Phenols from Cornstalk Alkali Lignin

Preparation by Destructive Distillation and Separation by Fractional Distillation

GROVER LEON BRIDGER¹ Iowa State College, Ames, Iowa

THE destructive distillation of lignin isolated from wood by the fuming hydrochloric acid and 72 per cent sulfuric acid methods has been studied by many investigators (5, 7). Lignin prepared from sources other than wood and by other methods has been largely neglected in destructive distillation studies. The only experiments of this kind on alkali lignin are those of Phillips (7) who prepared his lignin from corncobs. He compared the yields of products from the destructive distillation at atmospheric pressure of corncob lignin isolated by three methods—namely, the fuming hydrochloric acid, the 72 per cent sulfuric acid, and the alkali methods.

Of particular interest is the oil or tar obtained as one of the products from the destructive distillation of lignin. This tar amounts to 8-14 per cent (basis lignin) in the case of the fuming hydrochloric acid and 72 per cent sulfuric acid lignin, and 17-28 per cent in the case of the alkali lignin. Phillips obtained 7.5 per cent of tar (basis lignin) from the corncob fuming hydrochloric acid lignin, 7.8 per cent from the corncob 72 per cent sulfuric acid lignin, and 17.7 per cent from the corncob alkali lignin. Comparing these yields on the basis of the original corncobs, the order is reversed: for the hydrochloric acid lignin the yield is 1.9 per cent; for the 72 per cent sulfuric acid lignin, 1.5 per cent; and for the alkali lignin, 0.88 per cent. The yield of the tar is dependent on the pressure at which the distillation is carried out; for example, by distilling alkali lignin from corncobs at a pressure of 25 mm. of mercury in an atmosphere of carbon dioxide, Phillips and Goss (8) obtained a yield of 28.3 per cent of tar (basis lignin).

The oil or tar from all kinds of lignin contains a certain amount of material which is insoluble in sodium bicarbonate solution but which is soluble in sodium hydroxide solution and is therefore phenolic in nature. The amount of this phenolic fraction is from 20 to 35 per cent (basis tar) in the case of the fuming hydrochloric acid and 72 per cent sulfuric acid methods of isolation, and

¹ Present address, Chemical Engineering Department, Rice Institute, Houston, Texas. much higher (80 to 90 per cent) in the case of the alkali method of isolation. The only previous investigation of the nature of the phenolic fraction of the tar is that of Phillips and Goss, who used chemical methods to separate several phenols from the tar. They identified phenol, o-cresol, guaiacol, n-propyl guaiacol, creosol, and 1-vinyl-3-methoxy-4-hydroxybenzene in the phenolic portion of the tar. The fraction of the tar from which these compounds were isolated amounted to only 15 per cent of the crude tar, however, and no estimation of the amounts of the several compounds could be made by the methods of separation used.

In the present study the conditions of the destructive distillation of cornstalk alkali lignin for obtaining high yields of phenols were determined. It was found possible to distill fractionally the phenolic tar or the phenols extracted from the tar. In this way many of the constituent phenols of the tar were quantitatively separated and identified.

Destructive Distillation Experiments

PREPARATION OF LIGNIN. Shredded cornstalks (50 pounds or 22.7 kg.) were cooked with one-tenth their weight of sodium hydroxide and eight to ten times their weight of water for 2 hours at 90 pounds per square inch (6.3 kg. per sq. cm.) gage pressure in a spherical rotating cooker heated by direct steam. When cool the cook liquor was drained off and the pulp washed two or three times with water, the washings being added to the main portion of the liquor. After having been allowed to settle, the liquor) was filtered through cloth into a large open steam-heated kettle and evaporated until its specific gravity at 90° C. was 1.06. The volume of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined or Duriron leader of the liquor was then transferred to lead-lined the during the state of the liquor was then transferred to lead-lined to the state of the liquor was then transferred to lead-lined to the during the state of the liquor was then transferred to the state of the state o

kettles heated by steam jackets, and enough muriatic acid (25 per cent hydrogen chloride), was added to bring the excess acid concentration to at least 3 per cent by weight, about 0.2 pound of acid per pound of liquor being required. The acidified liquor was boiled gently for 2 hours, after which time the precipitated lignin was well coagulated and easily filtered. It was then washed free from acid with water and dried in the oven at 105°C. The yield of the ovendried lignin was 4.5 to 5.0 pounds or 9 to 10 per cent of the oven-dried cornstalks.

Apparatus and Procedure. For small-scale destructive distillations, a cast-iron retort, A,



FIGURE 1. SMALL-SCALE DESTRUCTIVE DISTILLATION APPARATUS

Alkali lignin from cornstalks has been destructively distilled under varying conditions of time, temperature, method of heating, and pressure. The conditions for optimum phenolic tar yield at an absolute pressure of 5.5 inches of mercury are (a) a final retort temperature of at least 400° C.; (\vec{b}) a time of heating sufficient to allow all the distillate to come over, the rate of heating not being important; (c) any convenient means of heating the retort, a direct flame giving as good results as a heating bath. The optimum pressure found for production of phenols was 2.2 inches of mercury

about 180 cubic inches (3 liters) in capacity was used (Figure 1). The retort was heated either by a direct gas flame or by a suitable bath which was in turn gas-heated. A tightly fitting cover was held in place by a yoke and small clamps, an asbestos composition gasket being used. The cover was fitted with a thermometer well which extended to within 0.25 inch (0.635 cm.) of the bottom of the retort. The temperature was determined either by a thermometer or an iron-constant an thermocouple connected to a suitable pyrometer. The vapor line through which the distillates passed led directly to a receiving flask, B, which was cooled in a water bath, C. Above this was a Liebig condenser, D, which further cooled the lighter constituents. The vapors were finally led through an ice-cooled trap, E, and thence to a small rotary vacuum pump, F, which maintained the system at the desired pressure. In making the distillations, the lignin was charged into the re-

In making the distillations, the lignin was charged into the retort, and the system was tightly closed. When the desired pressure had been attained, the ring burner which supplied the heat was turned on and the distillation was allowed to proceed until no more distillate came over at the maximum temperature used. The distillates from the receiver and from the trap were combined and the two layers separated in a separatory funnel. The weights of the aqueous layer, tar layer, and residual carbonized material were recorded, and the gas and loss calculated by difference; the per cent yields were calculated on the basis of the oven-dried lignin and also on the basis of the oven-dried stalks. The tar thus separated contained some dissolved water, the amount of which was not determined in the small-scale experiments.

For the large-scale experiments a similar system was used except that the retort consisted of a horizontal iron pipe, 8 inches (20.3 cm.) in diameter and 14 inches (35.6 cm.) in length. One end of the pipe was fitted with a flange and the other was closed by a circular piece of sheet iron which was welded on.

Effect of Time, Temperature, and Method of Heating

A number of distillations were made under various conditions of time, temperature, and methods of heating. In each run 0.441 pound (200 grams) of oven-dried lignin was used, and the pressure was maintained at 5.5 inches (14 cm.) of absolute, although still lower pressures would probably prove better.

The phenols were fractionally distilled in an efficient column both from the crude tar and from the chemically extracted phenolic portion of the tar. It was found possible to fractionate 40 to 55 per cent of the tar into constantboiling cuts. These fractions were identified in large part; phenol, o-cresol, p-cresol, guaiacol, 3,5-xylenol, and creosol were found. Alkali lignin can thus be considered a potential source of phenols which may become important in the future.

mercury absolute (23.5 inches vacuum). The retort was heated by baths of lubricating oil, sodium nitrate, and molten lead, and by direct flame.

The results are shown in Table I. The maximum retort temperature is the maximum temperature inside the retort as shown by the thermocouple in the well. The time of heating is the total time between the firing of the retort and the time when the fire was cut off. For the first three runs in Table I (II, IV, and VII) in which direct flame heating was used, the temperature inside the retort is an important factor in the yield of tar; at 300° C. the yield is much smaller than at 395° and 500° C. This fact is further borne out by run III, in which the lignin was heated no higher than 235° C. for 4.3 hours, after which time practically no distillate had been obtained. It was then heated an additional 4.5 hours at temperatures no higher than 360° C. The yields of tar were almost as great as those in the direct-flame heating runs. It can be concluded that the greater part of the distillate came over between about 250° and 400° C. Phillips (7) stated that 400° C. is the best temperature for the destructive distillation of alkali lignin from corncobs, which checks the present findings well.

The total time and rate of heating seemed relatively unimportant. For example, runs V and VI were both made with a heating bath of molten lead, the maximum temperature being about the same in each case. Although the time of run V is over twice that of run VI, the yields of tar and aqueous distillate are identical. This fact was also observed in other experiments.

It was thought that by heating the lignin more uniformly, overheating at the surface of the retort would be prevented and better yields of distillates might be obtained. Consequently, the several runs (III, V, and VI) using liquid heat-

TABLE I. EFFECT OF TEMPERATURE, TIME, AND METHOD OF HEATING ON YIELDS

Run No.	Method of Heating	Max. Retort Temp. °C.	Max. Bath Temp. ° C.	Time of Heating <i>Hours</i>	Aqueous dist.	asis Oven-I Tar	Pe Dried Lignin Carbon residue	Gas and loss	d of Products Aqueous dist.	asis Oven-I Tar)ried Stalks- Carbon residue	Gas and loss
	Direct flame Direct flame Direct flame	300 395 500	•••	$2.0 \\ 3.2 \\ 2.75$	7.0 11.1 14.5	$14.2 \\ 17.7 \\ 17.5$	$ 67.0 \\ 57.5 \\ 52.0 $	$11.8 \\ 13.7 \\ 16.0$	$0.70 \\ 1.11 \\ 1.45$	$1.42 \\ 1.77 \\ 1.75$	6.70 5.75 5.20	$1.18 \\ 1.37 \\ 1.60$
líí vi	Oil bath NaNOs bath Lead bath	235 360 420	290 420 490	4.3 4.5 2.0	Slight 7.5 10.6	Slight 14.4 17.6	$60.5 \\ 51.2$		Slight 0.75 1.06	Slight 1.44 1.76	6.05 5.12	Slight 1.76 2.06
v ⁻	Lead bath	390	490	4.25	10.6	17.7	56.6	15.1	1.06	1.77	5.66	1.51

ing baths were made. However, in no case were the yields of distillates better than those obtained by direct flame heating. It must then be concluded that the method of heating has no effect on the yields of distillates if the retort temperature is high enough.

It may be concluded from the above experiments, therefore, that the optimum conditions for the production of tar by destructive distillation of alkali lignin under 5.5 inches (14 cm.) of mercury absolute pressure are: (a) a final retort temperature of at least 400° C., (b) a time of heating sufficient to drive over all the distillate (the rate of heating is not very important), and (c) any convenient means of heating the retort (the method of heating is relatively unimportant, and a direct flame gives as good results as a heating bath).

Effect of Pressures Lower than Atmospheric

Once the above conditions (for 5.5 inches of mercury) were established, a number of distillations were carried out at varying pressures below atmospheric in order to observe the effect on the yield of the products. 0.441 pound (200 grams) of oven-dried lignin was used in each distillation. Direct flame heating was used, the maximum retort temperature being 400° to 500° C. The pressures were kept constant within 0.5 inch (1.27 cm.) of mercury. The absolute pressures recorded were based on a 29.0-inch (73.7-cm.) barometer reading. The time of heating was about 3 hours in all runs.

The results are given in Table II and shown graphically in Figure 2. At an absolute pressure of about 5 inches (12.7 cm.) of mercury the yield of total distillate and tar reached a distinct maximum. On the other hand, the aqueous distillate was sensibly constant throughout the entire range of pressure except in the very low range, where it dropped. Another interesting feature of Figure 2 is the abrupt increase in tar yield and consequently in total distillate yield when a very slight vacuum was maintained on the retort. The carbonized residue curve is roughly the inverse of the tar and total distillate curves.

TABLE II. EFFECT OF LOW PRESSURES ON YIELDS

Run	Abs. Pressure,	Basis	Oven-I	Per Coried Ligni	Gas and	ld of Produ ——Basis Aqueous	oven-3	Dried Stall	Gas and
INO.	In, Hg	aist.	rar	residue	TOSS	dist.	T ar	residue	TOSS
XIV XV XVI XIII IV VII IX XI XI VIII	$\begin{array}{c} 2.2 \\ 2.2 \\ 2.2 \\ 4.0 \\ 5.0 \\ 5.5 \\ 17.0 \\ 17.0 \\ 28.0 \\ 29.0 \\ (atm.) \end{array}$	$\begin{array}{c} 8.2\\ 11.0\\ 14.7\\ 13.8\\ 11.8\\ 11.1\\ 14.5\\ 14.4\\ 15.0\\ 15.0\\ 15.0 \end{array}$	$16.1 \\ 15.7 \\ 15.5 \\ 17.1 \\ 19.5 \\ 17.7 \\ 17.5 \\ 14.6 \\ 14.7 \\ 14.0 \\ 11.6 \\$	59.8 57.0 56.0 57.0 57.5 52.0 54.5 57.0 54.5 57.0 56.5 59.2	$15.9 \\ 16.3 \\ 13.8 \\ 15.4 \\ 11.7 \\ 13.7 \\ 16.0 \\ 16.5 \\ 12.2 \\ 14.5 \\ 14.2 \\ $	$\begin{array}{c} 0.82\\ 1.10\\ 1.47\\ 1.38\\ 1.18\\ 1.11\\ 1.45\\ 1.44\\ 1.61\\ 1.50\\ 1.50\\ 1.50 \end{array}$	1.61 1.57 1.55 1.71 1.95 1.77 1.75 1.46 1.46 1.47 1.40 1.16	5.98 5.70 5.37 5.70 5.75 5.20 5.45 5.65 5.92	1.591.631.381.541.171.371.601.651.221.451.42

Reducing the pressure in the retort might be expected to produce two major effects: (a) an increased rate of removal from the retort of the vaporized decomposition products and (b) lowering of the boiling points of the products and thus the temperature at which they would be vaporized. Both of these factors should increase the yield of distillate because of the smaller chance for complete decomposition of the intermediates into carbon or its oxides.

The abrupt increase in tar yield when the pressure was reduced to 1 inch of mercury below atmospheric may be explained by assuming that the first-mentioned factor was the determining one in this range. The increase in yield of tar due to the better removal of the vapors would certainly be more pronounced than that caused by the lowering of boiling point at this slight vacuum. The gradual increase in distillate resulting from a further decrease in pressure may be supposed to result from the lowered boiling points and, to some extent, from the increased speed of vapor removal. The reason for the decreasing yield after the pressure had been reduced below 5 inches is rather hard to explain on this basis, however.



AT LOW PRESSURES

It is interesting to compare the yields of tar obtained in the present study with those of Phillips (7). The best yield of wet tar obtained in the present experiments was 17.7 per cent (basis oven-dried lignin); Phillips and Goss obtained 28.3 per cent from corncob alkali lignin at 25 mm. of mercury absolute pressure. However, the lignin used in the present experiments represented 10 per cent of the cornstalks, whereas that of Phillips represented only 5 per cent of the corncobs because of milder conditions of extraction. The yields of tar, based on the original raw material, are thus 1.77 per cent (basis

oven-dried cornstalks) in the present study and 1.41 per cent (basis corncobs) in Phillips' experiments. The fact that the yields are so different when based on the lignin seems to indicate that the lignin of the raw material which requires more drastic conditions for its removal is considerably different from that which comes out with relatively mild extraction conditions. This was also shown by Phillips (6) in experiments on the fractional extraction of lignin from corncobs.

Composition of Tar

The separation of the tar into its major classes of compounds was accomplished by previous lignin investigators by successive extractions with sodium bicarbonate and sodium hydroxide solutions which were supposed to dissolve the

acidic and phenolic portions, respectively. The acids and phenols were recovered by acidification of these solutions, and the insoluble tar remaining from the above extractions was classed as neutral tar. This method of analysis gave in some cases very high percentages of phenols; Phillips (7), for example, found that 84 per cent of the tar from his destructive distillation experiments at atmospheric pressure was insoluble in sodium bicarbonate solution but soluble in sodium hydroxide solutions. He thus reported that the tar contained 84 per cent of phenols.

In studying tar from the low-temperature carbonization of coal, Morgan (3) found that sodium hydroxide extractions of the tar dissolved not only the phenols but also considerable amounts of other classes of compounds which, when separated from the phenols, were entirely insoluble in caustic solu-

tion. He found that one of the best methods of separating these phenate-soluble compounds was by the use of caustic soda saturated with salt, a reagent which extracts only the phenols, instead of the ordinary aqueous solution of sodium hydroxide. The phenate-soluble materials then remained behind with the neutral oils, and the phenols were thus selectively extracted.

This method of separation was tried on some of the tars from the first six runs, and it was found that they behaved similarly to the coal tar studied by Morgan. When aqueous 10 per cent sodium hydroxide was used to extract some of the lignin tar which had previously been extracted with sodium bicarbonate, about 90 per cent of it dissolved. When 10 per cent sodium hydroxide saturated with salt was used, however, only about 60 per cent of it dissolved. The tar which was insoluble in the caustic-brine extraction was now also insoluble in the ordinary 10 per cent sodium hydroxide solution. As a result of these tests the following method of separation and estimation, which is similar to that used by Morgan, was adopted:

1. The tar from each run, about 30 to 35 grams in quantity, was extracted with 50 ml. of 10 per cent sodium bicarbonate. Its loss in weight was recorded as acids.

2. The insoluble tar from the first step was dissolved in an equal volume of benzene and extracted with two 25-ml. portions of the caustic-brine reagent. After having been shaken with this reagent and allowed to stand, the mixture separated into three layers: the lower layer consisted of the alkaline solution of the phenols, the middle layer consisted of precipitated neutral tar, and the top layer consisted of a solution of the benzene-soluble tar. The benzene was necessary for good separation of the neutral tar and the phenate solution; unless it was present a suspension formed which was very difficult to break up. The phenols were separated and weighed. 3. The neutral tar was calculated by difference, no attempt

3. The neutral tar was calculated by difference, no attempt being made to estimate the quantities of the benzene-soluble and benzene-insoluble neutral tar because of the difficulty of separating them quantitatively.

The tar from each of runs VII to XVI, inclusive, was analyzed by the above procedure, and the results are recorded in Table III. The per cent composition of the tar was calculated both on the basis of the crude wet tar and on that of the original oven-dried lignin. The tar in each case contained some water, but this was not determined in the small-scale runs. The percentage of phenols increases with decreasing pressure, the percentage of neutral tar first increases and then falls off with decreasing pressure, and the percentage of acids remains sensibly constant. From the standpoint of phenol production it appears advantageous to decrease the pressure as much as possible, because the yield of phenols continues to increase at very low pressures, despite the drop in total tar yield. The yield of phenols is also shown graphically in Figure 2.

TABLE III. EFFECT OF LOW PRESSURES ON TAR CO
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Run No.	Abs. Pressure, In. Hg	Basis C Acids	Per Ces rude Tar Phenols	nt Comp (Wet) Neutral tar	osition of Basis O Acids	Tar ven-Dried Phenols	Lignin Neutral tar
XIV XV XVI XIII XII IX XI XI XI XI XVIII	2.2 2.2 4.0 5.0 17.0 28.0 29.0 (atm.)	$\begin{array}{c} 7.1 \\ 8.9 \\ 5.5 \\ 4.6 \\ 10.0 \\ 11.2 \\ 10.7 \\ 12.9 \end{array}$	$\begin{array}{c} 64.5\\72.0\\86.9\\57.2\\60.0\\49.0\\57.0\\53.2\\49.2\end{array}$	28.419.17.634.035.441.031.836.137.9	$1.1 \\ 1.4 \\ 0.9 \\ 1.5 \\ 0.9 \\ 1.4 \\ 1.6 \\ 1.5 \\ 1.5$	$10.4 \\ 11.3 \\ 13.4 \\ 9.8 \\ 11.7 \\ 7.1 \\ 8.4 \\ 7.5 \\ 5.7 \\ \end{array}$	$\begin{array}{c} 4.6\\ 3.0\\ 1.2\\ 5.8\\ 6.9\\ 4.7\\ 5.0\\ 4.4\end{array}$

In view of the rather large difference between the amount of phenols observed when the caustic-brine reagent is substituted for the usual aqueous caustic solution, it is probable that most of the values for the yield of phenols in the literature are considerably higher than the true values. The amounts found in the present study are large enough to make lignin an attractive potential source of phenols, however.

Fractionation of Distillates

APPARATUS AND METHOD. The fractionating column was constructed of 0.39-inch (10-mm.) inside-diameter Pyrex tubing. It was packed with 0.126-inch (3.2-mm.) inside-diameter singleturn glass helices (1), the packed section being 100 cm. in height. Around the packed section was a 0.55-inch (14-mm.) insidediameter Pyrex tube on which was wound 50 feet (15.2 meters) of Nichrome resistance wire to provide side heating, and this was in turn enclosed in a 1.26-inch (32-mm.) inside-diameter Pyrex tube which served as further insulation. The kettle consisted of a 500-ml. flask which was heated by an electrical heater. Reflux was furnished by a total condenser at the top of the column.

The fractionations were carried out using 150- to 250-ml. charges. A high reflux ratio (20-30 to 1) was maintained at all times and the still was operated at as high a boiling rate as possible without flooding. Adiabatic conditions were maintained in the column by close control of the side heat. Fractions were collected corresponding as nearly as possible to the constant-boiling portions of the fractionation curves. All fractionations were conducted at atmospheric pressure.

Fractionation of Tar

The tar from the large-scale destructive distillations was fractionated after various pretreatments. This tar was wet, containing 13 per cent water (wet basis) as determined in the following fractionations, and represented 14 per cent of the oven-dried lignin; the dry tar thus represented 12.2 per cent of the oven-dried lignin. In fractionation A the tar was given no pretreatment. In fractionation B the tar was predistilled in an ordinary distilling flask before being fractionated. For fractionation C the phenols were extracted from



the crude tar as follows: 204 grams of the crude wet tar were dissolved in an equal volume of benzene and extracted successively with 10 per cent hydrochloric acid, 10 per cent sodium bicarbonate, 10 per cent sodium hydroxide saturated with sodium chloride, and 10 per cent sodium hydroxide. The hydrochloric acid and sodium bicarbonate extracts were washed with benzene, and these washings were added to the residual solution of tar before the alkaline extractions. The alkaline extracts were combined and the phenols were recovered by acidification with 25 per cent sulfuric acid. The crude phenols thus obtained were distilled without fractionation before being charged into the fractionating column. The hydrochloric acid extract was made alkaline with sodium hydroxide solution, and a precipitate formed which was filtered, washed, and dried. It was a dark purple amorphous powder weighing 0.4 gram which partially dissolved in water to give a deep purple solution. This material was not further investigated; it probably consisted of a mixture of basic nitrogenous compounds, since it had a characteristic odor and evolved ammonia when boiled with sodium hydroxide solution. For purposes of comparison a fractionation of a commercial cresylic acid was made; this is designated as fractionation D.

The fractionations were carried out until decomposition of the material in the kettle set in, as evidenced by liberation of white fumes and lowering of the vapor temperature. The fractions from the lignin tar were in all cases colorless or very light shades of pink or yellow. On standing several days, however, they turned dark red or black. The fractions from fractionation C (extracted phenols) showed less tendency than the others to discolor, but after several weeks they were also dark in color. The fractions from the commercial cresylic acid remained light in color, however.



FIGURE 4. FRACTIONATION OF COM-MERCIAL CRESYLIC ACID (RUN D)

The results of the fractionations are shown in Figures 3 and 4, where the cumulative volume per cent of distillate (basis dry crude tar) is plotted against the vapor temperature in the top of the column. Sharp fractions were obtained in most cases. The material boiling below 182° C., the lower limit

of the phenolic temperature range, consisted entirely of water and in a few cases of a small amount of methanol; there was no evidence of light oils or other material of any kind. A summary of the recovery of material is shown in Table IV. The amounts of the dry crude tar, the dry charge to the fractionating column, the phenolic distillate (the distillate obtained above 182° C.), the residue in the still kettle, and the loss in the fractionation are shown both in weights and in percentages on the basis of the dry crude tar. Since the crude tar contained 13 per cent water, there were small amounts of water in the materials throughout the operations, but these have been subtracted for purposes of comparison.

_	Тı	BIE	IV R	RCOVE	AV FRO	M FI	3 A C'TT I O	NATT	ONS	
Run No.	Crude (Dr	Tar y)	Column	e to (Dry)	Phen Disti	olic llate	Resi	due	Lo	88
	Grams	%°	Grams	%a	Grams	%"	Grams	$\%^a$	Grams	%ª
$egin{array}{c} A \ B \ C \end{array}$	$236 \\ 125 \\ 178$	$100 \\ 100 \\ 100$	$236 \\ 104 \\ 88.5$	$100.0 \\ 83.2 \\ 49.6$	$119 \\ 69 \\ 58$	$50.5 \\ 55.2 \\ 32.6$	$76 \\ 11 \\ 15$	${}^{32.2}_{8.8}_{8.4}$	${}^{41}_{24}_{15.5}$	$17.3 \\ 19.2 \\ 17.5$
D ¢A	199 ll per ce	100 ents a	199 re on the	100.0 basis of	171 f the dr	85.9 y cruc	12 le tar.	6.0	16	8.1

The predistillation without fractionation (fractionation B) increased the yield of the phenolic distillate by almost 5 per cent (basis dry crude tar). Figure 3 shows that this is due in large part to the fact that decomposition set in earlier in the fractionation of the crude tar (fractionation A) than in that of the predistilled tar (fractionation B). The crude tar began to decompose at a vapor temperature of 233° and a kettle temperature of 312° C., whereas the predistilled tar began to decompose at a vapor temperature of 248° and a kettle temperature of 330° C. The recovery of phenolic distillate from the extracted and predistilled phenols (fractionation C) was somewhat poorer than that of the first two fractionations. This may be explained in part by the greater loss of material due to incomplete extraction, mechanical losses, etc. It is also possible that the phenolic distillates of fractionations A and \hat{B} contained substances other than phenols, but this seems unlikely because of the similarity in properties of the fractions of the extracted phenols and crude tar. Furthermore, rough experiments on the neutral portions of the tar indicated that they contained very little material boiling in the phenolic range. The losses were rather large because the material held up in the column packing after the fractionation was not removed but was included in the losses.

These results on the recovery of total phenols from the tar check the analyses made by the caustic-brine extraction method quite well. Table III shows that at a pressure of 28 inches of mercury absolute (the pressure of the large-scale runs) the tar contains about 53 per cent phenols (wet basis) or 61 per cent phenols (dry basis). The recovery of phenolic distillate in fractionations A and B was 50.5 and 55.2 per cent, respectively. Thus over 80 per cent of the total phenols (as estimated by the caustic-brine method) were recovered in fractionation A, and 91 per cent in fractionation B. The recovery of the crude predistilled phenols in fractionation Cwas 49.6 per cent of the dry crude tar which contained 61 per cent total phenols (dry basis); this recovery amounted to 81 per cent of the total phenols. The recovery of fractionated phenols in this run was 32.6 per cent of the dry crude tar, or 53 per cent of the total phenols. The smaller recovery in fractionation C may be attributed to the fact that the amount of charge was smaller than in the other fractionations which would magnify the percentage loss in the column holdup, and also to the fact that the residue in this fractionation consisted entirely of phenols whereas in fractionations A and B it was probably largely composed of neutral and acidic compounds.

Identification of Phenols

The yields of the various fractions from the three runs are shown in Table V. The boiling points and refractive indices are those of the material at the flat portions of the curves. The amounts of the various fractions were ascertained by drawing vertical lines through the mid-points of the transitions between the various fractions and recording the differences in abscissas between these lines. This method, of course, will include any compounds which may have been present in amounts too small to be fractionated out distinctly, but the sharp breaks in the curves indicate that few such compounds were present in appreciable amounts in the majority of cases. All of the fractions were cooled to -20° C, in an attempt to freeze them, but in most cases a glass or very viscous mass was obtained which could not be crystallized. For comparison, Table VI shows the boiling points and refractive indices of the more common phenols in the boiling range studied (2).

Since the fractions from run C (extracted phenols) seemed more pure than those of runs A and B, they were used exclusively for the chemical identification work; the details are as follows:

The fraction boiling at 183° C. was solid at room temperature and showed the characteristic crystal structure of phenol. It melted at 35° C. A nitro derivative was prepared according to Mulliken's procedure (4) which melted at 121.5- 122.5° C. (melting point of picric acid, 122.5° C.). The fraction was therefore phenol.

The fraction boiling at 191° C. was small and therefore not very pure. A picrate was prepared which melted at 87– 88° C. (melting point of the picrate of *o*-cresol, 88° C.). The fraction therefore contained *o*-cresol.

The fraction boiling at 201° C. gave an aryloxyacetic acid melting at 130–132° C. (melting point of the aryloxyacetic acid of p-cresol, 134–136° C.). The fraction therefore consisted chiefly of p-cresol.

The fraction boiling at 205° C. yielded a 3,5-dinitrobenzoyl ester which melted at $140-141^{\circ}$ C. (melting point of the 3,5-dinitrobenzoyl ester of guaiacol, 141° C.). It also gave a picrate melting at $87-88^{\circ}$ C. (melting point of the picrate of guaiacol, 86° C.). The fraction was therefore guaiacol.

	TABLE	V. FRA	CTIONATIO	N OF TARS				
Fraction Boiling at, C.	$\begin{array}{c} \text{Refractive} \\ \text{Index}, \\ n_{D}^{20} \end{array}$	Basis dry tar	-Per Cent Y: Basis oven-dried lignin	ield Basis oven-dried stalks	Chief Constituent			
	C	Crude Lig	nin Tar (Run	n A)				
183 191 201 207 215 222 233	$\begin{array}{c} 1.5405 \\ 1.5275 \\ 1.5195 \\ 1.5210 \\ 1.5230 \\ 1.5198 \\ 1.5198 \\ 1.5175 \end{array}$	$14.9 \\ 6.7 \\ 6.4 \\ 5.1 \\ 5.5 \\ 4.7 \\ 7.2$	1.820.830.780.620.670.570.88	$\begin{array}{c} 0.182 \\ 0.083 \\ 0.078 \\ 0.062 \\ 0.067 \\ 0.057 \\ 0.088 \end{array}$	Phenoi o-Cresol p-Cresol Guaiacol Xylenols Creosol			
Total	yield	50.5	6.17	0.617	e			
Predistilled Lignin Tar (Run B)								
182 189 201 208 218 225 248	$\begin{array}{c} \textbf{1.5422} \\ \textbf{1.5402} \\ \textbf{1.5400} \\ \textbf{1.5290} \\ \textbf{1.5310} \\ \textbf{1.5290} \\ \textbf{1.5240} \\ \textbf{1.5240} \\ \textbf{1.5468} \end{array}$	9.6 4.0 10.4 6.4 5.6 7.2 12.0	$1.18 \\ 0.49 \\ 1.27 \\ 0.78 \\ 0.68 \\ 0.88 \\ 1.46$	$\begin{array}{c} 0.118\\ 0.049\\ 0.127\\ 0.078\\ 0.068\\ 0.088\\ 0.146\\ \end{array}$	Phenol o-Cresol p-Cresol Gusiacol Xylenols			
Total	yield	55.2	6.74	0.674				
	Crude Predis	tilled Phe	nols from Lig	nin Tar (Ru	n <i>C</i>)			
183 191 205 208 216 220 225 231 240 249 Total	Solid 1.5407 1.5378 1.5378 1.5392 1.5345 1.5320 1.5299 1.5299 1.5299 1.5330 1.5299 1.53412 yield	6.8 1.1 2.8 4.4 5.6 1.7 2.8 1.1 2.2 32.6	$\begin{array}{c} 0.84\\ 0.13\\ 0.34\\ 0.52\\ 0.17\\ 0.68\\ 0.21\\ 0.34\\ 0.13\\ 0.27\\ \hline 3.97 \end{array}$	$\begin{array}{c} 0.084\\ 0.013\\ 0.034\\ 0.052\\ 0.017\\ 0.068\\ 0.021\\ 0.034\\ 0.013\\ 0.027\\ \hline 0.397 \end{array}$	Phenol o-Cresol p-Cresol Guaiacol 3,5-Xylenol Creosol			

The fraction boiling at 208° C. had a refractive index of 1.5345; it was small in amount and probably not very pure. An aryloxyacetic acid of this fraction melted sharply at 93° C. after recrystallization from water and petroleum ether. The fraction was not further identified.

The fraction boiling at 216° C. probably contained more than one compound. No sharp-melting 3,5-dinitrobenzoyl ester could be obtained, its melting point increasing from 98° to 126° C. on repeated recrystallization from ethanol, petroleum ether, and methanol. However, a small amount of a bromo derivative was isolated which melted sharply at 160° C.; this indicates that 3,5-xylenol was present (melting point of the tribromo derivative of 3,5-xylenol, 162.5° C.). The other constituent or constituents of this fraction were probably other isomeric xylenols, since there are several such compounds boiling in this region.

The small fraction boiling at 220 ° C. contained creosol since an aryloxyacetic acid prepared from it melted sharply at 86 ° C. (melting point of the aryloxyacetic acid of creosol is 84–85 ° C.) and a picrate melted at 97 ° C. (melting point of the picrate of creosol is 96.8 ° C.).

The fraction boiling at 231° C. yielded an aryloxyacetic acid melting at 74-76° C. It was not further identified.

The fraction boiling at 249° C. yielded a 2,4-dinitrophenyl ether which melted at $162-163^{\circ}$ C. after repeated recrystallization. A 3,5-dinitrobenzoyl ester melted at $157-160^{\circ}$ C. No known phenol could be found which yielded derivatives of these characteristics, and the fraction was not further identified.

The yields of the various fractions for the three fractionations are given in Table V. The yields are calculated on the basis of the dry crude tar, the oven-dried lignin, and the ovendried cornstalks, using a yield of 14 per cent of wet tar from the lignin and a yield of 10 per cent oven-dried lignin from the oven-dried cornstalks. These figures are for a distillation pressure of 28 inches of mercury absolute, and the yield of tar and phenols would be considerably higher from a highvacuum distillation (Table III).

Comparing these results with those of Phillips and Goss (8) who identified several phenols in lignin tar, it is observed that all of the compounds which they found, with the exception of n-propylguaiacol and 1-vinyl-3-methoxy-4-hydroxybenzene, were found in the present study. Phillips and Goss separated the phenolic compounds from the tar by alkaline extraction, steam distillation of the crude phenols, separation of the steam-volatile portion into solid and liquid potassium phenolates, and finally fractionation of the recovered phenols in a three-bulb fractionating column. Their recovery of the steam-volatile phenols was 15 per cent of the tar, and that of the total fractionated phenols was 9.1 per cent of the tar. Because of the relatively inefficient fractionation and because of the incomplete recovery of the phenols, no quantitative estimation of the amounts of the various compounds was possible. As a result of the present study it is believed that Table V gives a fairly accurate quantitative account of the distillable components of the lignin tar. The yields of phenol and o-cresol seem unusually high in fractionation A; poor fractionation was obtained in this region due to flooding, however, and they are probably too high. The yields of the other fractions in fractionations A and B agree fairly well. The vields in fractionation C are all smaller than those in fractionations A and B, and in some cases are in different proportions. This may be the result of incomplete extraction of some of the more difficultly alkali-soluble phenols.

Fractionation D (Figure 4), in which a commercial cresylic acid was used, indicates the similarity between coal-tar phenolic distillates and the lignin-tar phenols. In addition to mand p-cresols, a number of other compounds were present as indicated by the numerous plateaus. The separation of mand p-cresol (at 201° and 203° C.), although probably not complete, is an indication that the column was sufficiently efficient for the present purposes.

Fractionation of Aqueous Distillates

It is usually assumed that the principal constituents of the aqueous distillate from lignin are acetone, methanol, and acetic acid. The customary method for determining acetone in the distillate is by the iodoform reaction (Messinger method), that used for determining methanol is usually methoxyl determination, and that used for acetic acid is titration of the distillate with standard alkali (7). These three compounds have not been isolated quantitatively from the distillates, however, by any of the previous investigators. The usual yield of acetone reported in the literature ranges

TABLE VI. PHENOLIC COMPOUNDS ARRANGED IN ORDER OF IN-CREASING BOILING POINT

	B. P., ° C.	$\begin{array}{c} \text{Refractive} \\ \text{Index}, \\ n_{\text{D}}^{20} \end{array}$
Phenol 2-Methylphenol (o-cresol) 4-Methylphenol (p-cresol) 3-Methoxyphenol (guaiscol) o-Ethylphenol 2,4-Dimethylphenol (xylenol) 2,5-Dimethylphenol (xylenol) 2,5-Dimethylphenol (xylenol) m-Ethylphenol 3,3-Dimethylphenol (xylenol) 2-Methoxy-4-methylphenol 2-Methoxy-4-methylphenol 3,4-Dimethylphenol (xylenol) 1-Methyl-6-isopropylphenol 4-Methyl-6-isopropylphenol 2-Methyl-6-isopropylphenol 2-Methyl-6-isopropylphenol 2-Methyl-6-isopropylphenol 2-Methyl-5-isopropylphenol 1-Methyl-5-isopropylphenol 1-2-Dihydroxybanzene (catechol)	° C. 182 190.8 201.1 202.8 205.1 207.5 211.5 211.5 212 214 218 219.5 221.8 219.5 221.8 225.1 226 228. 228. 228. 228. 229. 231.8 237.9 245.5	$\begin{array}{c} n_{\rm D}^{20} \\ 1.5425 \ (41^{\circ} \ {\rm C.}) \\ 1.547 \\ 1.540 \\ 1.540 \\ 1.540 \\ 1.540 \\ 1.540 \\ 1.540 \\ 1.540 \\ 1.523 \\ 1.523 \\ 1.5234 \\ 1.5234 \\ 1.5234 \\ 1.524 \\ $
I-Hydroxy-4-methylphenol (homocatechol) Eugenol Isoeugenol	$252 \\ 253 \\ 267.5$	1.5425 (74° C.) 1.5439 (14° C.) 1.5680

from 0.10 to 0.20 per cent (basis lignin) for both alkali and fuming hydrochloric acid lignin, although Phillips (7) found as high as 1.0 per cent for 72 per cent sulfuric acid lignin. For methanol, 0.07 to 1.9 per cent (basis lignin) have been reported, 0.90 per cent being an average figure for alkali, 72 per cent sulfuric acid, and fuming hydrochloric acid lignin. The yield of acetic acid ranges from 0.05 to 0.30 per cent for alkali lignin and 0.9 to 1.3 per cent for the fuming hydrochloric acid and 72 per cent sulfuric acid lignins.

In order to compare the present aqueous distillates with those of previous investigators, the aqueous distillates from four of the large-scale distillations were analyzed using the customary methods previously mentioned. The results of the analyses are: acetone, 0.285 per cent; methanol, 0.28 per cent; and acetic acid, 0.432 per cent.

These figures were somewhat different from those reported in the literature; therefore a quantitative separation of the constituents by fractional distillation was attempted. The combined aqueous distillates from three large-scale runs were divided into two portions and fractionated in the column, one without any pretreatment and the other after it had been made alkaline with sodium hydroxide. In order to obtain a check on the efficiency of the column for such a separation, a control fractionation was made of a solution of acetone, methanol, and water in amounts corresponding to 0.10 and 0.79 per cent (basis lignin) for the acetone and methanol, respectively.

The results are shown in Figure 5. Good separation of the methanol was obtained, and the average yield from both fractionations is 0.84 per cent (basis oven-dried lignin). A separation of the acetone was not accomplished, however, and



on the basis of comparison with the control fractionation, it can be concluded that there was less than 0.10 per cent (basis lignin) present, since the initial boiling points and the first parts of the fractionation curves lie considerably higher than that for the control run. After the water had all

been removed in the first fractionation (no pretreatment of distillate) such a small amount of material remained in the kettle that it could not be fractionated further; the acetic acid (boiling point 118°C.) could therefore not be separated in this way.

In order to separate the acetic acid, the alkaline residue from the second fractionation was saturated with carbon dioxide and the liberated phenols were removed by filtration and ether extraction. The solution was then acidified with sulfuric acid, and the free acids were separated from the solution by four ether extractions. The ether solution was concentrated by distillation of the extract until the vapor temperature was 50° C. The total amount of oil remaining after the ether had been removed was only 0.1 per cent (basis lignin). It was distilled in a small flask; the temperature rose steadily from 50° to 255° C., almost all of the oil being distillable. It may be concluded that the amount of acetic acid (boiling point 118° C.) present was very small; the value (0.432 per cent) obtained by the usual titration method is therefore much too high. It may be concluded that the values obtained by the customary methods of analysis for acetone, methanol, and aceticacid may lead to considerable error when applied to the aqueous distillates from lignin. This is doubtless due to the presence of materials other than these three constituents which interfere with the reactions. It is likely that many of the values recorded in the literature are in error because of this fact.

Neutral Tar and Carbonized Residue

The neutral tar as separated by the caustic extraction method consisted of a benzene-soluble portion and a benzeneinsoluble portion. The latter was a light brown soft mass, which settled to the bottom of the benzene solution. These two fractions were entirely soluble in benzene in the presence of the phenols, as is evident from the method of separation used. No attempt was made to identify these materials.

The carbonized residue was a light, porous material which had about twice the volume of the original lignin. It was of a granular texture and was not sooty.

Discussion

In comparison to coal tar, wood tar, and other natural sources of phenols, the tar from alkali lignin has a far greater phenol content. The yield of the tar from the lignin is also larger than that of the tar from coal and wood destructive distillations. As a source of phenols, therefore, alkali lignin would be far superior to the present-day sources with respect to the yield. Offsetting this advantage, however, is the higher cost of production of the lignin and the difficulty of using the lignin carbonized residue as a substitute for coke and charcoal. The first of these disadvantages would be overcome by the development of a cheap method of recovering the lignin from soda and sulfate wood pulp liquors or of a cheap method of separating lignin from agricultural by-product materials. The second disadvantage would be overcome either by development of new uses for the carbonized residue sufficient to absorb its production or by modification of it in such a manner as to make it acceptable as a substitute for coke or charcoal. Preliminary tests indicate that good activated carbon may be made from it. By briquetting the carbonized residue it could be used for fuel and for many other purposes. In view of the increasing demand for phenolic compounds, lignin should thus be considered a potential source of phenols which may become important in the future.

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