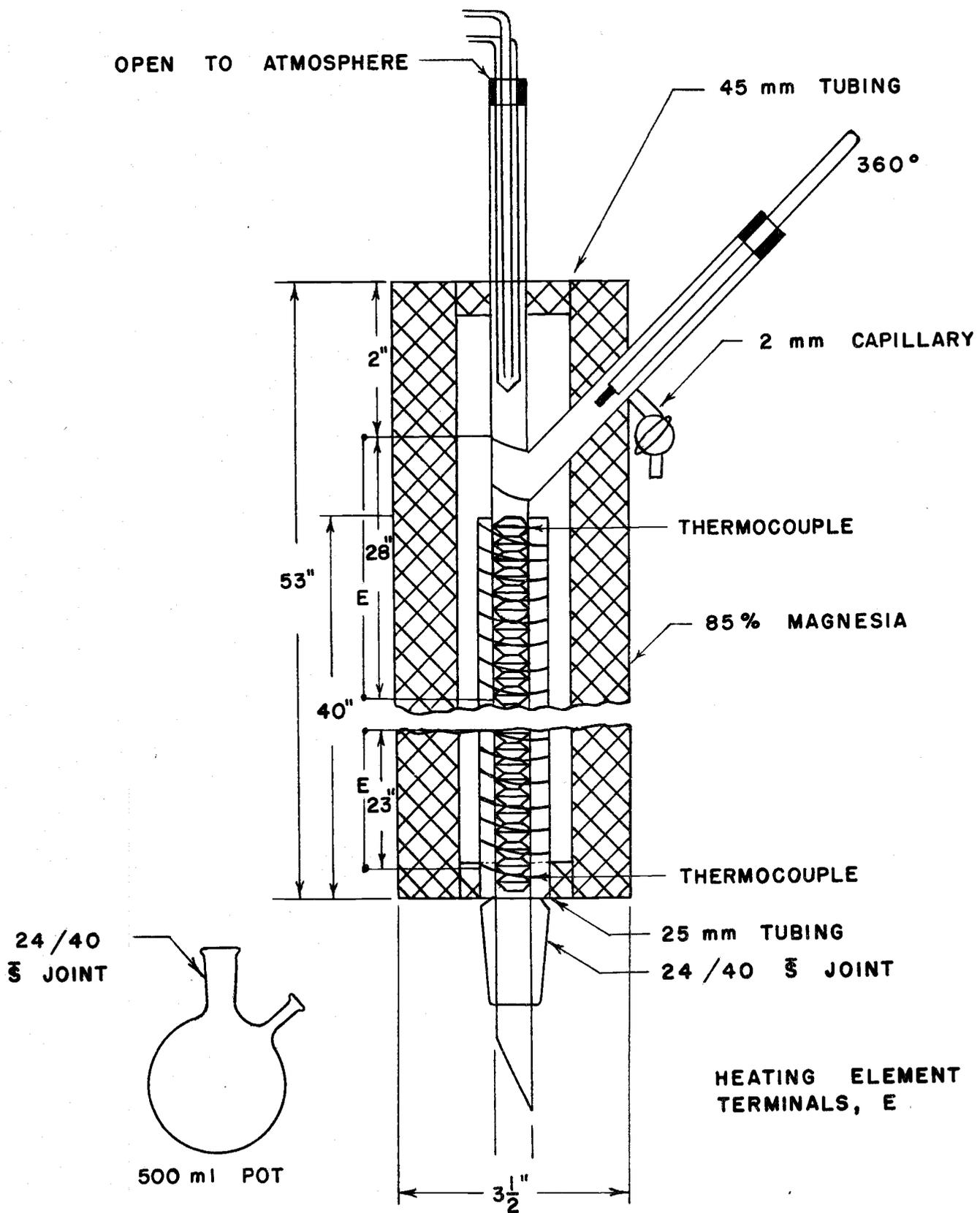


FIGURE 3. FRACTIONATING COLUMN

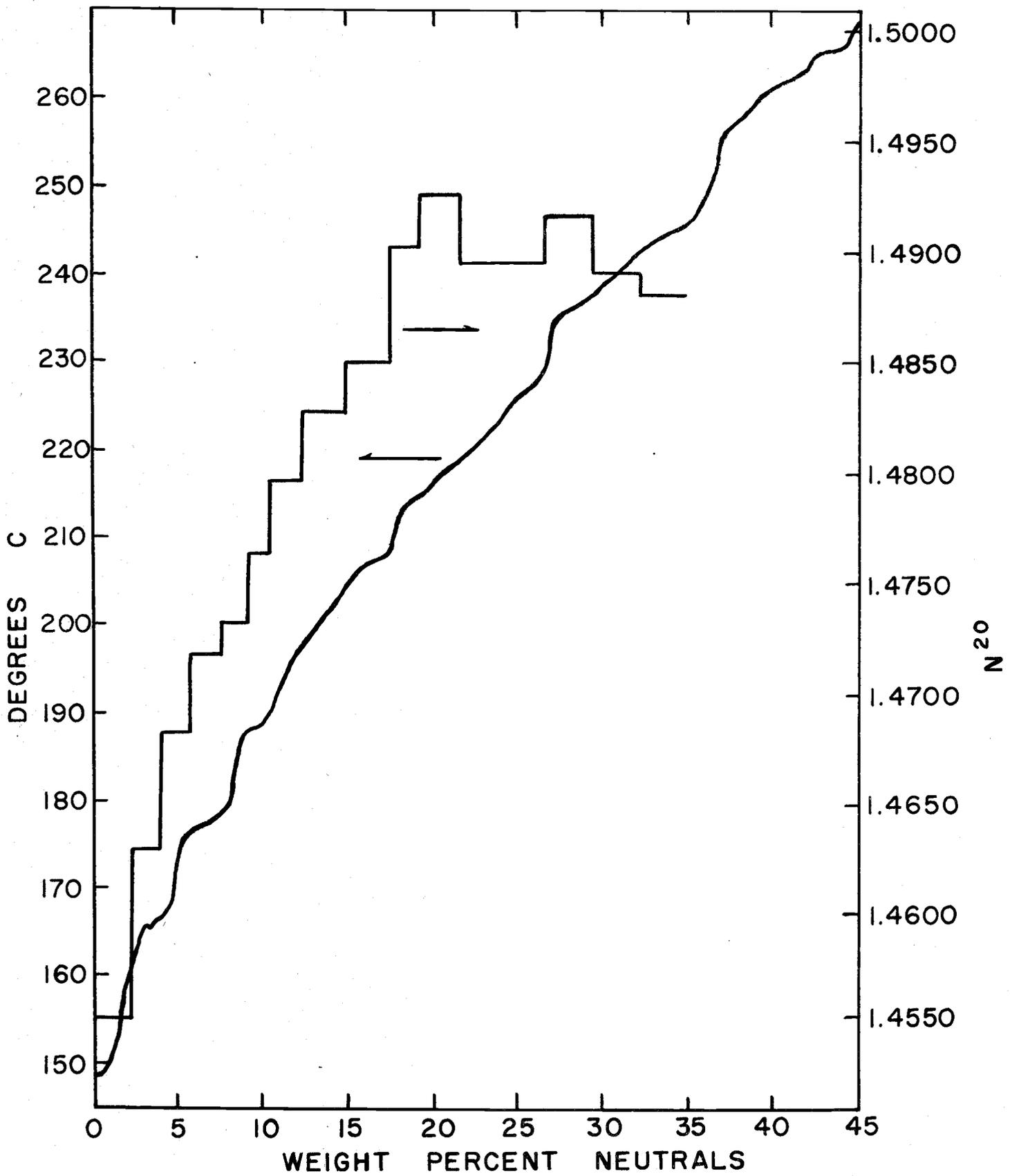


FIGURE 4. FRACTIONATION OF NEUTRALS

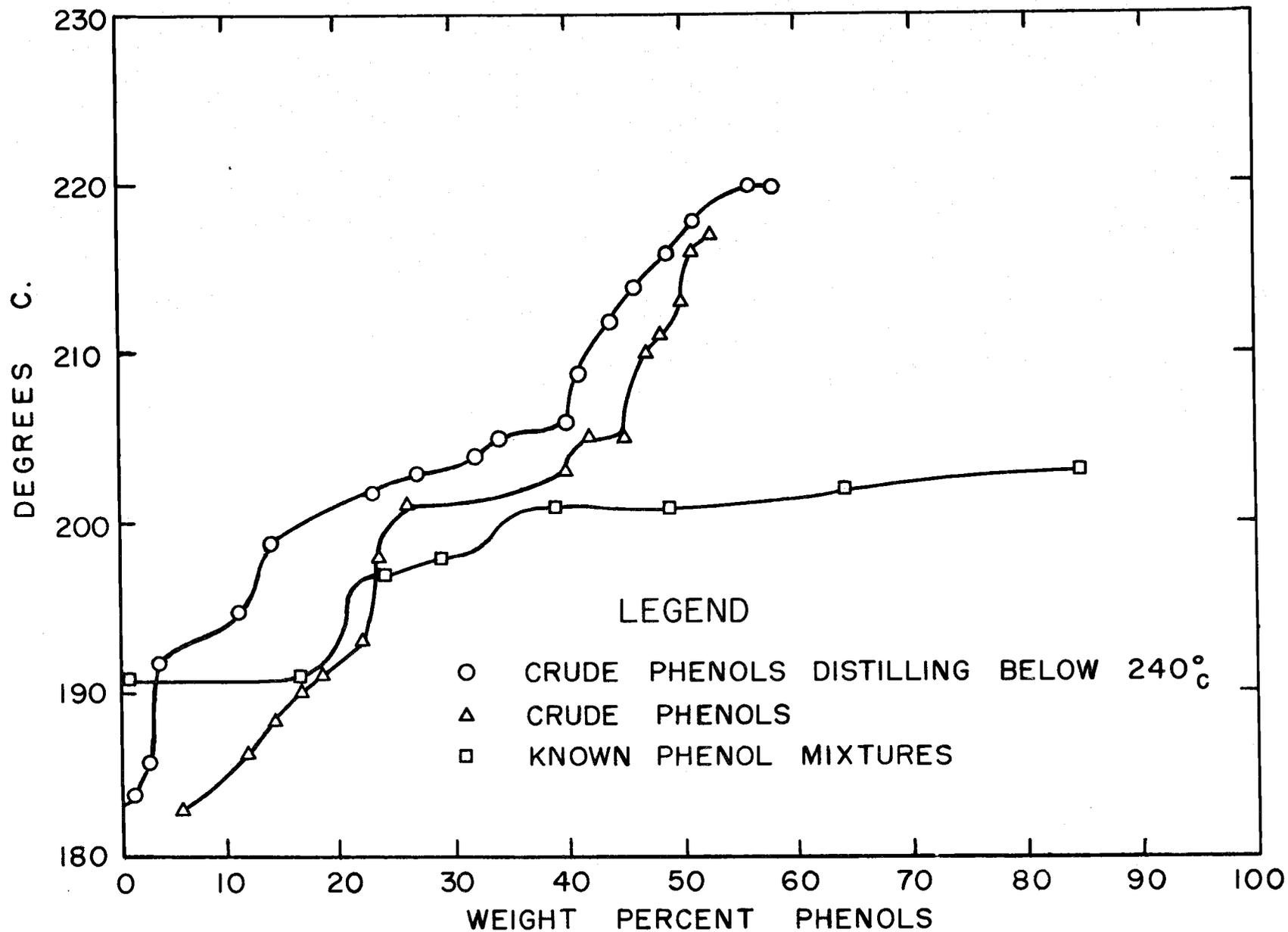


FIGURE 5. FRACTIONATION OF PHENOLS