Production and utilization of lignin from agricultural by-product materials

G. L. Bridger
Iowa State College

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PRODUCTION AND UTILIZATION OF LIGNIN FROM AGRICULTURAL BY-PRODUCT MATERIALS

by

G. L. BRIDGER

A Thesis Submitted to the Graduate Faculty for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Chemical Engineering

Approved:

Signature was redacted for privacy.

In charge of Major work

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Dean of Graduate College

Iowa State College
1938
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I. INTRODUCTION

A. Occurrence of Lignin

Most cellulose materials, such as woods, stalks, and straws are composed of three major constituents, namely; cellulose, hemicelluloses, and lignin. The hemicelluloses are differentiated from cellulose by their ease of hydrolysis with dilute acids to sugars and their solubility in sodium hydroxide solution. The lignin is believed to serve as an incrusting or binding material for the cellulose and hemicellulose cells. The relative proportions of these three major constituents in cornstalks, oak (a typical hardwood), and pine (a typical softwood) are shown in Table I (103).

TABLE I
Constituents of Cornstalks and Typical Woods

<table>
<thead>
<tr>
<th></th>
<th>Cornstalks</th>
<th>Oak</th>
<th>Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose (Cross and Bevan)</td>
<td>49.7%</td>
<td>58.0%</td>
<td>59.7%</td>
</tr>
<tr>
<td>Cellulose (Alpha)</td>
<td>26.5</td>
<td>33.0</td>
<td>37.1</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>30.5</td>
<td>19.6</td>
<td>10.2</td>
</tr>
<tr>
<td>Lignin</td>
<td>24.6</td>
<td>24.9</td>
<td>26.4</td>
</tr>
</tbody>
</table>

(Percentages are on the moisture-free basis)
The amount of lignin in nature is enormous; except for cellulose, it is the most abundant natural product in the vegetable kingdom (30). Agricultural by-product materials such as cornstalks, corncobs, oathulls, cottonstalks, and cereal straws are from one-fourth to one-third lignin. The annual production of cornstalks in the United States has been conservatively estimated to be 150,000,000 tons (104). The potential supply of lignin from this source is thus about 50,000,000 tons yearly; this enormous amount of material is at present almost entirely wasted.

One of the most promising sources of lignin from the standpoint of segregation is the waste liquors from pulp and paper mills. These plants use wood as the raw material and the lignin which is removed in producing paper and chemical pulp is present in the effluent liquors from the mills. This liquor is largely discarded or, in some instances, concentrated and burned, the soda being recovered by leaching the ash. In the soda pulp process alone in 1933 about 152,000 tons of lignin were present in the waste liquors (10).

One of the major research projects at the Iowa State College is the utilization of agricultural by-products. Cornstalks and corncobs have been given especial attention. The whole stalks have been used to manufacture artificial lumber, insulating boards, and plastics. The cellulose has been used in the manufacture of paper and chemical pulp. The pentosans have been used in the manufacture of furfural and
xylose. No important uses have been developed for the lignin, however. Since this is a major constituent of the stalks and cobs, a complete and economical utilization of them would demand a profitable use for the lignin. It is the purpose of this thesis to study methods of production and uses of lignin from agricultural by-product materials.

B. Chemistry of Lignin

Despite its great abundance, lignin is still one of the least comprehended of all vegetable substances. Perhaps this may be attributed to the fact that it has found no widespread uses as has cellulose. The research which has been done to date on lignin has led, in large part, to disappointing and indefinite conclusions. From the chemical point of view lignin is still a rather obscure and mysterious substance.

Although the greater part of the work done on the chemistry of lignin has been concerned with lignin isolated from wood, there seems to be no great difference between the lignin of wood and the lignin of the various agricultural waste materials. Even if this is not true, it will be fairly safe to discuss the chemistry of lignin from both sources simultaneously.

1. Isolation

There are two general methods for the isolation of lignin from the raw material, the first being that of removing all other components from the plant material leaving the lignin as
a residue, and the second that of dissolving the lignin from the cellulosic material and precipitating it from solution. Despite the many variations of both of these methods, it is generally agreed that the lignin obtained by any of them is different from that which existed in the original cellulosic material.

Of the many modifications of the first method of isolation, the one most used by lignin investigators is the Willstatter (II3) or fuming hydrochloric acid method. This consists of treating the cellulosic material with fuming hydrochloric acid at room temperature which treatment hydrolyzes the cellulose and other carbohydrates quantitatively and leaves the lignin as an insoluble residue. Another method of this kind which has been gaining favor among lignin investigators in recent years is the Klason (61) or 72 per cent sulfuric acid method. It consists of treating the cellulosic material with 72 per cent sulfuric acid in the cold to hydrolyze the cellulose and then boiling with 3 per cent sulfuric acid to complete the hydrolysis of the hemicelluloses.

In the second general method, the most common reagents for dissolving the lignin are alkalis and sulfites. When the cellulosic material is treated with a solution of sodium hydroxide at high temperatures, the lignin and hemicelluloses are dissolved and may be precipitated from solution by acidification. The hemicelluloses are removed by hydrolysis with dilute mineral acids. Similarly, lignin is removed from the
cellulosic material by treating it with acid sulfites, such as Ca(HSO₃)₂, usually under high pressure. The resulting "lignosulfonic acid" may be crystallized as the alkaline earth salts. Other methods of lesser importance are the extraction of lignin with organic solvents such as phenols, alcohols, and ethers. The yield of lignin from this second general method is always much less than that from the first, due to incomplete solution and to degradation of the lignin.

2. Physical properties and composition

Lignin as isolated by the various processes is an amorphous powder, ranging in color from light brown to black. The Willstatter and Klason lignins are practically insoluble in alkanis and organic solvents, while that extracted by the second general method is completely soluble in alkanis and more or less completely soluble in many organic solvents.

Lignin contains about 65 per cent C and 6 per cent H, there being much more carbon than would be required in a carbohydrate formula (14). Various empirical formulas have been given, a typical one being C₄₃H₄₂O₁₄ (formula weight = 782). The apparent molecular weight of methanol lignin in solutions of organic solvents is between 4,000 and 10,000 (67).

3. Constitution

Despite the large number of researches which have been carried out, the constitution of lignin still remains unknown. In the first place, it has never been satisfactorily demonstrated
that lignin is a single compound. Although the lignins from
various sources and isolated in various ways are similar in a
general qualitative way, there is enough variation in their
physical and chemical properties to keep one from concluding
that they are all identical. Furthermore, it is not even cer-
tain that the lignin isolated from a single source is only
one compound.

What is known definitely about the constitution of lignin
can be stated very briefly (42): It contains methoxyl groups,
in number varying from 3 to 7, and hydroxyl groups, usually
about 5 in number, per unit of about 800 to 900 formula weight.
Less certain, though quite probable, is the presence of
acetyl, aldehyde, and ethylenic linkages. The nature of the
nucleus is quite unknown, it being supposed that it is aromatic
or hydroaromatic in nature. This last speculation results
from the fact that many aromatic substances are obtained from
lignin on degradation by oxidation, reduction, caustic fusion,
dry distillation, etc. These methods are usually considered
too drastic to permit a definite conclusion to be drawn,
however.

A recent structural formula for lignin which has been pro-
posed is that of Fuchs (31). This structure is
4. Reactions and derivatives

Although the constitution of lignin is unknown, a number of well defined reactions are known. Lignin is quite highly reactive with many of the common reagents, and these reactions and the resulting derivatives will be described briefly.

Lignin is very easily oxidized even under mild conditions. With reagents such as ozone, hydrogen peroxide, and other mild oxidizing agents, lignin is degraded to simple organic acids, such as formic, acetic, malonic, and oxalic acids. Under more drastic conditions such as heating with 10 normal sodium hydroxide at 300°C, lignin yields aromatic acids in small amounts. When lignin is oxidized with nitric acid, oxalic acid is the chief product.

On heating with red phosphorus and hydriodic acid at 250°C, lignin yields a mixture of hydrocarbons, in amount about 32 per cent. This reduction is very similar to that of cellulose and other carbohydrates. By hydrogenating under high pressure in the presence of catalysts, lignin may be converted completely into liquid and gaseous products.
Lignin may be nitrated readily by treating with 5 normal nitric acid in the cold. The product is an amorphous powder similar to lignin itself, but having an orange color and a characteristic odor. This nitrated product may be reduced, diazotized, and coupled to form dyes.

The most important sulfonation products of lignin are the lignin sulfonic acids obtained by treating the lignin-containing material with sulfurous acid and acid sulfites. The lignin in the sulfite liquor from pulping wood is present as a salt of the sulfonic acid or as the free acid which may be precipitated out as lead, calcium, or barium salts or as the free acid. A great deal of work has been done on the chemistry of these lignin sulfonic acids, but it is not agreed whether they are one or many compounds. It is fairly certain, however, that the lignin sulfonic acids still contain methoxyl and hydroxyl groups.

Lignin is very easily chlorinated by chlorine gas, derivatives containing up to about 45 per cent of chlorine having been obtained. Antimony pentachloride and sulfuryl chloride have also been used for the chlorination. Bromine derivatives may be prepared. The readiness with which lignin reacts with the halogens is used as an argument for assuming that it contains ethylenic linkages.

Lignin may be acetylated easily, the best method being treatment with acetic anhydride in pyridine; as many as three
or four acetyl groups may be introduced into the molecule. This is, of course, good evidence for the presence of the hydroxyl groups.

Alkyl groups may be introduced into lignin by the usual reagents such as dimethyl sulfate, diazomethane, etc. The alkyl groups enter at the hydroxyl groups and when completely alkylated, the lignin is no longer soluble in alkali; this is to be expected if its alkali solubility is due to the formation of phenolates.

Lignin is not hydrolyzed under ordinary conditions, a fact which is evident from the methods of its isolation. By heating lignin with dilute acids in sealed tubes at 170-180°C, complete demethoxylation occurs, however. It may also be demethoxylated by treatment with hydriodic acid.

C. Production of Lignin

1. General

A process for producing lignin from its raw materials should permit as complete recovery as possible of the two other main constituents, namely; cellulose and hemicelluloses. It should not cause the lignin to suffer excessive degradation and it should be economically feasible.

Most processes for producing cellulose from cellulosic materials have been developed with little attention as to degradation or recovery of the other constituents present.
Since a large amount of lignin is found in industrial waste liquors from pulp and paper plants, the proposed methods for producing lignin will be discussed from the point of view of recovery from these waste liquors. It should be pointed out, however, that if sufficiently valuable uses are developed for lignin, the "waste liquors" may become the principal product of manufacture and the cellulose a by-product. It should also be noted that while most of the industrial waste liquors are from pulp and paper mills using wood as the raw material, the liquors from similar processes using agricultural by-products as the raw materials would be very similar in composition and would, with little variation, respond to any treatment which is successful with the wood liquors.

2. Soda liquors

When cellulosic material is treated with a solution of caustic soda, the lignin and hemicelluloses dissolve more or less completely, depending on conditions of concentration, temperature, etc., and the cellulose remains unattacked. This is the basis of the well known "soda pulping process". The lignin is more easily removed than the hemicelluloses, but always various amounts of the latter are present and must be separated from the lignin by some means. When the filtered liquor from such a cook is acidified, both extracted substances are precipitated. Upon boiling the mixture with dilute mineral
acids, however, the hemicelluloses are hydrolyzed, yielding soluble and volatile substances, and the lignin remains in fairly pure state as an insoluble residue.

Numerous processes have been worked out for the recovery of lignin from the black liquors of the soda pulp process using this principle, but as far as is known they are not being used commercially. Nevertheless such a process would be attractive as a means of recovering lignin from agricultural wastes, because it would be relatively simple, and would give a pure product. Only about one half of the lignin could be recovered in this process.

An alternate process is the precipitation of part of the lignin from the soda liquors with carbon dioxide. The filtrate from the precipitation still contains enough organic matter to permit burning the concentrated liquor to recover the soda and produce heat for the evaporation. By a preliminary treatment of the liquors with alcohol the hemicelluloses may also be recovered. The liquor from this treatment would probably not be suitable for fuel, however.

3. Sulfite liquors

In the sulfite process the lignin is present in the form of a sulfonic acid, and can only be recovered as an alkaline earth salt or as the free sulfonic acid. Howard (53) has successfully accomplished this in a very economical manner. His process consists of treating the sulfite liquor from wood
pulping with a lime reagent in four steps. In the first step
is recovered a CaHSO₃ precipitate which may be re-used for
pulping; in each of last three steps the lignin sulfonic acid
salts are precipitated. The effluent from the last step con-
tains the soluble carbohydrates and is much less objectionable
because of its greatly reduced oxidizing ability and toxicity
to stream life.

4. Sulfate liquors

Sulfate liquors are alkaline and contain the lignin as a
sodium salt, as in the soda liquor. Considerable sulfur is
present also and the lignin suffers more degradation than in
the soda process. The methods described for recovery of lignin
from soda liquors can be used but the product is not as pure
nor is the yield as great.

5. Other waste liquors

Among the many other proposed pulping processes, those
which are most promising technically and interesting from the
standpoint of lignin recovery are the so-called chlorine
(19)(94), nitric acid (3)(82), and alcohol (2) processes.
Although they are either not being used at the present time
or at most to a very limited extent, they may become important
in the future. Chloro- and nitro- lignin may be recovered from
the liquors of the first two processes respectively; and from
the last, the alcohol process, a lignin may be recovered which
utilization of lignin.

It utilizes more than an insignificant quantity of lignin, but none has been developed which
is utilized and traded for lignin, but none has been developed which
wastes, lignin has found no major use. Many outlets have been
despite its great abundance in agricultural and industrial

D. Utilization of Lignin

With the methods of treatment are simpler.

With the methods of treatment are simpler.

Lignin is utilized in Germany. The lignin correspondences observed
to the processes not used in the United States but is said to be ex-
pleasure. The lignin being treated as a residue. This
the cellulose and hemicelluloses of wood are converted into ferment-
ate the same acid in the sonotherm process (2), which
hydrolysis occurred in the berseum process (6), or with dilute
hydrolysis with running
of the hemicelluloses of wood. By hydrolysis with running
another inducement in which lignin is a by-product is that

hemicelluloses, and essential oils.

are recovered of the cooking lees, and recovered of the lignin.

The advantages of this process
is best as a solid residue. The advantages of this process
is that upon distillation off the alcohol, the lignin

when reduced they separate into two layers, the lignin being in the

equal parts of button and water at high pressures.

The process consists of cooking the gelledcoated material with
the process consists of cooking the gelledcoated material with
have shown that plantations are one of the best sources to use (6).

reason then any other kind of isolated lignin. Recent studies
The uses to which lignin in the free state (as differentiated from lignin not separated from its raw material) are being put at present may be summed up briefly. Lignin from sulfite liquors, as recovered by the Howard process, is being used to produce tanning and dispersing agents (56), vanillin, pigments (54), insecticides (56), wood preserving agents (56), and thermo-setting resins (55). The total quantity of lignin used in these ways is very small compared to the total amount available in sulfite liquors. The disposal of sulfite liquors is a serious problem; they cannot be evaporated and burned as can soda liquors, and legislation against running them into streams is becoming more widespread. Sulfite liquor has found some use in road treatment; it is claimed to be an effective dust preventive.

The lignin in soda and sulfate liquors is not recovered at all; the chief method of disposal of this liquor is evaporation, burning, and leaching of the ash to recover the soda. Heat for the evaporation is supplied by the burning of the liquor. No commercial process in this country at present produces or uses lignin from any source other than pulp and paper mill liquors. In Europe, however, the saccharification of wood is an important industry and it produces large amounts of by-product lignin. The only use to which this is put is fuel.

On the other hand, the number of proposed uses for lignin is large. These will be mentioned briefly in the following
paragraphs and some of them discussed more fully in a later chapter. Many of these proposed schemes have been tried on a semi-commercial scale, others are relatively new, but none has thus far reached commercial importance. Some of them show great promise, and will undoubtedly be used in the future on a large scale.

Perhaps the oldest proposal for lignin utilization is destructive distillation either of recovered lignin or of evaporated waste liquors. The products of destructive distillation are similar to those from wood; lignin yields more carbonized residue, tar, and methanol than does wood, however. The yield and nature of the products depends greatly on the method of separating the lignin from the other plant constituents. It is of particular interest in this thesis that lignin prepared by the alkali method yields the greatest amount of tar and that this tar has a higher phenolic content than any other lignin tar. Numerous destructive distillation studies have been made but none has thus far proved economical on a large scale. The chief reason for this is that practically all the attention has been turned to production of methanol, acetone, and acetic acid. These compounds are now being made synthetically and competition between them and the distillation products is keen. Little or no attention has been given to the production of phenols from the tar of the distillation. Because of increasing price and demand for phenols, this latter
possibility should be investigated.

A more recent use for lignin is in the preparation of resins and plastics. The various kinds of lignin can be made to react with aldehydes, amines, phenols, and other reagents to form different types of resins, some of which may be molded into plastics. The Forest Products laboratory has developed several interesting plastics from the lignin in sawdust. Another type of molding compound has been prepared from alkali lignin in this laboratory.

It has been found that when lignin is subjected to alkali fusion it is converted chiefly into catechol, protocatechuic acid, oxalic acid, and "lignic acid". The first three of these compounds are valuable technically and if they could be produced economically from lignin a utilization of a considerable amount of it could be accomplished. Because of conflicting data in the literature and difficulty in reproducing results no actual development has been made in this field, however.

A very promising way of utilizing lignin appears to be hydrogenation. Lignin can be hydrogenated to yield alcohols and glycols (1) or by more complete hydrogenation, hydrocarbons can be produced. Although work in this field has not been extensive, the results indicate that high yields of the products may be obtained. Inasmuch as great interest is being evidenced at present over the hydrogenation of coal, it would seem that a similar process for lignin should be of much value,
It is a solution of both of these parts is necessary before
the various sources and second, a study of uses for
a study of economical means of production or recovery of
problem naturally divided into two main parts: first,
in view of the preceding facts, it is seen that the

Purpose of Study

derivatives.

of iron derivatives such as the nitro, chloro, and ester.
Preparation of these work has been done on the nitration
itself (46) with pressure oxidation (28); and fermentation
iron and copper with phenol, ammonia, or iron
preparation of derivatives of ferrous nitration, reduction, and dehydrogenation
hydrazides of iron (44) or anthraquinone (50) to methylene.
Among the less important proposed uses for iron are

use.

were not as good as some of the commercial ferrihydries now in
were obtained with definite ferrihydride values, although they
were applied with success to waste sulfitic liquors and products
ammonia at high temperatures and pressures. These have been
ammoniunitization (50), whereas the iron is treated with aquous
from iron. Perhaps the most interesting method is that of
Many attempts have been made to produce a good ferrihydride

since results indicate that iron is probably more adapted

- 22 -


a profitable outlet for lignin can be realized.

The methods of production studied in the present investigation were recovery of lignin from soda liquors by strong acid and carbon dioxide precipitation, and extraction of lignin from the raw materials with butanol-water solutions. These methods were chosen because they yield a purer product than do most others, because the other constituents of the raw material are not destroyed but may be recovered, and because relatively little work has been done on them.

In the utilization studies emphasis has been placed on alkali lignin because it has definite advantages over the other kinds of lignin in many respects. The uses for lignin which were investigated in this study were destructive distillation, particularly as concerns phenol production and preparation of plastics.
experiments on their suetate indicate hydroxylation and
reproduction. In 1967, Hombrey and Anderson (48) carried out similar
experiments and were described by and of the
earlier treatments, and those studies of different
were noted. They isolated the lignin into a straight-surface
extractable solid, no difference in the yields of lignin before
and woody. They used sodium, hydroxylation, and
pretreatment or lignin from the straight solid yield of concentrate
-In 1981 Hombrey and Whitehead (49) studied the pre-

Keeza (60) in 1962.

From the aqueous phase, each solid lignor was separated and
extracted in a straighter way.
Attempts at the lignin to be part-
(F6) between organic wood) He found this lignin to be part-
material, and obtained a yield of 25.1% per cent of extral lignin
materials, and obtained the reusability of lignor with materials
and lignin. Some pretreatment of the power of pretreatment hydroxide in
acids.

I. Theoretically Studies

A. Pretreatment of Alkali Lignin with Strong Acids

II. Production of Lignin - Historical
as the precipitant.

In the same year Beckmann and Liesche (5)(6)(7) began an important investigation of methods of preparing alkali lignin. They used three methods of preparation: (1) Precipitation from alkaline cook liquors with a 2.5 per cent excess of hydrochloric acid followed by boiling for 5-10 minutes to dissolve the hemicelluloses, thus making filtration of the lignin easy, (2) separation of the hemicelluloses from the alkaline liquors by adding 1-2 volumes of alcohol prior to the precipitation with acid, thus permitting recovery of both hemicelluloses and lignin, and (3) extraction of the raw material with a solution of alkali in alcohol, which dissolves the lignin but not the hemicelluloses, followed by the usual acidification with hydrochloric acid. They studied the physico-chemical properties of the various fractions. Another study of the alkali lignin prepared by precipitation from the alkaline solution with hydrochloric acid was that of Fringsheim and Fuchs (96a). In 1924 Powell and Whittaker (95) published the results of an extensive study of alkali lignin from flax. They cooked the flax with 10 per cent sodium hydroxide solution at 130°C, acidified the liquor while hot, and filtered the precipitated mass, which amounted to 20-22 per cent of the original flax. This "lignin" probably contained considerable hemicelluloses, since no effort was made to remove them from the liquor by hydrolysis. A few years later, Powell and Whittaker (96) studied alkali lignin
from several species of wood in a similar manner. A rather complete study of the methods of preparation and the nature of alkali lignin was published by Mehta (72) in 1925.

A new type of alkali lignin, termed "metalignin", was described by Dorse and Barton-Wright (20) in 1927. This was prepared by cooking spruce with 4 per cent sodium hydroxide solution at 8 atmospheres. The lignin which was precipitated from the liquors with hydrochloric acid had only half the molecular weight of the ordinary alkali lignin. In this year Phillips (85) began a study of alkali lignin from corn-cobs. A yield of 3.5 per cent of the weight of the cobs was obtained by extracting them with alcoholic sodium hydroxide solution at room temperature. In a later paper (86) fractional extraction of the lignin was accomplished, a total of 9.0 per cent of the cobs being recovered as lignin.

In 1932, Macklin and Mass (68) made a study of the removal of lignin from spruce by concentrated solutions of sodium hydroxide (20-40%) at 160°C. They found that lignin is almost insoluble in the 40 per cent sodium hydroxide solutions.

Although sodium hydroxide is by far the most common reagent for extracting alkali lignin, others are occasionally used. An example of this is the use of ammonia, which was described by Peterson (84).
2. Proposed commercial processes

The first proposal to use acid precipitation on a large scale as a means of recovering lignin from soda liquors was that of Rinman (97) in 1909. He stated that after the acid treatment the liquors should be heated slowly in order to obtain a grainy precipitate. Almost simultaneously Hough (52) in this country was granted a patent on the precipitation with sulfuric acid and destructive distillation of the organic materials in soda liquors.

No further work was published until 1923 when Bradley and McKeefe (11) took out a patent on the treatment of soda liquor with nitre cake (NaHSO₄) to precipitate the liquor. In 1926 Greenwood (33) proposed the treatment of soda liquors with sulfuric acid in the presence of a solvent such as gasoline which dissolved any liberated resinous substances.

B. Precipitation of Alkali Lignin with Carbon Dioxide

The fact that lignin is soluble in caustic alkali solutions is usually accounted for by assuming that the hydroxyl groups in the lignin are phenolic in nature and therefore form soluble phenolates with the alkali. Since phenols are too weakly acidic to be soluble in sodium bicarbonate or sodium carbonate, it is possible to precipitate them from their
alkaline solution by passing in carbon dioxide which neutralizes the alkali and liberates the phenols from their alkaline salts. If lignin is thus in the form of a phenolate in its alkaline solution, it should be precipitated by the introduction of carbon dioxide.

The first recorded experiment in the literature testing this hypothesis is that of Klassen and Segerfelt (62) in 1910. They treated black liquor from a soda-sulfate cook with carbon dioxide and obtained a precipitate which contained 59.36 per cent C, 4.77 per cent H, and 6.72 per cent Na. On acidification of this material with sulfuric acid and purification by chloroform extraction, a lignin containing 63.31 per cent C, 5.24 per cent H, and 11.96 to 12.76 per cent CH₂O- was obtained. The filtrate from the carbon dioxide precipitation was acidified with sulfuric acid and a further precipitate was obtained which seemed identical with the carbon dioxide precipitated lignin.

Rinman (98) in 1911 precipitated a substance from black liquor which was one-third soluble in alcohol. The filtrate from the carbon dioxide precipitation gave another precipitate with sulfuric acid. The two substances seemed different, however. The first was very weakly acidic and was called "humus substances" while the second was more strongly acidic and therefore called "humic acids".

Helmberg and Wintzell (49) in 1921 precipitated lignin
from a pine soda-sulfate black liquor with sulfuric acid, hydrochloric acid, acetic acid, and carbon dioxide. All of the precipitates seemed to be identical. The filtrate from the carbon dioxide precipitation gave very little additional precipitate on acidification with hydrochloric acid. The lignin obtained above was separated into an alcohol-insoluble fraction and an alcohol-soluble fraction. The former was called $\alpha$-lignin and contained 65.73 per cent C and 5.80 per cent H. The latter was called $\gamma$-lignin and contained 67.02 per cent C and 6.19 per cent H.

The precipitation of lignin by carbon dioxide has been used as a means of purification for certain kinds of lignin. For example, Compton, Greig, and Hibbert (17) and Hibbert and Rawley (47) found that lignin extracted from spruce wood by means of methanol was completely precipitated from its sodium hydroxide solution by carbon dioxide and they used this as a means of purifying it.

There have been also a number of patents covering technical processes for recovering lignin from the black soda liquors of paper and pulp mills using carbon dioxide as the precipitant. The first of these processes (1911) was that of Rinman (99) who precipitated "humus substances" from black liquors with carbon dioxide and destructively distilled them to obtain alcohol, acetone, tar, etc. The soda was recovered from the residual liquor by precipitation as the bicarbonate with ammonia and carbon dioxide.
Neil (81) in 1912 treated black liquor with carbon dioxide and coagulated the resulting precipitate with sodium aluminate or sodium zinicate. The filtrate was oxidized with oxygen or ozone and causticized with lime. There was thus no evaporation in the process.

Veitch and Merrill (110) in 1913 found that they could precipitate about half the organic matter from southern pine black liquor by saturating it with carbon dioxide at 19 lbs./in² pressure, heating to 100°C, cooling, and filtering. The filtrate gave a further precipitate with hydrochloric acid. The carbon dioxide precipitate was destructively distilled.

Drewsen (22) in 1919 obtained sodium acetate from black liquors by heating them under pressure, treating with carbon dioxide, concentrating, and causticizing with lime thus obtaining a dry mixture which was treated with carbon dioxide and water. This mixture was finally heated to 160°-200° and leached with cold water to obtain the sodium acetate.

Bradley and McKeefe (12) in 1923 effected a simultaneous precipitation and concentration by spraying black liquor into a heated atmosphere containing carbon dioxide or sulfur dioxide. The resulting liquor was causticized. They also (13) precipitated the liquor containing a basic aluminum compound with carbon dioxide. This precipitate was destructively distilled to form a distillate and a residue of intimately mixed carbon and alumina.

A patent assigned to the Euromerican Cellulose Products
Company (24) in 1926 describes a process for recovering
pentosans (probably containing much lignin also) from soda
liquors of grasses by carbon dioxide precipitation.

Dorner (21) obtained a patent on a carbon dioxide pre-
cipitation process for recovering substances for use as
animal foods or for fermentation from black soda liquors.

The most recent industrial work on carbon dioxide pre-
cipitation is that of the Mead Corporation (71). Black soda
liquors are treated with fuel gas containing carbon dioxide,
heated to coagulate the lignin, and cooled. The lignin is
then filtered, washed with water, dilute sulfuric acid, and
again with water. It is dried on a drum drier and pulverized.

In this process only about 20 per cent of the total organic
matter is removed from the liquor, which can be concentrated
and burned as usual to recover the soda. This process is in
the development stage and if it reaches commercial production
it should make available a cheap supply of alkali lignin.

C. Production of Lignin by Butanol-Water
Extraction

The use of aliphatic hydroxy compounds for extracting
lignin from its raw materials is fairly recent, the first
published account being that of Gruse (35) in 1920, who isolated
lignin from wood by heating it with ethyl alcohol and
hydrochloric acid. Since that time a large number of similar preparations using various compounds has been published. The literature on this subject is thoroughly reviewed by Phillips (88) up to 1934 and more recent work is cited by Welker (111).

The use of butanol was first studied in 1927 by Hagglund and Urban (38) who cooked pine wood with butanol to which had been added a small amount of hydrochloric acid as a catalyst. In 1936 Aronovsky and Gortner (2) published the results of a critical study of the pulping of aspen wood with a large number of aqueous solutions of aliphatic monohydroxy and polyhydroxy alcohols and of glucose, mannitol, dioxane, and urea. The most promising results were obtained from the use of butanol-water solutions. Pulps analyzing as high as 85 per cent \( \alpha \)-cellulose were obtained; over 90 per cent of the lignin and pentosans were removed from the wood. A desirable feature of the butanol-water pulping is the fact that butanol-water mixtures are miscible in all proportions at the pulping temperatures, but are only slightly miscible at ordinary temperatures. When the cook liquors are drained from the pulp and cooled, they therefore separate into two layers, one of which is chiefly alcohol containing the bulk of the lignin, while the other layer is chiefly water and contains the bulk of the pentosans. The liquors are acidic and it is unnecessary to use additional acid as a catalyst.

Because of the above advantages, the butanol-water process seems the most attractive of the many proposed processes
from the standpoint of lignin recovery. It was therefore used in the present work in studying lignin production.
III. PRODUCTION OF LIGNIN - EXPERIMENTAL

A. Precipitation of Alkali Lignin with Strong Acids

In none of the previous studies on acid precipitation of lignin from alkaline liquors (Chap. II) was the effect of excess acid concentration on the yield and filtering properties of the lignin reported. In only one case was the concentration of excess acid stated; Beckmann and Liesche (5) stated that 2.0 - 2.5 per cent excess hydrochloric acid was used in their experiments. When this concentration was tried with alkaline cook liquor from cornstalks, the lignin and pentosans were precipitated in a fine state and could not be filtered through paper even after prolonged boiling. When a large excess of acid was used, a black, charred precipitate formed which could be filtered but which had apparently undergone some decomposition. In order to determine the optimum conditions of precipitation, a series of acid precipitations using sulfuric, hydrochloric, and nitric acids was made.

1. Preparation of soda liquors

Dried cornstalks (305 grams) were cooked with 20 times their weight of 4 per cent sodium hydroxide solution (as recommended by Mehta (72)) for two hours at atmospheric pressure.
The liquor was drained from the pulp, which was washed with water, the washings being combined with the first liquor. The combined liquor was evaporated to about 2.5 liters, when it had a specific gravity of 1.03 at 20°C. It was filtered through filter paper, using a Buehner funnel and suction. This liquor will be designated as liquor A.

Another liquor used for some of the experiments on the effect of boiling time was prepared by cooking 1 pound of cornstalks with 0.1 pounds of sodium hydroxide and 20 pounds of water for 3 hours in an open kettle. After filtering and washing the pulp, the combined liquor and washings were evaporated to a volume of about 1 gallon, its specific gravity then being 1.019 at 20°C. The amount of sulfuric acid necessary to neutralize the liquor was determined by boiling 100 ml. portions with varying amounts of standard acid for 15 minutes, filtering the precipitated lignin and titrating the filtrate with standard sodium hydroxide using phenolphthalein as an indicator. The results of several titrations gave 1.03 ml. of 50 per cent sulfuric acid (9.65 mols/liter) per 100 ml. as the amount necessary for neutralization. This liquor will be designated as liquor B.

2. **Effect of excess acid concentration**

Sulfuric acid was used first since it is the cheapest of all strong mineral acids. It was found in a few preliminary runs that adding the concentrated acid tended to produce a
charred precipitate, therefore it was diluted to 50 per cent by volume (9.41 mols/liter) before being added to the caustic liquor. A number of precipitations were made in the following way. One hundred ml. of liquor A was used in each case, the acid being added to the cold liquor. The mixture was then boiled for 15 minutes, cooled and filtered. It was soon found that neither Gooch nor alundum crucibles could be used, since they quickly became stopped up with the fine precipitate. The following procedure was finally adopted: The precipitated mixture was filtered into an ordinary funnel containing a filter paper which had been dried and weighed. The precipitate was washed well with water, dried at 120°C, and weighed with the paper. Although this method is not as precise as might be desired, it proved sufficiently accurate for the purpose. Blanks indicated that the loss in weight of the filter paper in the process was about 0.010 grams, which correction was applied to the yields obtained. In order to obtain directly the concentration of excess acid in the solution the filtrate was titrated with standard sodium hydroxide (4.00 mols/liter) using phenolphthalein as an indicator.

The same procedure was followed for the precipitations with hydrochloric acid and nitric acid except that the boiling of the acidified liquor was carried out under reflux. Concentrated hydrochloric acid (10.7 mols/liter) and 50 per cent by volume nitric acid (7.85 mols/liter) were used.

The results of the several experiments are shown in Table II. The weight of precipitates and the volume of sodium
<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Speed</th>
<th>Direction</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:00</td>
<td>0</td>
<td>North</td>
<td></td>
</tr>
<tr>
<td>10:30</td>
<td>2</td>
<td>East</td>
<td></td>
</tr>
<tr>
<td>10:45</td>
<td>3</td>
<td>South</td>
<td></td>
</tr>
<tr>
<td>11:00</td>
<td>4</td>
<td>West</td>
<td></td>
</tr>
<tr>
<td>11:20</td>
<td>5</td>
<td>North</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- Speed is measured in miles per hour (mph).
- Direction is indicated relative to cardinal points.
- Notes are for additional information specific to each point of travel.
hydroxide (4.00 mols/liter) required for neutralization of the excess acid are plotted against the total volume of acid added in Figure 1. The intercepts of the sodium hydroxide titration curves on the x-axis represent the amount of acid necessary for neutralization of the liquor. This amount is 0.0716 gram-equivalents for the sulfuric and hydrochloric acid precipitations, and 0.0738 gram-equivalents for the nitric acid precipitations. It is evident that more than half the total acid added in the good filtration range was in excess of the neutralization equivalent. It is also seen that for each acid there is a critical concentration below which the precipitate is difficult to filter and above which it is well flocculated and easy to filter. This concentration is about 7 per cent by weight for sulfuric acid, 1.8 per cent for hydrochloric acid, and 4.5 per cent for nitric acid. For sulfuric and hydrochloric acids the yield of precipitate is the same above the critical concentration; for nitric acid however it is lower for all concentrations. The product obtained in the lower concentrations for these two acids was in every case charred when it was dried; this is probably due to the presence of unhydrolyzed pentosans. The material resulting from the higher concentrations was a brown powder which did not char or melt on drying.

Nitric acid did not give as good results as either sulfuric or hydrochloric acids. The filtrations were not as satisfactory, the yield of lignin was lower and in the higher concentration range (>$5$ mols/liter) the greater part of the
lignin was consumed either by oxidation or nitration or both. Probably some nitration took place in all the runs, since the precipitates were more highly colored than usual. This is borne out further by the fact that in the sulfuric and hydrochloric acid precipitation, the amount of acid necessary for neutralization of the liquor was apparently greater for the nitric acid than for the other two acids. The additional nitric acid was probably that used in reacting with the lignin.

It can be concluded from these experiments that for good precipitation and easy filtration of lignin from alkaline solutions by strong acids a critical concentration of excess acid for each acid must be exceeded. Since the precipitates obtained in the lower range of concentration settle well, however, it would be possible to concentrate the lignin by a thickening process using much less acid and then complete the flocculation by treatment with stronger acid. Nitric acid is unsatisfactory for the precipitations because it attacks the lignin and decreases the yield. It is also more expensive than hydrochloric and sulfuric acids.

Hydrochloric acid seemed to give better results than sulfuric acid as regards uniformity of product and ease of filtration and it was consequently used in most of the work. It is, however, much more expensive than sulfuric acid. Using current market prices for 60°Be sulfuric acid ($13.00/ton) and 20°Be hydrochloric acid ($23.00/ton) the prices per pound-
equivalent for the two acids are:

Sulfuric acid: \( (98)(13.00)/(2000)/(0.777)(2) = $0.41 \)

Hydrochloric acid: \( (36.5)(23.00)/(2000)/(0.315) = $1.33 \)

It is seen that on a commercial scale, sulfuric acid would be much more economical, even though a larger excess is required (7 per cent for sulfuric as compared to 1.8 per cent for hydrochloric) since the same number of pound-equivalents are necessary for neutralization of the liquor.

3. Effect of time of heating

In all of the above experiments, the time of boiling the acidified liquors was 15 minutes. To determine the effect of longer times of heating, two precipitations of liquor A were made in the low excess acid concentration range using longer times of boiling. One run using an excess acid concentration of 4.9 per cent sulfuric acid required 1 hour boiling for complete flocculation and the other with 2.0 per cent sulfuric acid required 3 hours boiling. The yields of lignin were 0.511 grams and 0.501 grams, respectively.

In a study of the recovery of lignin from soda liquors, McCortney (70) concluded that by heating the acidified liquor which has an excess hydrochloric acid concentration of 0.026 per cent at 90-95°C for 3 hours, the lignin settled well and was easily filtered. Such a procedure would be in general agreement with the above results since it was found that by
increasing the time of heating the amount of acid necessary could be materially reduced. Since there might be advantages in this method, it seemed desirable to test it and compare the results with those of the method already described.

Several precipitations were made by adding varying amounts of acid to 100 ml. portions of liquor B and heating them at 90-95°C. in a water bath for 3 hours. The results are given in Table III.

**TABLE III**

Precipitation of Alkali Lignin at Low Acid Concentrations

<table>
<thead>
<tr>
<th>Volume of liquor B (ml.)</th>
<th>Volume of H₂SO₄ (5.65 mols/1) (ml.)</th>
<th>Filtration</th>
<th>Concentration of excess acid (weight per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.00</td>
<td>Would not filter</td>
<td>----</td>
</tr>
<tr>
<td>100</td>
<td>2.00</td>
<td>&quot;</td>
<td>0.092</td>
</tr>
<tr>
<td>100</td>
<td>3.00</td>
<td>Fair-filtrate cloudy</td>
<td>0.187</td>
</tr>
<tr>
<td>100</td>
<td>4.00</td>
<td>Good-filtrate clear</td>
<td>0.275</td>
</tr>
<tr>
<td>100</td>
<td>5.00</td>
<td>&quot;</td>
<td>0.364</td>
</tr>
<tr>
<td>100</td>
<td>6.00</td>
<td>&quot;</td>
<td>0.452</td>
</tr>
</tbody>
</table>

The precipitates in the last four runs were light tan amorphous particles which dried to a light powder in air, but which charred to a hard black mass when dried in the oven at 105°C.
It is evident that although less acid was required to effect satisfactory precipitation than in the 15 minute runs, much more was needed than McCortney found to be sufficient. This can probably be attributed to the fact that McCortney used litmus paper to determine the neutral point of the liquor, a procedure which was found to be quite unreliable. Also he used hydrochloric acid which seems to be somewhat more effective than sulfuric acid for the precipitation, but not nearly enough to account for the difference between 1.8 per cent and 0.036 per cent.

A few precipitations were made using 4.00 and 5.00 ml. of 50 per cent sulfuric acid per 100 ml. of liquor B and heating them to boiling over a direct flame for 2-3 hours. The precipitates were just as easily filtered as in the 90-95°C runs.

4. Large scale preparations

A number of large scale preparations were made using both sulfuric and hydrochloric acids, and using various excess acid concentrations and various lengths of heating time. The results were consistent with the small scale experiments as regards yields and filtration. The procedure finally adopted for preparation of large batches of lignin follows:

Shredded cornstalks (50 pounds) were cooked with one-tenth their weight of sodium hydroxide and 8 to 10 times their weight of water for 2 hours at 90 pounds per square inch 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 at this point was 12 to 15 gallons. The liquor was then transferred to lead-lined or Duriron kettles heated by steam jackets and enough muriatic acid (25 per cent HCl) was added to bring the excess acid concentration to at least 3 per cent by weight, about 0.2 pounds of acid per pound of liquor being required. The acidified liquor was boiled gently for two hours, after which time the precipitated lignin was well coagulated and easily filtered. It was then washed free of acid with water and dried in the oven at 105°C. The yield of the oven-dried lignin was 4.5 to 5.0 pounds or 9 to 10 per cent of the oven-dried cornstalks.

5. Discussion

The acid precipitation process has certain characteristics which should be considered before applying it to a large scale plant. A flow sheet of such a plant using sulfuric acid as the precipitant is shown in Figure 2.

The essential steps are evaporation of the liquor, precipitation with acid, filtration of the lignin, and concen-
tration of the acid.

The chief advantages of the process are:

(1) A fairly good recovery of alkali lignin of good purity.

(2) Elimination of the necessity for waste liquor disposal.

The principal disadvantages of the process are:

(1) Large heat consumption; this would probably be the chief expense. Heat must be supplied both for the evaporation and for the acid concentration; it is not possible to burn any part of the organic matter in the liquor.

(3) The sodium hydroxide could not be recovered and re-used.

(3) The cost of the acid would be a large item since only that in excess of the neutralization equivalent can be recovered.

(4) Rather large quantities of sodium sulfate would be a by-product of the process. This might be marketed, but the income would not pay for the acid and alkali consumption.

(5) The form in which the hemicelluloses might be recovered is limited. Probably some furfural could be recovered, from the hydrolysis vapors. Most of the hemicelluloses are probably in the acid liquors as sugars and they would have to be recovered before the concentration of the acid, if at all.

The cost of producing lignin by this process is estimated in the following calculations. A basis of 1000 pounds of cornstalks will be used and the quantities of chemicals, etc.
as stated in the large-scale procedure will be used with the substitution of sulfuric acid for hydrochloric acid. No cost for the black liquor will be included except that of the caustic soda, which is not recovered. Current prices for the chemicals will be used.

Cost of chemicals needed:

100 pounds of caustic soda: (100)($0.023) = $2.30

100 pounds of sulfuric acid: (amount for neutralization) (100)($0.0065) = 0.65

Cost of evaporation (assume initial and final weights of liquor 15,000 and 2,500 pounds, respectively):

$0.22/(1000) = 2.75

Cost of filtration (assume maximum value given by Tyler for cost of filter press operation)*:

($4.00)(100)/(2000) = 0.20

Total cost per 100 pounds of lignin = $5.80

This cost does not include operating expenses and overhead for the equipment other than that used for evaporation and filtration. On the other hand, the sodium sulfate resulting as a by-product should have some value which would offset this expense. It should be pointed out that the amount of evaporation used in the above calculations is entirely arbitrary; a good product is obtainable over a wide range of concentration of the black liquor. An economical balance

between the amount of evaporation and the other variables should be struck. The cost of the lignin would thus probably be reduced quite materially.

It is evident that this method of recovery is rather expensive and that unless rather valuable products could be obtained from the lignin, the process would probably be uneconomical.

B. Precipitation of Alkali Lignin with Carbon Dioxide

It is seen in the Historical chapter (II) that there is considerable disagreement among the above investigators as to whether the carbon dioxide and mineral acid fractions are identical, whether the carbon dioxide fraction is a free phenol or a sodium salt, and whether all or only part of the lignin can be precipitated by carbon dioxide. Some of the above discrepancies can probably be explained by the fact that the lignins prepared were from varied sources; perhaps different raw materials contain lignin which is different in regard to its solubility in sodium bicarbonate and sodium carbonate solutions. The present experiments were performed to determine whether cornstalk lignin could be completely or partially precipitated with carbon dioxide.
1. Experiments with isolated alkali lignin

   a. Fractionation of cornstalk alkali lignin. Fifty grams of air-dried alkali lignin (45 grams oven-dried) prepared from cornstalk black liquor by precipitation with hydrochloric acid and removal of pentosans by hydrolysis were dissolved in a solution of 500 ml. of water and 25 grams of sodium hydroxide. One hundred ml. portions of this solution were precipitated by bubbling in carbon dioxide until the solution was acid to phenolphthalein (10-15 min.).

Precipitation No. 1: The precipitate was allowed to stand but very little settling occurred. Filtration was attempted by suction but the paper was soon stopped by the slimy mass. After standing 3 days, the mixture was heated whereupon the precipitate went back into solution. Carbon dioxide was again bubbled in, the mixture heated to coagulate it, and it was then cooled and filtered. The filtrate was treated with hydrochloric acid. The yields of the two oven-dried fractions were:

   \[
   \begin{align*}
   \text{CO}_2 \text{ precipitate: } & \quad 1.6 \text{ gms. or 1.6 per cent of orig. stalks.} \\
   \text{HCl} \quad & \quad 4.2 \text{ gms. or 4.2 per cent} \\
   \end{align*}
   \]

Precipitation No. 2: The precipitated mixture was boiled for 5 minutes and allowed to cool. The precipitate was now well coagulated in large lumps and easily filtered. The filtrate was acidified with hydrochloric acid and boiled for 5 minutes. The yields of the oven-dried fractions were:
CO_2 precipitate: 4.7 gms. or 4.7 per cent of orig. stalks
HCl " 2.1 gms. or 2.1 per cent " " "

Another precipitation was made in the same way except that the filtrate from the first carbon dioxide precipitation was re-saturated with carbon dioxide and boiled, but no further precipitate formed. The filtrate was then precipitated with hydrochloric acid as usual. The yields were:

CO_2 precipitate: 3.4 gms. or 3.4 per cent of orig. stalks
HCl " 3.4 gms. or 3.4 per cent " " "

Precipitation No. 3: This was carried out the same as No. 2 except that instead of boiling the carbon dioxide-saturated liquor it was heated for an hour in a boiling water bath. The coagulation was not so good and the filtration was somewhat more difficult.

CO_2 precipitate: 3.5 gms. or 3.5 per cent of orig. stalks
HCl " 3.0 gms. or 3.0 per cent of orig. stalks

Precipitation No. 4: This was carried out the same as No. 2 except that the solution was heated to boiling before the carbon dioxide was passed in.

CO_2 precipitate: 3.2 gms. or 3.2 per cent of orig. stalks
HCl " 3.7 gms. or 3.7 per cent of orig. stalks

b. Reprecipitation of the carbon dioxide fraction. Five gms. of the carbon dioxide fraction, 2.5 gms. of sodium hydroxide, and 50 ml. of water were mixed and carbon dioxide bubbled in. The mass became gelatinous and practically solid, so 50 ml. more of water were added and the solution was heated
to boiling for 5 minutes. The coagulation was not good, so 3.25 gms. of sodium carbonate were added to bring the salt concentration up to the value of the previous precipitations. More carbon dioxide was passed in and the solution heated again. The coagulation was now good and the cooled mixture was easily filtered. Upon re-saturating the filtrate with carbon dioxide and heating, no more precipitate was found. The filtrate was then acidified with hydrochloric acid and a small amount of precipitate recovered.

\[ \text{CO}_2 \text{ precipitate: 3.7 gms. or 74 per cent of orig. carbon dioxide lignin} \]

\[ \text{HCl precipitate: 0.7 gms. or 14 per cent of orig. carbon dioxide lignin} \]

Total recovery: 88 per cent of orig. carbon dioxide lignin

To see whether precipitation with hydrochloric acid changed the action of the carbon dioxide lignin toward carbon dioxide, 5.0 gms. of the carbon dioxide lignin were warmed with 50 ml. of water until solution took place. Three ml. of dilute hydrochloric acid (10%) were added and the mixture boiled for 5 minutes. After cooling, the precipitate was filtered, dried, and weighed. It amounted to 4.5 gms. or 90 per cent of the original carbon dioxide lignin. The precipitate was now reddish-brown in color as is the usual alkali lignin and was insoluble in water. It was redissolved in sodium hydroxide solution and precipitated as above. The results were:
CO₂ precipitate: 3.66 gms. or 73.2 per cent of orig.
carbon dioxide lignin

HCl precipitate: 0.56 gms. or 11.2 per cent of orig.
carbon dioxide lignin

Total recovery: 84.4 per cent of orig. carbon dioxide lignin

9. Reprecipitation of the hydrochloric acid fraction.
Five grams of the hydrochloric acid fraction were dissolved in 50 ml. of water and 2.5 gms. of sodium hydroxide. The solution was saturated with carbon dioxide, boiled, and filtered, but no precipitate was found. It was then precipitated with hydrochloric acid in the usual way and 4.5 gms. or 90 per cent of the original hydrochloric acid lignin were recovered.

d. Properties of the two fractions. The above experiments show that cornstalk alkali lignin as prepared by the mineral acid precipitation method can be separated into two fractions by precipitation with carbon dioxide. A typical fractionation may be represented as follows:

\[
\begin{align*}
\text{Cornstalks} & \rightarrow \text{Alkali Lignin (100%)} \\
& \rightarrow \text{NaOH \text{ soln. solution \ Alkaline CO₂ (9%)} \\
& \rightarrow \text{Filtrate HCl HCl Lignin (8.4%)}
\end{align*}
\]

That the carbon dioxide and hydrochloric acid fractions are not the same was shown by the reprecipitations of the two fractions. These may be represented by:
The two fractions are almost entirely represipitated by the carbon dioxide and hydrochloric acid, respectively. The difference in the two fractions may be accounted for by assuming that the carbon dioxide fraction contains phenolic hydroxyl groups but no carboxyl groups and that the hydrochloric acid fraction contains carboxyl groups. The presence of carboxyl groups in alkali lignin has not been proven by previous lignin investigators, however.

The carbon dioxide fraction was lustrous black in appearance and could be easily ground to a black powder. It was soluble in hot and cold water; it was only slightly soluble in hot alcohol and insoluble in cold. It was insoluble in both hot and cold ether and benzene. Its ash content was 7.6 per cent, this ash being greenish-brown in color.

The hydrochloric acid fraction had the usual reddish-brown granular appearance of the ordinary alkali lignin. It was insoluble in cold alcohol but partially soluble in hot alcohol. It was insoluble in hot and cold water, cold ether and cold benzene, and very slightly soluble in hot ether and
hot benzene. It contained 0.5 per cent of a white ash.

e. Effect of pentosans on carbon dioxide precipitation.
The main difference between the alkaline lignin solutions studied in the preceding paragraphs and the black soda liquors from cornstalks is that the latter contain large amounts of pentosans in a colloidal condition. A few preliminary experiments had shown that lignin was not easily precipitated from soda liquors by carbon dioxide by the procedure of the preceding experiments, so a number of experiments were performed on synthetic mixtures of lignin and pentosans. The pentosans used were prepared from black soda liquor by precipitation with alcohol (106).

The procedure used was the same as in the previous precipitations. Various proportions of lignin and pentosans were tried and the filtering properties of the carbonated solutions noted. Most of the carbonated solutions were heated to boiling before filtering but a few were not.

The results of the experiments are given in Table IV. The presence of pentosans is seen to prevent the coagulation of the lignin by carbon dioxide, probably because it acts as a protective colloid. The lignin was undoubtedly precipitated from solution as evidenced by the thickening of the solution, but it would not settle or filter.
TABLE IV  
Precipitation of Synthetic Lignin-Pentosan Alkaline Solutions with Carbon Dioxide

<table>
<thead>
<tr>
<th>Weight of lignin/pentosans (gms.)</th>
<th>Weight of NaOH (gms.)</th>
<th>Weight of H₂O (gms.)</th>
<th>Heating</th>
<th>Remarks</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>15</td>
<td>100</td>
<td>None</td>
<td>Filtered.</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>15</td>
<td>100</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Boiled

<table>
<thead>
<tr>
<th>Weight of lignin/pentosans (gms.)</th>
<th>Weight of NaOH (gms.)</th>
<th>Weight of H₂O (gms.)</th>
<th>Heating</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>15</td>
<td>100</td>
<td>5 min.</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>15</td>
<td>100</td>
<td>5 min.</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>&quot;</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>15</td>
<td>100</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

2. Experiments with soda liquor

a. Treatment of soda liquor with carbon dioxide. Black liquor from a soda cook of cornstalks (ratio of cornstalks to sodium hydroxide = 1011) was subjected to precipitation by the
methods outlined above. This liquor had a specific gravity of 1.01 at 20°C, contained 5.02 per cent total solids (determined by drying at 105°C), and contained 1.55 per cent ash. By titration of the filtrate from a hydrochloric acid precipitation it was found that the liquor contained 0.251 equivalents of alkalinity as sodium hydroxide, sodium carbonate, and sodium lignate.

One hundred ml. portions of this liquor were saturated with carbon dioxide whereupon they became murky in appearance. On heating no coagulation occurred and the entire solution passed through a filter paper without separation of a precipitate. Ten gms. of sodium chloride were added and the solutions heated again, but the results were no better.

Two liters of the liquor were saturated with carbon dioxide until the liquor was colorless to phenolphthalein and it was heated for an hour in an autoclave at a pressure of 150 lbs./in² (172°C). On removal the liquor was again basic to phenolphthalein, so it was re-saturated with carbon dioxide and allowed to stand for several days. Perceptible settling occurred but the precipitate was difficult to filter; it very quickly made the paper impermeable.

A portion of the black liquor was concentrated to one-fourth of its original volume; it now contained 1.00 equivalents per liter of alkalinity and 6.45 per cent alkali lignin. Two 100 ml. portions were saturated with carbon dioxide, boiled for 5 minutes, and allowed to cool. A heavy viscous precipitate
settled. One of the samples could not be filtered cold, so it was again heated to boiling and filtered hot with much difficulty. There were recovered 3.30 gms. of precipitate or 51 per cent of the total alkali lignin. The other sample was heated again with 5 gms. of sodium bicarbonate and cooled. It could now be filtered with difficulty and there were recovered 5.7 gms. or 88 per cent of the total alkali lignin.

b. Removal of Pentosans with alcohol. While it was found possible, under certain conditions, to filter the lignin precipitated from the black liquor with carbon dioxide, the filtration was not as satisfactory as could be desired. Since it was shown that the pentosans prevented good coagulation and filtration, it would be advantageous to remove them from the liquor prior to the carbon dioxide treatment. This can be done by adding alcohol to the liquor whereupon the pentosans are precipitated. This dehydrates the pentosans, which are hydrophilic colloids, thus flocculating them. This is one of the best ways of separating pentosans or hemicelluloses from wood. It was first used by Thomsen (106) in 1879.

A number of experiments were performed on soda liquor which had been evaporated to a specific gravity of 1.14 (20°C). Various amounts of industrial denatured alcohol ("Ponsolve") were added to 100 ml. portions of the liquor. It
was agitated, filtered using suction, and the precipitate dried to constant weight at 70°C. The results are shown in Table V. Good filtration was observed in all cases; at least 1.23 volumes of alcohol were necessary to coagulate all the pentosans, however. The pentosans as recovered in this way were black, granular, solids; upon washing with alcohol, they became light brown or yellow in color. They have a high ash content, probably because the solubility of the inorganic compounds is decreased when the alcohol is added.

**TABLE V**

**Removal of Pentosans from Soda Liquor with Alcohol**

<table>
<thead>
<tr>
<th>Volume of soda liquor (ml.)</th>
<th>Volume of alcohol (ml.)</th>
<th>Weight of precipitate (gms.)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>67</td>
<td>10.8</td>
<td>Good filtration</td>
</tr>
<tr>
<td>100</td>
<td>83</td>
<td>12.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>15.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>100</td>
<td>133</td>
<td>17.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>100</td>
<td>167</td>
<td>17.0</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Several precipitations were then made with carbon dioxide, after preliminary removal of the pentosans. The soda liquor used had a specific gravity of 1.133 at 20°C, contained 59.3 per cent solids (by drying to constant weight at 105°C) and contained 8.77 per cent ash (both percentages on the basis of the soda liquor). One hundred ml. of the liquor were
treated with 150 ml. of alcohol and the pentosan precipitate filtered off. The alcohol was removed from the filtrate by distilling without a fractionating column until excessive foaming prevented further distillation. The residue was then cooled and treated with carbon dioxide until it was colorless to phenolphthalein. The precipitate was coagulated by boiling for 5 minutes and it was then filtered, dried, and weighed. The filtrate was acidified with hydrochloric acid and the resulting precipitate was filtered, dried, and weighed. In order to determine the total amount of recoverable alkali lignin present, samples of the liquor were also precipitated with hydrochloric acid, omitting the other steps.

The results are shown in Table VI.

**TABLE VI**

<table>
<thead>
<tr>
<th>Precipitation of Lignin from Pentosan-Free Soda Liquor</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total HCl: CO₂ : lignin from: Pentosans: alcohol : Remarks</td>
<td>Volume of:</td>
</tr>
<tr>
<td>lignin : lignin: filtrate : (%) : distillate:</td>
<td>(%) : (%) : (%) : (ml.)</td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
<td>--</td>
</tr>
<tr>
<td>8.28 5.20 2.36 14.61 113</td>
<td>Pentosans not washed.</td>
</tr>
<tr>
<td>8.28 5.30 3.09 11.35 105</td>
<td>Pentosans washed with alcohol.</td>
</tr>
</tbody>
</table>

All percentages are on the basis of the soda liquor. A total of 25.13 per cent of the total solids was removed from the liquor in the first case and 19.74 per cent was removed in
the second case. The total of the carbon dioxide and hydrochloric acid fractions is slightly less than the total hydrochloric acid fractions in the first case, but slightly more in the second. This apparent discrepancy is probably caused by the presence of much ash in the carbon dioxide fraction or possibly by incomplete drying. It was possible to recover only about two-thirds of the alcohol by distillation. Filtration was easy and rapid in all cases.

c. Large scale precipitation. In order to test the above process using large scale laboratory equipment, a large batch of soda liquor (35.5 pounds) was prepared. It had a specific gravity of 1.175 at 20°C, contained 31.5 per cent total solids and contained 12.1 per cent ash. The alcohol precipitation was carried out by pouring the alcohol (Ponsolve) into the agitated liquor. The precipitated pentosans were filtered in a 6 inch filter press using 50 lb./in² pressure. Filtration was accomplished quite rapidly; an attempt to wash the cake with alcohol failed, however. The alcohol was distilled from the filtrate in a large batch steam heated still. The residue was carbonated by bubbling in carbon dioxide. Coagulation of the lignin was brought about by boiling the mixture in a large copper kettle. The sludge was filtered in the 6 inch filter press, washed with cold water, and dried at 105°C.

A quantitative flowsheet of the recovery is shown in Figure 3. The quantities of the various materials are given both in pounds and in weight percentage of the soda liquor.
All weights of solids are on a bone-dry basis and percentages of ash are on the basis of the bone dry solids. The recovery of pentosans and alcohol checks the small scale runs well, but the lignin recovery is much lower. This low lignin yield was probably due to incomplete coagulation in the heating process; it was difficult to maintain the carbonated liquor at a boil without much foaming.

3. Discussion

In most of the previously proposed carbon dioxide precipitation processes (see Chap. II) only a fraction of the organic matter is removed from the soda liquor. For example, the Mead process (71) removes 20 per cent of the organic matter from the liquor while the remaining 80 per cent is used as fuel in the furnaces. Such a process represents a compromise between complete recovery of the organic matter and no recovery whatever.

In the process proposed in the present study more than half the organic matter is recovered. A flowsheet of this process is shown in Figure 4. Most of the pentosans and part of the lignin is recovered. Some of the organic matter remaining in the liquor is precipitated out when lime is added for the causticization and the remainder is recirculated back, with the caustic. The alcohol recovery is shown as only one step; if excessive foaming were encountered, however, it might
be necessary to distill off part of the alcohol after the carbonation. No evaporation of the liquor is shown in the flow sheet but it might be economically advantageous to evaporate before the alcohol precipitation step since less alcohol would then be required. The carbon dioxide from the lime burning could be used for the carbonation or, if desirable, flue gas containing carbon dioxide could be used.

The chief advantages of this process are:

1. No chemical consumption except that due to mechanical losses.
2. Good recovery of both lignin and pentosans.
3. Recovery of the soda; probably as much soda could be recovered as NaOH as is recovered by the current practice of causticizing the burned liquor leachings.
4. Elimination of the waste liquor disposal problem.

Some disadvantages are:

1. A large quantity of alcohol would have to be kept on hand necessitating a large investment and a fire hazard.
2. Fuel would be necessary to burn to calcium carbonate to lime. If flue gases were used for the carbonation, however, it might be more economical to dispense with the burning and buy new lime for the causticization.
3. All the lignin cannot be recovered by this process; the yield is only about one-half of that in the mineral acid precipitation.

Since the chemical costs in this process are small in
comparison with the mechanical costs, it is impossible to make an accurate estimate of the total cost of recovering the lignin and pentosans without actually designing a plant. This cost would unquestionably be much lower than that of the mineral acid precipitation process. A preliminary cost estimate by the Mead Corporation (71) on their process gave a probable price of $0.06 per pound for their lignin. This includes profit and is undoubtedly a very conservative estimate. It can be safely stated that the process proposed in this thesis could produce lignin at the same price and probably at a much lower one.

C. Preparation of Lignin by Butanol-
Water Extraction

In a study of this kind there are a large number of variables to be considered, the more important of which are time of cooking, pressure (or temperature) of cooking and ratio of butanol to water. Aronovsk y and Gortner (2) made all their cooks at a pressure of 150 lbs./in\(^2\) (188\(^\circ\)C). Most of their cooks were for a period of from 2 to 4 hours; they did not make a systematic study of the effect of time, however. They made a number of cooks with different ratios of butanol to water, and found that equal volumes of the two materials gave the best results.
The present study consists of an investigation of the effect of time and pressure on lignin removal from cornstalks. Since the chief object in studying this process was to prepare lignin, the only analyses made on the pulps were for lignin.

Some of the data given in this section are taken from the thesis of Welker (111).

1. Method of cooking cornstalks

Two hundred grams of air dried shredded cornstalks (of known moisture content) were cooked with 1500 ml. of butanol (technical grade) and 1500 ml. of water for 2 hours at the specified pressure in a small steel autoclave. When the cook was completed the liquor was drained out while still hot and cooled in a condenser. The hot pulp was removed from the vessel and pressed in the screw press, the liquor thus obtained being added to the main portion. The pulp was then washed with at least 3 portions of water, dried at 105°C, and weighed.

The liquors on cooling separated into two layers. The alcoholic layer on top contained the lignin and other alcohol-soluble materials; the aqueous layer on the bottom contained the sugars, starches, acids, etc. Both layers were dark brown in color. At the interface in the alcoholic liquor there was always an insoluble substance which gave the appearance of an
emulsion. This was filtered off by suction; if the emulsion still persisted it was easily separated by heating and cooling again. When complete separation had taken place the two layers were filtered and their volumes noted.

2. Recovery of lignin and alcohol from alcoholic liquor

The two layers from the cock liquors were separated as previously described and filtered with the use of suction. Filtration was accomplished very easily with the alcoholic layers; the aqueous layers were filtered with difficulty in some cases, however.

The alcoholic liquors were concentrated by distillation in a large flask. The distillate was clear and in the first part of the distillation a considerable amount of water separated out, which was acidic to litmus. It was possible to concentrate the liquor to about 1/10 of its original volume, remove the concentrate while hot, and allow the lignin to precipitate out on cooling, it being then easily filtered from the mother liquor. If the evaporation was carried too far, however, the precipitated lignin could not be easily filtered from the very viscous mother liquor. The lignin thus separated became soft and plastic when heated in the drying oven at 105°C; if the adhering mother liquor was removed by washing with ether, however, it remained solid. In most cases the product was a hard, dark brown solid.

The lignin and other extractives in the mother liquor were
recovered either by evaporating the liquor to dryness or by diluting it in a large volume of water, whereupon the lignin, etc., was precipitated. The product from evaporation was usually a viscous liquid when hot which set to a plastic or solid mass upon cooling. In the dilution method the product was usually a heavy black liquid, heavier than the water from which it was precipitated. On standing several days it gradually became solid. It is probable that this material in the mother liquor contained other extractives than the lignin which tended to prevent its hardening.

The aqueous layer contained hydrolysis products, acids, and other water-soluble extractives, together with some dissolved butanol. No attempt was made to examine or recover these. The residue from the evaporation at 105°C of the aqueous layer was a black, charred, material which smelled of burnt sugar.

3. Method of determination of lignin in pulps

The pulps from all the runs except the first two (which were lost) were analyzed for lignin to determine the extent of lignin removal. The modified 72 per cent H₂SO₄ method (100) was used. The benzene-alcohol extraction was omitted in all the analyses except those of the original cornstalks since Aronovsky and Gortner (2) showed that pulps prepared by the butanol-water method contain little or no benzene-alcohol extractives. In preparation for the analyses, the pulps were ground in a Wiley mill and the 60-100 mesh screenings were used.
They were dried at 105°C.

4. Effect of time of cook on lignin removal

A number of cooks were made for different lengths of time while the pressure was held constant at 100 lbs./in² (156°C). The time of cool recorded was the interval between the attainment of the stated pressure and the shutting off of the burner. Usually about one-half hour was required for heating the charge up to the required temperature and a somewhat longer time was required for cooling to about 100°C.

The results of these cooks is shown in Table VII. The per cent loss in weight was calculated by dividing the loss in weight of the stalks by their initial dry weight. The per cent solids in the alcohol layer was determined by drying an aliquot portion of this layer to constant weight at 105°C. The per cent lignin remaining in the pulp is shown calculated on the basis of the dry pulp, the dry stalks, and the original lignin. In order to compare the loss in weight due to lignin removal to total loss in weight, the per cent removal of lignin has been calculated on the basis of the dry stalks. This was found by subtracting the per cent lignin in the pulp from the per cent lignin in the original stalks (both on the basis of the original stalks).

The results are shown graphically in Figure 5. It is seen that under the conditions of the experiments, most of the loss in weight occurs in the first four hours, the curve for the total loss in weight flattening off after this time.
### TABLE VII

**Effect of Time of Butanol-Water Cook on Lignin Removal**

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (hrs.)</th>
<th>Weight of dry stalks (gms.)</th>
<th>Weight of dry pulp (gms.)</th>
<th>% Loss in (% solids in basis dry stalks)</th>
<th>% Solids in alcohol layer (Basis dry stalks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>orig. stalks</td>
<td>1.0</td>
<td>192</td>
<td>154</td>
<td>14.7</td>
<td>5.61</td>
</tr>
<tr>
<td>1</td>
<td>2.0</td>
<td>192</td>
<td>137</td>
<td>28.8</td>
<td>7.14</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>192</td>
<td>139</td>
<td>27.7</td>
<td>11.2</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>192</td>
<td>115</td>
<td>40.2</td>
<td>6.94</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>192</td>
<td>112</td>
<td>41.8</td>
<td>14.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% Lignin in pulp</th>
<th>% Removal of basis dry pulp</th>
<th>% Removal of basis dry stalks</th>
<th>% Removal of basis original</th>
<th>% Removal of lignin (Basis dry stalks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.4</td>
<td>24.4</td>
<td>100.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>19.20</td>
<td>13.88</td>
<td>56.9</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>17.66</td>
<td>10.55</td>
<td>43.2</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>15.51</td>
<td>9.04</td>
<td>37.0</td>
<td>15.4</td>
<td></td>
</tr>
</tbody>
</table>
TABLE VIII

Effect of Pressure of Butanol-Water Cook on Lignin Removal

<table>
<thead>
<tr>
<th>Cook No.</th>
<th>Pressure (lb/in²)</th>
<th>Temp. (°C)</th>
<th>Weight of dry stalks</th>
<th>Weight of dry pulp</th>
<th>% Loss in weight</th>
<th>% Solids in alcohol</th>
<th>% Lignin in pulp Basis dry pulp</th>
<th>% Removal of lignin (Basis dry stalks) Basis original stalks: dry stalks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orig. stalks</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>119</td>
<td>192</td>
<td>171.5</td>
<td>11.2</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>128</td>
<td>190</td>
<td>159</td>
<td>16.4</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>75</td>
<td>149</td>
<td>196</td>
<td>155</td>
<td>21.0</td>
<td>5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>158</td>
<td>192</td>
<td>139</td>
<td>27.7</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>165</td>
<td>177</td>
<td>182</td>
<td>104.0</td>
<td>43.0</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>186</td>
<td>184</td>
<td>97.7</td>
<td>46.9</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>240</td>
<td>194</td>
<td>182</td>
<td>87.2</td>
<td>52.1</td>
<td>26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% Lignin in pulp Basis dry pulp: % Removal of lignin (Basis dry stalks: Basis original stalks: dry stalks)

<p>| 24.4 | 24.4 | 100.0 | 0.0 |
| 20.3 | 18.0 | 73.8 | 6.4 |</p>
<table>
<thead>
<tr>
<th>21.0</th>
<th>17.6</th>
<th>72.1</th>
<th>6.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.2</td>
<td>13.9</td>
<td>57.0</td>
<td>10.5</td>
</tr>
<tr>
<td>18.2</td>
<td>10.4</td>
<td>42.6</td>
<td>14.0</td>
</tr>
<tr>
<td>18.0</td>
<td>9.6</td>
<td>39.2</td>
<td>14.8</td>
</tr>
<tr>
<td>16.3</td>
<td>7.8</td>
<td>32.0</td>
<td>16.6</td>
</tr>
</tbody>
</table>
The curves for per cent lignin removal and per cent solids in the alcohol layer coincide fairly closely. This indicates that the solids in the alcohol layers were principally lignin at the particular pressure used. These curves show quite clearly that almost two-thirds of the loss in weight is not due to lignin removal but to removal of water-soluble materials from the stalks. This means that the hemicelluloses are more easily removed by the butanol-water cooks than the lignin, since the former are the chief constituents of the water-soluble materials.

5. Effect of pressure of cook on lignin removal

The second series of cooks were made at a constant cooking time (2 hours) and at varying pressures. While the temperature is probably a more important factor than the pressure of the cook, they are interdependent quantities; the pressure measurements seemed more reliable than the temperature measurements, therefore they were used in interpreting the results.

Similar data were observed for these cooks as for the first series and the results are given in Table VIII and shown graphically in Figure 6. The curve for per cent total loss in weight begins to flatten at the highest pressures, indicating that further increase in pressure would probably cause little additional loss in weight. The curve for per cent lignin removal also is beginning to flatten in this
high pressure region, even though less than 70 per cent of
the lignin has been removed. The per cent lignin removal
and per cent solids in the alcohol layer curves do not
coincide as in the first series of cooks. The fact that the
per cent solids in the alcohol layer is so much higher at
higher pressures indicates that considerable non-ligneous
material was soluble in the alcohol in this pressure range.

In cooks 10 and 11 the lignin was recovered as
quantitatively as possible as a check on the results obtained
above. In cook 10 the alcoholic layer was concentrated to
1/8 of its original volume, cooled, and the precipitated
lignin filtered off. On drying it weighed 13.1 gms. The
mother liquor was evaporated to dryness at 105°C and a residue
of 25.9 gms. was obtained. Adding 1.5 gms. for the amount
previously removed for the solids determination, the total
recovery, 40.5 gms., checks fairly well with that calculated
from the liquor analysis, 41 gms. In cook 11 the liquor was
all evaporated to dryness, 49.7 gms. being obtained, as
compared with 47 gms. calculated from the analysis.

It thus is possible in the butanol process to recover
all the lignin removed in the pulping. This is not possible
with any of the pulping processes being used commercially at
present; usually about one-half of the lignin is destroyed.
Whether it would be preferable to recover the lignin by
crystallization from the concentrated solution or by evapora-
tion to dryness would depend somewhat on the use to which the
lignin would be put; the crystallization method probably yields the purer lignin, however.

6. Discussion

The butanol process for preparing lignin has certain advantages and disadvantages which may be listed here. A flowsheet of the process as proposed by Aronovsky and Gortner (2) is shown in Figure 7.

Chief among its advantages are:

1. Complete recovery of a very pure lignin, along with separation and recovery of the cellulose and the hemicellulose portions of the raw material.

2. No chemical consumption except that due to mechanical losses which could probably be reduced to a very low figure.

3. Comparative ease of recovery of the lignin from the cook liquors.

Some disadvantages are:

1. Necessity for maintaining high pressure plant to withstand the rather corrosive acidic liquors. It should be mentioned that the corrosion problem here would probably not be as great as in a sulfite pulping plant, however, which also operates at high pressures.

2. A large quantity of rather expensive pulping liquor would have to be kept on hand, thus requiring a large investment, even though the actual consumption would be low.
of steam is much lower than that of water.

Since no evaporation occurs, the latent heat of evaporation in the external process and that of the water of condensation would be smaller than that of the water.

At any rate then, for the other process, because the quantity of coal used in the internal recovery and the evaporation costs should be the same, more coal and probably a higher cost of production than before. The cost of production is higher than before. It is therefore the

although it is impossible to make an estimate of the
IV. UTILIZATION OF LIGNIN - HISTORICAL

A. Destructive Distillation

1. Yields of products obtained by previous investigators

The destructive distillation of wood has been an important industry in the past; recently it has met with competition because of the development of synthetic methanol, acetone, and acetic acid. While destructive distillation of wood and agricultural by-products might be considered a utilization of lignin in the raw state, cellulose and other constituents are simultaneously distilled and the products mixed. Considerable experimental work has been done on the destructive distillation of the agricultural by-product materials and it is possible that this will become an important industry.

When lignin is isolated and then destructively distilled, some of the products are the same as those from the distillation of the raw material, but others are quite different. Methanol, acetone, and acetic acid are obtained from both materials; a carbonized residue is obtained from the lignin which is somewhat different in physical properties from charcoal; the gas is similar in both cases; the greatest difference in any of the products is in the tar. Tar from wood contains a relatively small amount of phenols; tar from lignin is in some cases practically entirely phenolic.
The yields of the products of lignin distillation depend greatly on the method of separation of the lignin. Phillips (87) distilled lignin prepared from corncobs by three different methods. Table IX shows his results together with similar data for cellulose, pentosans, corncobs, birch wood, and pine wood (37).

**TABLE IX**

**Destructive Distillation Products from Several Materials**

<table>
<thead>
<tr>
<th></th>
<th>Lignin</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fuming: 72% :Alkali (Atmos.:Alkali 25 mm.:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCl :H₂SO₄: Pressure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>58.5% 65.0% 52.2% 50.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillate</td>
<td>15.0 15.0 15.5 11.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tar</td>
<td>7.5 8.0 17.7 28.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas and Loss</td>
<td>19.0 12.0 13.5 9.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.7 1.08 1.90 0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.1 0.91 0.08 0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>0.56 1.03 0.12 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|          | Cellulose:sans :Corncobs:Beech Wood:Pine Wood |
|          | (xylen): |          |          |
| Carbon   | 38.8% 31.6% 41.4% 35.0% 37.8% |          |          |          |
| Aqueous  |                |          |          |          |
| Distillate | 41.1 43.7 35.4 34.9 30.1 |          |          |          |
| Tar      | 4.2 6.7 8.2 8.1 8.1 |          |          |          |
| Gas and Loss | 15.9 18.0 20.0 22.0 24.0 |          |          |          |
| Methanol | -- -- 0.7 2.07 0.96 |          |          |          |
| Acetic acid | 1.39 7.4* 2.6 5.04 3.19 |          |          |          |
| Acetone  | 0.07 -- 0.6 0.20 0.20 |          |          |          |

*(Total acids calculated as acetic; no acetic acid present, however.*)
Since the yield of lignin prepared by the alkali method is much smaller than that made by the other two methods, the yields of tar are about the same when based on the original cellulosic material. The yields are affected greatly by the pressure at which the distillations are carried out, as is shown in the fourth column. These data are those of Phillips and Goss (89) who distilled lignin at a pressure of 25 mm. in an atmosphere of carbon dioxide.

Of particular interest in the oil or tar obtained as one of the products from the destructive distillation of lignin. This tar amounts to 6 to 14 per cent (basis lignin) in the case of the fuming HCl and 72 per cent $\text{H}_2\text{SO}_4$ lignin, and 17 to 28 per cent in the case of the alkali lignin as Table X. Phillips obtained 7.5 per cent of tar (basis lignin) from the corn cob fuming HCl lignin, 7.8 per cent from the corn cob $72$ per cent $\text{H}_2\text{SO}_4$ lignin, and 17.7 per cent from the corn cob alkali lignin. Comparing these yields on the basis of the original corn cobs, the order is reversed, however: for the fuming HCl lignin the yield is now 1.9 per cent; for the 72 per cent $\text{H}_2\text{SO}_4$ lignin, 1.5 per cent; and for the alkali lignin, 0.88 per cent.

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 HCl and 72 per cent H$_2$SO$_4$ methods of isolation, and 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 (39), who used chemical methods to separate several phenols from the tar. They identified phenol, o-cresol, guaiacol, m-propyl 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.

Most previous work has been on lignin isolated from wood by either the fuming HCl (Willstatter) or 72 per cent H$_2$SO$_4$ (Klason) method. The most convenient way to survey this previous work is by a comparison of the yields of products of the various investigators. Such a comparison is shown in Table X. In general, lowering the pressure of the distillation increased the yield of tar. Alkali lignin gave higher yields of tar than did any other kind.

The yields of methanol, acetone, and acetic acid obtained by those investigators who determined them are given in Table XI. There is a rather wide variation in all three cases; this is probably caused by errors in the analytical methods.

The composition of the tar for those cases where it was determined is shown in Table XII. It is seen that the alkali
<table>
<thead>
<tr>
<th>Investigator</th>
<th>Method</th>
<th>Pressure</th>
<th>Yields (Basis lignin)</th>
<th>Source</th>
<th>Investigator</th>
<th>Method</th>
<th>Pressure</th>
<th>Yields (Basis lignin)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hagglund</td>
<td>Wood</td>
<td>Fuming</td>
<td>HCl Atmos.</td>
<td>--</td>
<td>Heuser</td>
<td>Wood</td>
<td>Fuming</td>
<td>HCl Atmos.</td>
<td>--</td>
</tr>
<tr>
<td>1918 (36)</td>
<td>(Pine)</td>
<td></td>
<td></td>
<td>9.6</td>
<td>1919 (45)</td>
<td>(Spruce)</td>
<td></td>
<td></td>
<td>13.0</td>
</tr>
<tr>
<td>Schildbrand</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
<td>Fischer</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1920 (27)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Schrader</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tropsch</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
<td>Gaulis</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1921 (107)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heuser</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tropsch</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
<td>Bratz</td>
<td>Aspen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1922 (108)</td>
<td>(Spruce)</td>
<td></td>
<td></td>
<td></td>
<td>Szelenio</td>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-2 mm</td>
<td>21.6 14.2 10.2 53.8</td>
<td></td>
<td>and Gomory</td>
<td>(Beach &amp;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1928 (105)</td>
<td>Oak</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1-12 mm</td>
<td>15 21 10 54</td>
<td></td>
<td>Phillips</td>
<td>Cobs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1929 (87)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>72%</td>
<td>19 15 7.5 58.5</td>
<td></td>
<td>Phillips</td>
<td>Alkali</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>12 15 8 65</td>
<td></td>
<td>Goss</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1932 (69)</td>
<td></td>
<td>25 mm</td>
<td>9.3 11.7 28.3 50.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nasakin, Gaag</td>
<td>Wood</td>
<td>Fuming</td>
<td>HCl Atmos.</td>
<td>23.0 13.5 6.5 57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&amp; Kaminiski</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investigator</td>
<td>Method of Isolation</td>
<td>Acetone %</td>
<td>Methanol %</td>
<td>Acetic acid %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>--------------</td>
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<td>--------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hagglund (36)</td>
<td>Fuming HCl</td>
<td>0.10</td>
<td>0.67</td>
<td>0.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heuser and Skjoldbrand (45)</td>
<td>&quot; &quot;</td>
<td>0.19</td>
<td>0.90</td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Heuser and Bratz (43)</td>
<td>&quot; &quot;</td>
<td>0.20</td>
<td>0.84</td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phillips (87)</td>
<td>Fuming HCl</td>
<td>0.6</td>
<td>0.7</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>72% H₂SO₄</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkali</td>
<td>0.13</td>
<td>1.9</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Alk. 25 mm</td>
<td>0.10</td>
<td>0.65</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nasakin, Gaag &amp; Kaminskii (78)</td>
<td>Fuming HCl</td>
<td>0.2</td>
<td>0.45</td>
<td>1.2</td>
<td></td>
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</table>
TABLE XII
Composition of Tar in Previous Investigations

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Isolation</th>
<th>Method of Neutral</th>
<th>Total Acidic</th>
<th>Acids (sol. in NaOH)</th>
<th>Phenols (sol. in HCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fischer and Schroder (27)</td>
<td>Fuming</td>
<td>HCl</td>
<td>66.1</td>
<td>33.9</td>
<td>16.4</td>
</tr>
<tr>
<td>Tropsch (106)</td>
<td>Fuming</td>
<td>HCl</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Pietet and Gaulis (93)</td>
<td>Fuming</td>
<td>HCl</td>
<td>11</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Phillips (87)</td>
<td>Alkali</td>
<td></td>
<td>7.2</td>
<td>92.6</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Lignin tar contains by far the highest percentage of phenols. For this reason it was chosen for investigation.

2. Activation of carbonized residue

In developing a destructive distillation process for lignin an outlet for all the products and by-products should be available. The carbonized residue is the largest single product of the distillation and a utilization or disposal of it would be essential. This carbon is light, porous, friable, of fairly good strength, and of low ash content.

One of the chief uses for carbons of this type is in making activated carbon. Most activated carbons are made by carbonizing vegetable materials, such as wood, waste paper...
mill liquors, and agricultural by-products. Any vegetable
material giving a char of sufficient mechanical strength may
be used in producing an activated carbon (69).

There are numerous references in the literature to pre-
paration of activated carbon by evaporation and carbonization
of soda liquors, but very few are preparations from lignin or
other organic matter separated from the liquors. The latter
method would have the advantage of yielding a purer, more
uniform, and more nearly ash-free carbon. A process such as
this was described by Naugle (80) in 1925. The lignin was
separated, mixed with sodium fluoride to volatilize silicon,
and carbonized. The residue was washed with hydrochloric
acid and dried. Darling (18) acidified soda liquor from corn-
stalks, spray-dried it, and then destructively distilled it
at 300°C. The residual carbon was activated. Another process
involved destructive distillation of alkali lignin and treatment
of the carbonized residue with soda ash and acids to reduce
its ash content (15).

B. Plastics from Lignin Tar and from Lignin

1. Phenolic tar resins and plastics

Since the major use for phenols today is in the preparation
of resins and plastics of the phenol-formaldehyde type, the
most obvious use for the phenolic tar from lignin is in pre-
paring these products. In commercial practice, the most widely
used phenolic compounds are phenol and the cresols, the latter usually being used in the form of a mixture of m- and p-cresols, termed "creosolic acid". These compounds are present in lignin tar and they can be separated from the tar and used in making resins and plastics by the same methods used in the case of coal tar. It would be much more desirable from the standpoint of economy and yield, however, if the resins and plastics could be made either directly from the crude tar or from the total crude phenols separated from the tar.

The use of phenol and some of its homologues in making resins and plastics has been known since Baekeland's classical work in 1909. It is not, however, general practice to prepare them directly from crude phenolic mixtures containing a large number of phenols or from coal tar which contains phenols. There has been very little research on this method of preparation and it will be reviewed as follows:

Glund and Breuer (32) in 1919 prepared resins from low temperature coal tar fractions by treating them with formaldehyde in the presence of ammonium chloride as a catalyst. The resins were soluble and fusible. Karpai (59) in 1925 converted the phenolic constituents of a coal tar into non-volatile condensation products by reacting them with formaldehyde. The unreacted portion of the tar was removed by steam distillation. Ehrmann (23) in 1929 prepared resins and lacquers by treating coal tar fractions with formaldehyde.
A rather thorough study of the preparation of resins and molding compounds from low temperature coal tar fractions, by treatment with paraformaldehyde in the presence of basic catalysts such as pyridine, was made by Morgan and Megson (76) in 1931. They used a "one-stage" process and removed the unreacted portion of the fractions by washing the product with warm benzene. The fractions they used contained about 50 per cent phenolic bodies. Resins of high dielectric resistance and molded objects of good strength were obtained.

No work on the preparation of resins or plastics from lignin tar has been reported in the literature. Since lignin tar is so much richer in phenols than is coal tar (60-90 per cent as compared to about 4 per cent), it seemed worth while to investigate its use in preparing plastics.

2. Lignin plastics

Studies on the preparation of resins and plastics from lignin have been few but promising products have been developed. Resins were produced by Phillips and Weihe (92) from corn-cob alkali lignin by condensing it with furfural and with various aromatic amines in the presence of alkaline or acidic catalysts. These resins were tested as stains, varnishes, and binders for compressed boards, and good results were obtained. Lignin isolated from wood by the acid hydrolysis method has been converted into molding materials by reacting it with phenols or amines. This type of plastic has been developed
by Fischer and Horn (29) in Germany and by Batesman and associates (3) of the Forest Products Laboratory in this country. The methods used by the latter workers were subjecting sawdust to (1) acid hydrolysis, (2) water hydrolysis in the presence of the reacting material, (3) chlorination, or (4) esterification. The materials produced by all these methods involve a reaction with the lignin, although it is not isolated in every case.

No report has been found in the literature of the preparation of molding materials from alkali lignin, with one possible exception. Bergstrom (9) described the preparation of resins from the "resinates" in soda liquors. The method of isolating these "resinates" was not described but it may be that they contained alkali lignin.
V. UTILIZATION OF LIGNIN - EXPERIMENTAL

A. Destructive Distillation

1. Small scale distillations

a. Apparatus and procedure. For the small-scale destructive distillations, a cast iron retort (A) of about 180 cubic inches capacity was used (See Figure 6). This 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 1/4 inch of the bottom of the retort. The temperature was determined using either a thermometer or an iron-constantan 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 retort, and the system was tightly closed. When the de-
sired 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.

B. 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 200 grams of oven-dried hydrochloric acid precipitated alkali lignin was used and the pressure was maintained at 5.5 inches of mercury absolute (23.5 inches vacuum). The retort was heated by baths of lubricating oil, sodium nitrate, molten lead, and by direct flame.

The results are shown in Table XIII. 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. Referring to the first three runs in the table (II, IV, and VII) in which direct flame
TABLE XIII
Effect of Temperature, Time, and Method of Heating on Yields

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Direct flame</td>
<td>300</td>
<td>----</td>
<td>2.0</td>
</tr>
<tr>
<td>IV</td>
<td>&quot;</td>
<td>395</td>
<td>----</td>
<td>3.2</td>
</tr>
<tr>
<td>VII</td>
<td>&quot;</td>
<td>500</td>
<td>----</td>
<td>2.75</td>
</tr>
<tr>
<td>III</td>
<td>Oil bath</td>
<td>235</td>
<td>290</td>
<td>4.3</td>
</tr>
<tr>
<td>VI</td>
<td>NaNO₃ bath</td>
<td>360</td>
<td>420</td>
<td>4.5</td>
</tr>
<tr>
<td>V</td>
<td>Lead bath</td>
<td>420</td>
<td>490</td>
<td>2.0</td>
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</tbody>
</table>

Percent Yield of Products

<table>
<thead>
<tr>
<th>Basis Oven-Dried Lignin</th>
<th>Basis Oven-Dried Stalks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Distillate</td>
<td>Carbon Tar</td>
</tr>
<tr>
<td>Aqueous Tar</td>
<td>Carbon Res.</td>
</tr>
<tr>
<td>7.0</td>
<td>14.2</td>
</tr>
<tr>
<td>11.1</td>
<td>17.7</td>
</tr>
<tr>
<td>14.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Slight</td>
<td>Slight</td>
</tr>
<tr>
<td>7.5</td>
<td>14.4</td>
</tr>
<tr>
<td>10.6</td>
<td>17.6</td>
</tr>
<tr>
<td>10.6</td>
<td>17.7</td>
</tr>
<tr>
<td>7.55</td>
<td>14.44</td>
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<tr>
<td>10.6</td>
<td>17.6</td>
</tr>
<tr>
<td>17.7</td>
<td>56.6</td>
</tr>
<tr>
<td>Slight</td>
<td>Slight</td>
</tr>
<tr>
<td>7.55</td>
<td>14.44</td>
</tr>
<tr>
<td>10.6</td>
<td>17.6</td>
</tr>
<tr>
<td>10.6</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Slight 17.6 51.2 20.6 1.06 1.76 5.12 2.06
| 10.6                    | 17.7                   | 56.6                    | 1.06 1.77 5.66 1.51 |
heating was used, it is seen that 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°C 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, after which time no more distillate was obtained. 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 at temperatures between 250°C and 400°C. Phillips (87) stated that a temperature of 400°C is the best 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 heating 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 of mercury absolute pressure are: (1) a final retort temperature of at least 400°C; (2) a time of heating sufficient to drive over all the distillate, the rate of heating not being very important; and (3) any convenient means of heating the retort, the method of heating being relatively unimportant, a direct flame giving as good results as a heating bath.

e. 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. Two hundred grams of oven-dried hydrochloric acid precipitated alkali lignin were used in each distillation. Direct flame heating was used, the maximum retort temperature being 400 to 500°C. The pressures were kept constant within 1/2 inch of mercury. The absolute pressures recorded are based on a 29.0 inch barometer reading. The time of heating was about 3 hours in all runs.

The results are given in Table XIV and are shown graphically in Figure 9. It is seen that at an absolute
TABLE XIV

Effect of Low Pressures on Yields

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>XIV</td>
<td>2.2</td>
<td>8.2</td>
<td>16.1 59.8 15.9 0.82 1.61</td>
</tr>
<tr>
<td>XV</td>
<td>2.2</td>
<td>11.0</td>
<td>15.7 57.0 16.3 1.10 1.57</td>
</tr>
<tr>
<td>XVI</td>
<td>2.2</td>
<td>14.7</td>
<td>15.5 56.0 13.6 1.47 1.55</td>
</tr>
<tr>
<td>XIII</td>
<td>4.0</td>
<td>13.8</td>
<td>17.1 53.7 15.4 1.28 1.71</td>
</tr>
<tr>
<td>XII</td>
<td>5.0</td>
<td>11.8</td>
<td>19.5 57.0 11.7 1.18 1.95</td>
</tr>
<tr>
<td>IV</td>
<td>5.5</td>
<td>11.1</td>
<td>17.7 57.5 13.7 1.11 1.77</td>
</tr>
<tr>
<td>VII</td>
<td>5.5</td>
<td>14.5</td>
<td>17.5 52.0 16.0 1.45 1.75</td>
</tr>
<tr>
<td>IX</td>
<td>17.0</td>
<td>14.4</td>
<td>14.6 54.5 16.5 1.44 1.46</td>
</tr>
<tr>
<td>XI</td>
<td>17.0</td>
<td>16.1</td>
<td>14.7 57.0 12.2 1.61 1.47</td>
</tr>
<tr>
<td>X</td>
<td>28.0</td>
<td>15.0</td>
<td>14.0 56.5 14.5 1.50 1.40</td>
</tr>
<tr>
<td>VIII (Atmos.)</td>
<td>15.0</td>
<td>11.6 59.2 14.2 1.50 1.16</td>
<td>5.92 1.42</td>
</tr>
</tbody>
</table>
pressure of about 5 inches 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 pressure
range, where it dropped. Another interesting feature of the
graph is the abrupt increase in tar yield and consequently in
total distillate yield when a very slight vacuum was maintain-
ed on the retort. This was subsequently checked in later
work (73). The carbonized residue curve is roughly the inverse
of the tar and total distillate curves.

Reducing the pressure in the retort might be expected to
produce two major effects: (1) an increased rate of removal from
the retort of the vaporized decomposition products and (2)
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 inter-
mediates 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 explain-
ed 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 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. It might be postulated that the removal of the initial products of the decomposition at very low pressures was accomplished so rapidly that complete decomposition to tar was not attained.

It is interesting to compare the yields of tar obtained in the present study with those of Phillips and Goss (89). The best yield of wet tar obtained in the present experiments was 17.7 per cent (basis oven-dried lignin) while Phillips and Goss obtained 28.3 per cent from corn cob alkali lignin at 25 mm. of mercury absolute pressure. However, the lignin used in the present experiments represented 10 per cent of the cornstalks, while that of Phillips represented only 5 per cent of the corn cobs, because of milder conditions of extraction. The yields of tar, based on the original raw material is thus 1.77 per cent (basis oven-dried cornstalks) in the present study and 1.41 per cent (basis corn cobs) 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 (86) in experiments on the fractional extraction of lignin from corncobs.

d. Composition of tar. The separation of the tar into its major classes of compounds has been accomplished by previous lignin investigators by successive extractions with sodium bicarbonate solution and sodium hydroxide solution 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 (87) for example found that 8 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 (75) 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 solution. He found that one of the best methods of separating these phenate-soluble compounds from the phenols 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
A good separation of the neutral tar and the phenate solution
for the benzene-saturated tar, the benzene was necessary for
adapted neutral tar, and the top layer consisted of a satu-
solution of the phenates, the middle layer consisted of pre-
te three layers; the lower layer contained the astringent
with the reagent and allowed to stand, the mixture separated
portions of the astringent-buffer reagent. After having been shaken
in an equal volume of benzene and extracted with two 25 ml.

The insoluble tar from the first step was dissolved
and the solution was recrystallized as acetate.

A quantity was extracted with 50 ml of 10 per cent sodium-
buffer. The tar from each can, about 50 to 25 grams in
is similar to that used by Moreau, was adopted:
which gives the total method of separation and estimation,
10 per cent sodium hydroxide solution. As a result of these
separate buffer solution was now also insoluble in the acety-
ate or 16 dissolved. The tar which was insoluble in the
the saturated with salt was need, however, only about 60 per
about 80 per cent of it dissolved. When 10 per cent sodium hydrox-
which had previously been extracted with sodium phenate
10 per cent KCl was used to extract some of the phenate
similarly to the coal tar studied by Moreau. When aqueous
from the first stage, and it was found that they behaved
This method of separation was tried on some of the tars
separately extracted.

separately extracted.

beginning with the neutral oil, and the phenols were thus

- 100 -
unless it was present a suspension formed which was very difficult to break up. The phenol solution was separated, acidified, and the resulting phenols separated and weighed.

(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 XIV. The per cent composition of the tar has been calculated both on the basis of the crude wet tar and on the basis of the original oven-dried lignin. The tar in each case contained some water, but this was not determined in the small scale runs. It is seen that the percentage of phenols increases with decreasing pressure, that the percentage of neutral tar first increases and then falls off with decreasing pressure, and that 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 9.

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
TABLE XV

Effect of Low Pressures on Tar Composition

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Pressure (inches Hg.)</th>
<th>Acid</th>
<th>Phenols</th>
<th>Total</th>
<th>Neutral</th>
<th>Acid</th>
<th>Phenols</th>
<th>Total</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIV</td>
<td>2.2</td>
<td>7.1</td>
<td>64.5</td>
<td>26.4</td>
<td>1.1</td>
<td>10.4</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XV</td>
<td>2.2</td>
<td>8.9</td>
<td>72.0</td>
<td>19.1</td>
<td>1.4</td>
<td>11.3</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVI</td>
<td>2.2</td>
<td>5.5</td>
<td>86.9</td>
<td>7.6</td>
<td>0.9</td>
<td>13.4</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIII</td>
<td>4.0</td>
<td>8.8</td>
<td>57.2</td>
<td>34.0</td>
<td>1.5</td>
<td>9.8</td>
<td>5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>17.0</td>
<td>10.0</td>
<td>49.0</td>
<td>41.0</td>
<td>1.4</td>
<td>7.1</td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XII</td>
<td>5.0</td>
<td>4.6</td>
<td>60.0</td>
<td>35.4</td>
<td>0.9</td>
<td>11.7</td>
<td>6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XI</td>
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<td>57.0</td>
<td>31.8</td>
<td>1.6</td>
<td>8.4</td>
<td>4.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>28.0</td>
<td>10.7</td>
<td>53.2</td>
<td>36.1</td>
<td>1.5</td>
<td>7.5</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>29.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Atmos.)</td>
<td>12.9</td>
<td>49.2</td>
<td>27.9</td>
<td>1.5</td>
<td>5.7</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
amounts found in the present study are large enough to make lignin an attractive potential source of phenols, however.

2. Distillation of butanol and carbon dioxide lignin

In order to compare the different kinds of lignin for destructive distillation purposes, experiments were made on samples of butanol and carbon dioxide lignin. There was not available enough of these lignins from cornstalks, so samples from wood were used. The butanol lignin was furnished through the courtesy of the Commercial Solvents Corporation of Terre Haute, Indiana, and the carbon dioxide lignin was furnished through the courtesy of the Mead Corporation of Chillicothe, Ohio. Although the lignins were prepared from wood, the results should be comparable to those obtained on the cornstalk lignin, because in most lignin reactions the method of isolation is a much more important characteristic than the source of the lignin.

Distillations were made on both kinds of lignin at atmospheric pressure and at 7 inches of mercury absolute pressure. The results are shown in Table XVI. The percentage yields are based on the oven-dried lignin. Data for the hydrochloric acid precipitated alkali lignin from cornstalks are also shown for comparison. The butanol lignin gave identical yields of tar with the cornstalk alkali lignin. The yields of phenols were greater in the case of the cornstalk alkali lignin. Lowering the pressure had no effect on the yield of tar in the case of the butanol lignin but it materially increased the yield of phenols.
TABLE XVI

Distillation of Several Kinds of Lignins

<table>
<thead>
<tr>
<th>Lignin Used</th>
<th>Pressure of Distn. (in. Hg.)</th>
<th>Aqueous Yield of Products (Basis lignin)</th>
<th>Carbon : Gas &amp;</th>
<th>Distillate: Tar: Res.: Loss: Phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanol</td>
<td>Atmos.</td>
<td>23.5</td>
<td>17.5</td>
<td>51.5: 7.5: 6.61</td>
</tr>
<tr>
<td>Butanol</td>
<td>7</td>
<td>11.3</td>
<td>17.4</td>
<td>44.4: 26.9: 8.95</td>
</tr>
<tr>
<td>CO₂</td>
<td>Atmos.</td>
<td>12.7</td>
<td>23.2</td>
<td>48.3: 15.8: 9.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>7</td>
<td>14.5</td>
<td>21.2</td>
<td>50.9: 13.4: 9.5</td>
</tr>
<tr>
<td>Cornstalk alkali</td>
<td>Atmos.</td>
<td>15.0</td>
<td>11.6</td>
<td>59.2: 14.2: 5.7</td>
</tr>
<tr>
<td>Cornstalk alkali</td>
<td>5.5</td>
<td>14.5</td>
<td>17.5</td>
<td>52.0: 16.0: 10.0</td>
</tr>
</tbody>
</table>

The CO₂ lignin gave the highest yield of tar of any of the lignins but the yield of phenols was still slightly lower than that from the cornstalk lignin. This was the only case observed in which lowering the pressure lowered the yield of tar.

If the yields of phenols from the different lignins are compared on the basis of the original raw material, however, the order is changed. While no exact data were available on the percentage of the original wood that the butanol and carbon dioxide lignin represented, an estimate may be made by assuming that the butanol lignin represents 90 per cent of the total lignin in the wood (aspen) which contained 25 per cent of the original wood. The best yields of phenols on the basis
In the larger report in which heat transfer was better than was to be expected, probably because it was carried out under conditions of the distillation of ethylene and smooth as in the small scale experiments. The yield of tar in the heat run was higher in the small scale distillations. No distillation was en-
TABLE XXII. The results compare quite favorably with those shown in the results of several of the experiments are shown in the over a pitch furnace and was heated by gas.

A diameter and 25 inches in length. The report was constructed of a 10 inch pipe 12 inches in diameter and 10 inches in length. The report was constructed of a 10 inch pipe 12 inches in diameter and 10 inches in length. The report was constructed of a 10 inch pipe 12 inches in diameter and 10 inches in length. The report was constructed of a 10 inch pipe 12 inches in diameter and 10 inches in length.

The difference in the apparatus was in the size of the report, the only and preparative large quantities of the tar. The only made for the purpose of obtaining the yields on a large scale:

hydrocarbonate and preheated. 0 per cent. carbon dioxide 100:

2. Large scale distillations

0.5 per cent.

Concentrate alkali 100 mgm. 1.0 per cent. carbon dioxide 100:

of raw materials are then burned. 1.0 per cent.

106 -
TABLE XVII
Large Scale Destructive Distillations

<table>
<thead>
<tr>
<th>Pressure of Distillation (inches Hg.)</th>
<th>Weight of Lignin used (lbs.)</th>
<th>Per cent yield of products (basis oven-dried lignin)</th>
<th>Distillate</th>
<th>Tar</th>
<th>Residue</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>3.68</td>
<td>12.5</td>
<td>12.4</td>
<td>56.7</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>3.66</td>
<td>10.9</td>
<td>12.3</td>
<td>57.7</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>3.02</td>
<td>11.9</td>
<td>12.9</td>
<td>59.7</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>Atmos.</td>
<td>10.89</td>
<td>15.8</td>
<td>13.0</td>
<td>52.8</td>
<td>18.4</td>
<td></td>
</tr>
</tbody>
</table>

4. Fractionation of Tar and identification of fractions

a. Apparatus and method. The fractionating column was constructed of 0.39 inch inside diameter Pyrex tubing. It was packed with 0.126 inch inside diameter single-turn glass helices (25), the packed section being 40 inches in height. Around the packed section was a 0.55 inch inside diameter Pyrex tube on which was wound 50 feet of Nichrome resistance wire to provide side heating, and this was in turn enclosed in a 1.26 inch 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 main-
tained 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.

b. Fractionation of tar. The tar from the large scale
destructive distillations carried out at 27 inches of mercury
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
percent 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: 203 grams of the crude wet tar
was 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. 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
The results of the experiments are shown in Figures 10 and 11. However, the results remained the same in color.

After dark in October, the reaction from the commoner occurred.

The reaction from the commoner occurred.

From the commoner occurred.

The reaction from the commoner occurred.

Identification of the mixture of water and steam from the commoner occurred.

Identification of the mixture of water and steam from the commoner occurred.

Identification of the mixture of water and steam from the commoner occurred.

Identification of the mixture of water and steam from the commoner occurred.
there was no evidence of light oils or other material of any kind. A summary of the recovery of material is shown in Table XVIII. The amounts of the dry crude tar, the dry charge to the fractionating column, the "phenolic distillate" (which is 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 15 per cent water there were small amounts of water in the materials throughout the operations, but these have been subtracted for purposes of comparison.

TABLE XVIII
Recovery from Fractionations

<table>
<thead>
<tr>
<th>Run</th>
<th>Crude Tar (dry)</th>
<th>Charge to Column (dry)</th>
<th>Phenolic</th>
<th>Distillate</th>
<th>Residue</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Gms.</td>
<td>%</td>
<td>Gms.</td>
<td>%</td>
<td>Gms.</td>
<td>%</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>---</td>
<td>------</td>
<td>---</td>
<td>------</td>
<td>---</td>
</tr>
<tr>
<td>A</td>
<td>256</td>
<td>100</td>
<td>256</td>
<td>100.0</td>
<td>119</td>
<td>50.5</td>
</tr>
<tr>
<td>B</td>
<td>125</td>
<td>100</td>
<td>104</td>
<td>83.2</td>
<td>69</td>
<td>55.2</td>
</tr>
<tr>
<td>C</td>
<td>178</td>
<td>100</td>
<td>188.5</td>
<td>49.6</td>
<td>58</td>
<td>32.6</td>
</tr>
<tr>
<td>D</td>
<td>199</td>
<td>100</td>
<td>199</td>
<td>100.0</td>
<td>171</td>
<td>85.9</td>
</tr>
</tbody>
</table>

(All percentages are on the basis of the dry crude tar.)

It is seen that the predistillation without fractionation (fractionation B) increased the yield of the phenolic distillate by almost 5 per cent (basis dry crude tar). Referring to Figure 10, it is seen 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 pre-
distilled tar (fractionation B). The crude tar began to de-
compose at a vapor temperature of 233° C and a kettle
temperature of 312° C, whereas the predistilled tar began to
decompose at a vapor temperature of 248° C 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 fraction-
ations A and 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 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. Referring to Figure 9, it is seen that
at a pressure of 27 inches of mercury absolute (the pressure
of the large scale runs) the tar contained 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 per cent 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 of the total phenols were recovered in fractionation B. The recovery of the crude predistilled phenols in fractionation C was 49.6 per cent of the dry crude tar which contained 61 per cent total phenols (dry basis), this recovery amounting 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 hold-up, 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.

b. Identification of phenols. The yields of the various fractions from the three runs are shown in Tables XIX, XX, and XXI. 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 midpoints of the transitions between the various fractions and recording the differences in abscissas between these lines. This method, of course, will
TABLE XIX

Fractionation of Crude Lignin Tar (Run A)

<table>
<thead>
<tr>
<th>Fraction: Refractive:</th>
<th>Basis:</th>
<th>Basis:</th>
<th>Basis:</th>
<th>Per cent Yield:</th>
</tr>
</thead>
<tbody>
<tr>
<td>boiling: Index:</td>
<td>tar:</td>
<td>lignin:</td>
<td>Stalks:</td>
<td>Constituent:</td>
</tr>
<tr>
<td>at (°C.):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>183</td>
<td>1.5405</td>
<td>14.9</td>
<td>1.82</td>
<td>0.182</td>
</tr>
<tr>
<td>191</td>
<td>1.5275</td>
<td>6.7</td>
<td>0.83</td>
<td>0.063</td>
</tr>
<tr>
<td>201</td>
<td>1.5195</td>
<td>6.4</td>
<td>0.78</td>
<td>0.078</td>
</tr>
<tr>
<td>207</td>
<td>1.5210</td>
<td>5.1</td>
<td>0.62</td>
<td>0.062</td>
</tr>
<tr>
<td>215</td>
<td>1.5230</td>
<td>5.5</td>
<td>0.67</td>
<td>0.067</td>
</tr>
<tr>
<td>222</td>
<td>1.5198</td>
<td>4.7</td>
<td>0.57</td>
<td>0.057</td>
</tr>
<tr>
<td>233</td>
<td>1.5175</td>
<td>7.2</td>
<td>0.88</td>
<td>0.088</td>
</tr>
<tr>
<td>Total Yield</td>
<td>50.5</td>
<td>6.17</td>
<td>0.617</td>
<td></td>
</tr>
</tbody>
</table>

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TABLE XX

Fractionation of Predistilled Lignin Tar (Run B)

<table>
<thead>
<tr>
<th>Fraction refractive index (nD)</th>
<th>Basis</th>
<th>Basis</th>
<th>Basis</th>
<th>Basis</th>
<th>Chief Constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>boiling point at (°C)</td>
<td>tar</td>
<td>lignin</td>
<td>stalks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>182</td>
<td>1.5422</td>
<td>9.6</td>
<td>1.18</td>
<td>0.118</td>
<td>Phenol</td>
</tr>
<tr>
<td>189</td>
<td>1.5402</td>
<td>4.0</td>
<td>0.49</td>
<td>0.049</td>
<td>α-Cresol</td>
</tr>
<tr>
<td>201</td>
<td>1.5400</td>
<td>10.4</td>
<td>1.27</td>
<td>0.127</td>
<td>p-Cresol</td>
</tr>
<tr>
<td>208</td>
<td>1.5290</td>
<td>6.4</td>
<td>0.78</td>
<td>0.078</td>
<td>Guaiacol</td>
</tr>
<tr>
<td>218</td>
<td>1.5310</td>
<td>5.6</td>
<td>0.68</td>
<td>0.068</td>
<td>3,5 xylenol</td>
</tr>
<tr>
<td>225</td>
<td>1.5290</td>
<td>7.2</td>
<td>0.88</td>
<td>0.088</td>
<td>Cresol</td>
</tr>
<tr>
<td>248</td>
<td>1.5468</td>
<td>12.0</td>
<td>1.46</td>
<td>0.146</td>
<td></td>
</tr>
<tr>
<td>Total Yield</td>
<td>55.2</td>
<td>6.74</td>
<td>0.674</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE XXI

Fractionation of Crude Predistilled Phenols from Lignin Tar (Run C)

<table>
<thead>
<tr>
<th>Fraction boiling (°C)</th>
<th>Refractive Index</th>
<th>Per cent Yield</th>
<th>Phenol</th>
<th>o-Cresol</th>
<th>p-Cresol</th>
<th>Guaiacol</th>
<th>3,5 Xylenol</th>
<th>Cresol</th>
<th>3,5 Xylenol</th>
<th>Creosol</th>
</tr>
</thead>
<tbody>
<tr>
<td>183</td>
<td>Solid</td>
<td>6.8</td>
<td>0.84</td>
<td>0.084</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>191</td>
<td>1.5407</td>
<td>1.1</td>
<td>0.13</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>201</td>
<td>1.5378</td>
<td>2.8</td>
<td>0.34</td>
<td>0.034</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>205</td>
<td>1.5392</td>
<td>4.3</td>
<td>0.52</td>
<td>0.052</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>208</td>
<td>1.5348</td>
<td>1.4</td>
<td>0.17</td>
<td>0.017</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>216</td>
<td>1.5320</td>
<td>5.6</td>
<td>0.68</td>
<td>0.068</td>
<td>3,5 Xylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>1.5300</td>
<td>1.7</td>
<td>0.21</td>
<td>0.021</td>
<td>Creosol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>1.5299</td>
<td>2.8</td>
<td>0.34</td>
<td>0.034</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>231</td>
<td>1.5330</td>
<td>2.8</td>
<td>0.34</td>
<td>0.034</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>240</td>
<td></td>
<td>1.1</td>
<td>0.13</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>249</td>
<td>1.5412</td>
<td>2.2</td>
<td>0.27</td>
<td>0.027</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Yield</td>
<td></td>
<td>32.6</td>
<td>3.97</td>
<td>0.397</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 XXII shows the boiling points and refractive indices
of the more common phenols in the boiling range studied.

Since the fractions from Run C (extracted phenols) seemed
more pure than those of Runs A and B, they were used ex-
clusively for the chemical identification work, the details
of which are described as follows:

The fraction boiling at 182°C was solid at room tempe-
tature and showed the characteristic crystal structure of phenol.
It melted at 35°C. A nitro derivative was prepared according
to Mulliken's procedure (77) which melted at 121.5 - 122.5°C
(m.p. 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 (m.p. 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 (m.p. of the aryloxyacetic acid of
p-cresol = 134-136°C). The fraction therefore consisted
### TABLE XXII

Phenolic Compounds Arranged in Order of Increasing Boiling Point

<table>
<thead>
<tr>
<th>Compound</th>
<th>B.P. (°C)</th>
<th>Refractive Index nD^20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>182</td>
<td>1.5425 (41°)</td>
</tr>
<tr>
<td>2-methylphenol (o-cresol)</td>
<td>190.8</td>
<td>1.547</td>
</tr>
<tr>
<td>4-methylphenol (p-cresol)</td>
<td>201.1</td>
<td>1.540</td>
</tr>
<tr>
<td>3-methylphenol (m-cresol)</td>
<td>202.3</td>
<td>1.540</td>
</tr>
<tr>
<td>2-methoxyphenol (guaiacol)</td>
<td>205.1</td>
<td></td>
</tr>
<tr>
<td>o-ethylphenol</td>
<td>207.5</td>
<td></td>
</tr>
<tr>
<td>2,4-dimethylphenol (xylanol)</td>
<td>211.5</td>
<td></td>
</tr>
<tr>
<td>2,5-dimethylphenol (xylanol)</td>
<td>211.5</td>
<td></td>
</tr>
<tr>
<td>2,6-dimethylphenol (xylanol)</td>
<td>212.1</td>
<td></td>
</tr>
<tr>
<td>m-ethylphenol</td>
<td>214.0</td>
<td></td>
</tr>
<tr>
<td>2,3-dimethylphenol (xylanol)</td>
<td>218.1</td>
<td></td>
</tr>
<tr>
<td>p-ethylphenol</td>
<td>219.0</td>
<td></td>
</tr>
<tr>
<td>3,5-dimethylphenol (xylanol)</td>
<td>219.5</td>
<td></td>
</tr>
<tr>
<td>2-methoxy, 4-methylphenol (cresol)</td>
<td>221.8</td>
<td>1.537</td>
</tr>
<tr>
<td>3,4-dimethylphenol (xylanol)</td>
<td>225.1</td>
<td></td>
</tr>
<tr>
<td>1-methyl, 6-isopropylphenol</td>
<td>226.0</td>
<td>1.5218</td>
</tr>
<tr>
<td>4-methyl, 6-isopropylphenol</td>
<td>229.0</td>
<td>1.5234</td>
</tr>
<tr>
<td>2-methyl, 6-isopropylphenol (thymol)</td>
<td>231.8</td>
<td></td>
</tr>
<tr>
<td>1-methyl-5-isopropylphenol (carvacrol)</td>
<td>237.9</td>
<td>1.524</td>
</tr>
<tr>
<td>1,2 dihydroxybenzene (catechol)</td>
<td>245.0</td>
<td></td>
</tr>
<tr>
<td>1,2 dihydroxybenzenes (catechol)</td>
<td>245.0</td>
<td></td>
</tr>
<tr>
<td>1-hydroxy, 4-methylphenol (homocatechol)</td>
<td>252.0</td>
<td>1.5425 (74°)</td>
</tr>
<tr>
<td>Eugenol</td>
<td>253.0</td>
<td>1.5439 (14°)</td>
</tr>
<tr>
<td>Isoeugenol</td>
<td>267.5</td>
<td>1.5680</td>
</tr>
</tbody>
</table>
chiefly of p-cresol.

The fraction boiling at 205\(^{\circ}\)C yielded a 3,5-dinitro benzoyl ester which melted at 140-141\(^{\circ}\)C (mp. of the 3,5-dinitro benzoyl ester of guaiacol = 141\(^{\circ}\)C). It also gave a picroate melting at 87-88\(^{\circ}\)C (m.p. of the picroate of guaiacol = 86\(^{\circ}\)C). The fraction was therefore guaiacol.

The fraction boiling at 208\(^{\circ}\)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\(^{\circ}\)C after recrystallization from water and petroleum ether. The fraction was not further identified.

The fraction boiling at 216\(^{\circ}\)C probably contained more than one compound. No sharp melting 3,5-dinitro benzoyl ester could be obtained, its melting point increasing from 98\(^{\circ}\)C to 126\(^{\circ}\)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\(^{\circ}\)C which indicates that 3,5-xylenol was present (m.p. of the tribrom derivative of 3,5-xylenol = 162.5\(^{\circ}\)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\(^{\circ}\)C contained cresol since an aryloxyacetic acid prepared from it melted sharply at 86\(^{\circ}\)C (mp. of the aryloxyacetic acid of cresol = 84-86\(^{\circ}\)C) and a picroate melted at 97\(^{\circ}\)C (m.p. of the picroate of cresol = 96.8\(^{\circ}\)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-dinitro phenyl ether which melted at 162-163°C after repeated recrystallization. A 3,5-dinitro benzoyl ester melted at 157-160°C. No known phenol could be found yielding derivatives of these characteristics and the fraction was not further identified.

The yields of the various fractions as given in Tables VI, VII, and VIII are calculated on the basis of the dry crude tar, the oven-dried lignin, and the oven-dried cornstalks, assuming 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 27 inches of mercury absolute and the yield of tar and phenols would be considerably higher from a high vacuum distillation (see Table XIV).

Comparing these results with those of Phillips and Goss (89) who identified several phenols in lignin tar, it is observed that all of the compounds which they found, with the exception of m-propyl guaiacol and 1-vinyl-3-methoxy-4-hydroxy benzene, 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 3-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 Tables XIX, XX, and XXI give a fairly accurate quantitative account of the distillable component 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 yields 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 11) in which a commercial cresylic acid was used, indicates the similarity between coal tar phenolic distillates and the lignin tar phenols. In addition to m- and p- cresols, a number of other compounds were present as indicated by the numerous plateaus. The separation of m- p- cresol (at 201°C and 203°C), although probably not complete, is an indication that the column was sufficiently efficient
for the present purposes.

5. 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 (87). 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 from 0.10 per cent to 0.20 per cent (basis lignin) for both alkali and fuming hydrochloric lignin, although Phillips (87) found as high as 1.0 per cent for 72 per cent sulfuric lignin. For methanol, 0.07 per cent to 1.9 per cent (basis lignin) have been reported, 0.90 per cent being an average figure for alkali, 72 per cent sulfuric, and fuming hydrochloric lignin. The yield of acetic acid ranges from 0.05 per cent to 0.30 per cent for alkali lignin and 0.9 per cent to 1.3 per cent for the fuming hydrochloric lignin and 72 per cent sulfuric lignin.

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, so a quantitative separation of the constituents by fractionational 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 having 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 per cent and 0.79 per cent (basis lignin) for the acetone and methanol, respectively.

The results are shown in Figure 12. 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) there remained such a small amount of material in
the kettle that it could not be fractionated further; the acetic acid (b.p. 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 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°C to 255°C., almost all of the oil being distillable. It may be concluded that the amount of acetic acid (b.p. 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 therefore that the values obtained by the customary methods of analysis for acetone, methanol, and acetic acid 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.
6. Activation of carbonized residue

The following experiments were performed for the purpose of developing an activated carbon from the carbonized residue of alkali lignin destructive distillation.

a. Methods of activation. For the air activation, the carbonized residue was ground to pass a 50 mesh screen and placed in a Pyrex tube one inch in diameter. This tube was wrapped in asbestos paper and placed in a two inch iron pipe. The pipe was heated by a series of Bunsen burners and the temperature was noted by means of a thermocouple which was placed in the carbon through the end of the tube. Air was passed through the tube at a low velocity and the temperature was held at 350°C for a period of 1 hour except in Run 4 in which 4 hours was the heating time. The carbon was then removed and cooled in a desiccator.

The zinc chloride activation was carried out in two ways. In the first, 100 gms. of 50 mesh carbon were mixed with 87 gms. of zinc oxide and 130 ml. of hydrochloric acid (sp. gr. = 1.19) and allowed to stand for two days. The mixture was placed in a cast iron retort and heated slowly until a temperature of 400°C was attained. The residue was then cooled, washed with water until the washings were neutral to litmus, and dried.

The other method of zinc chloride activation was to
prepare a mash of equal parts of lignin and saturated zinc chloride solution and to heat this mash slowly in the small scale destructive distillation apparatus described previously. The temperature in the retort was kept below $350^\circ$C. The residue in the retort was ground to 50 mesh, washed with water until the washings were neutral to litmus, and dried. The yield of tar from this distillation was very much smaller than in the previous runs.

b. Methods of testing. Two methods of testing the activated carbons were used, namely; methylene blue adsorption and iodine adsorption.

The methylene blue test was made by adding a standard solution of methylene blue (0.320 gms./liter) in 5 ml. portions to a known weight of carbon in a separatory funnel, shaking, and testing the solution by withdrawing a drop onto a spot plate. The solution was added until a blue color was observed on the spot plate.

The iodine test was made by agitating 1 gm. of 200 mesh carbon with 50 ml. of 0.2 N iodine solution (in KI) for 3 minutes. The mixture was then filtered, the first portion of the filtrate discarded, and an aliquot portion of the filtrate titrated with 0.1 N sodium thiosulfate solution with starch as the indicator.

c. Results. The activated carbons from several preparations were tested by the two methods to compare their
adsorptive power. Tests were also made on a commercial activated carbon (powdered Hydrolarco) and on a commercial bone char for purposes of comparison.

The results of the methylene blue test are shown in Table XXIII.

TABLE XXIII

Adsorption of Methylene Blue by Activated Carbons

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Method of Activation</th>
<th>Grams of dye adsorbed per gm. of carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air - 1 hour heating</td>
<td>0.0096</td>
</tr>
<tr>
<td>2</td>
<td>Air - 1 hour heating</td>
<td>0.0064</td>
</tr>
<tr>
<td>4</td>
<td>Air - 4 hours heating</td>
<td>0.0207</td>
</tr>
<tr>
<td>5</td>
<td>ZnCl₂ - starting with lignin carbon</td>
<td>0.0334</td>
</tr>
<tr>
<td>6</td>
<td>ZnCl₂ - starting with lignin</td>
<td>0.0672</td>
</tr>
<tr>
<td>-</td>
<td>Hydrolarco</td>
<td>0.0496</td>
</tr>
</tbody>
</table>

It is seen that of the air activated carbons, the one with the longest heating time was the best although it was not as good as the zinc chloride carbons or the Hydrolarco. The zinc chloride carbon made by starting with the lignin was better than the Hydrolarco, while the other zinc chloride carbon was not as good.

The results of the iodine test are shown in Table XXIV.
TABLE XXIV
Adsorption of Iodine by Activated Carbons

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Method of Activation</th>
<th>Grams of iodine adsorbed per gram of carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Air - 4 hours heating</td>
<td>0.161</td>
</tr>
<tr>
<td>5</td>
<td>ZnCl₂ - starting with carbon</td>
<td>0.266</td>
</tr>
<tr>
<td>6</td>
<td>ZnCl₂ - starting with lignin</td>
<td>0.311</td>
</tr>
<tr>
<td>-</td>
<td>Hydrodarco</td>
<td>0.356</td>
</tr>
<tr>
<td>-</td>
<td>Bone char</td>
<td>0.210</td>
</tr>
</tbody>
</table>

The results are, in general, the same as in the methylene blue test except that the Hydrodarco was slightly superior to the zinc chloride carbon of Run 6.

These results show that the carbonized residue from the destructive distillation of lignin can be activated to produce carbons as good or better than commercial products. The zinc chloride method, which gave the best results, is more expensive than the air method of activation, but it should be possible by further research to improve the quality of the air activated product since the present investigation was not exhaustive in scope.

B. Plastics from Alkali Lignin Tar and from Alkali Lignin
1. Alkali lignin tar plastics

No study has been made of the preparation of plastics from alkali lignin tar, as has been pointed out in the historical chapter. The following experiments were made to determine whether the crude lignin tar or fractions of it could be used in the preparation of plastics of the phenol-formaldehyde or Bakelite type.

a. Procedure. Both the so-called one-stage and two-stage methods were used in making the resins. The former consists of using an excess of formaldehyde, carrying out the dehydration of the resin after the reaction has been completed. The latter consists of using an excess of the phenolic material, dehydrating the resin at a high temperature, and then completing the reaction by the addition of hexamethylenetetramine.

In the one-stage process equal weights of the phenolic material and 40 per cent formaldehyde were refluxed for 2 hours over a water bath, using 1 per cent of hexamethylenetetramine based on the phenolic material as a catalyst. At the end of the reaction the aqueous layer was poured off and further dehydration was accomplished by heating the mixture in an enamel pan over a direct flame at a temperature not greater than 110°C. The heating was continued until a small portion of the resin became brittle on cooling. The resin was then cooled and removed from the pan as a brittle, hard solid.
In the two-stage process, the phenolic material was refluxed with half its weight of 40 per cent formaldehyde for 4 hours in a water bath, using 1 per cent of hexamethylenetetramine based on the phenolic material as a catalyst. The water layer was then poured off and further dehydration was accomplished by heating over a direct flame in an enamel pan at a temperature not greater than 150°C. The resin was cooled to 90°C and hexamethylenetetramine was then added in excess, about 10 per cent of the weight of the phenolic material being used. Heating was continued at a temperature not greater than 110°C until a small portion of the resin became brittle on cooling. The resin was then cooled and removed from the pan.

In preparing the molding powders, 60 parts of each resin was ground to pass through a 20 mesh screen, mixed with 40 parts of wood flour as a filler and 1 part of hexamethylenetetramine as a catalyst, and the mixture was ground in a ball mill for at least half an hour. The powders were dried at 80°C for 15 or 20 minutes immediately before molding.

Ten gram portions of the powders were preformed and molded in a Carver press at 150-160°C and 5000 lb./in² pressure for 10 minutes. In most cases the samples were removed from the mold while still hot. They were in the shape of a disc, 1-1/2 inches in diameter.

The strength of the samples was tested on a modified
Paige impact tester. The tester has a five pound weight. This weight was allowed to drop on the samples from heights which were increased by one inch increments until the sample broke.

Water absorption was determined by immersing the samples in running water at $20^\circ C$ for 24 hours and observing the increase in weight.

b. Preliminary experiments. The first series of experiments was made to test the suitability of the crude lignin tar and more or less purified fractions of it for making plastics. Resins were made from crude lignin tar, distilled lignin tar which boiled over the range of 180-270$^\circ C$, and from a phenolic fraction which had been separated from the tar by alkaline extraction, acidification, and fractional distillation in the 4 foot glass column. This last fraction was redistilled immediately before using and it had a light yellow color. Its boiling range was 180-207$^\circ C$ and consisted chiefly of phenol and cresols. For purposes of comparison, resins were also made from pure phenol and from a commercial cresylic acid. The fractionation curve of this cresylic acid is shown in Figure 11.

In the one-stage process, all the resins were solid except the crude and distilled lignin tar resins which were pitch-like in consistency. The two-stage process yielded solid resins in every case. Molding powders were prepared from the solid resins and samples were molded. A sample of
a commercial Bakelite molding powder having the same proportions of filler was also molded as a check.

The solid resins were hard, brittle, and gave a conchoidal fracture. The phenol and fractionated lignin phenol resins were light amber in color and they molded to tan and red-brown plastics, respectively. The cresylic acid resins were dark red in color and molded to red-brown plastics. The lignin tar resins were black in color and molded to black plastics. All of the powders molded well and formed smooth products which took a high polish. All of the plastics from the lignin phenols had a tendency to run out of the mold to some extent during the initial part of the molding. The lignin tar plastics were much worse in this respect than were the fractionated lignin phenol plastics.

The results of this series of experiments are shown in Table XXV.

The best plastic of all from the standpoint of strength was that from the fractionated lignin phenols. This plastic had practically the same water absorption as the commercial Bakelite. The cresylic acid plastics had the lowest water absorption of all, but their strength was not as good as that of some of the others. The lignin tar plastics were the poorest of all, but they had sufficient strength and low enough water absorption to make them satisfactory for many uses. None of the plastics was appreciably affected in
### TABLE XXV

Plastics from Lignin Tar and its Fractions

<table>
<thead>
<tr>
<th>No.</th>
<th>Resin material</th>
<th>Process</th>
<th>% Yield</th>
<th>Strength</th>
<th>% Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Phenol</td>
<td>one-stage</td>
<td>82</td>
<td>18</td>
<td>0.25</td>
</tr>
<tr>
<td>8</td>
<td>Cresylic acid</td>
<td>one-stage</td>
<td>102</td>
<td>10</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>Cresylic acid</td>
<td>two-stage</td>
<td>111</td>
<td>7</td>
<td>0.22</td>
</tr>
<tr>
<td>9</td>
<td>Crude lignin tar</td>
<td>one-stage</td>
<td>79</td>
<td>--</td>
<td>----</td>
</tr>
<tr>
<td>10</td>
<td>Crude lignin tar</td>
<td>two-stage</td>
<td>96</td>
<td>4</td>
<td>0.97</td>
</tr>
<tr>
<td>11</td>
<td>Distilled lignin tar</td>
<td>one-stage</td>
<td>71</td>
<td>--</td>
<td>----</td>
</tr>
<tr>
<td>12</td>
<td>Distilled lignin tar</td>
<td>two-stage</td>
<td>107</td>
<td>5</td>
<td>1.46</td>
</tr>
<tr>
<td>13</td>
<td>Fractionated lignin phenols</td>
<td>two-stage</td>
<td>99</td>
<td>21</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Commercial Bakelite</td>
<td>-- --</td>
<td>--</td>
<td>14</td>
<td>0.41</td>
</tr>
</tbody>
</table>
appearance by the 24 hour immersion in water.

These results show that plastics as good or better than those made from pure phenol or commercial cresylic acid can be made from lignin tar phenols if they are sufficiently purified. Plastics made from the crude and distilled lignin tar were not as good as the others, probably because of the presence of either unreacted phenols or non-phenolic compounds.

g. Plastics from crude lignin phenols. The phenols may be separated from the non-phenolic compounds of the lignin tar by a caustic extraction process such as has been described in the section on fractionation of the lignin tar. In order to test the suitability of the total phenolic fraction of the tar as a plastic raw material, thereby eliminating any deleterious effects due to the non-phenolic compounds, the following experiments were carried out.

The crude phenolic fraction of the lignin tar which was separated by the caustic extraction method was used; it was distilled without fractionation immediately before use. The first series of resins was made by the two-stage process with different lengths of reaction time; these are designated as the "A" resins. A resin was made by the one-stage process and is designated as resin "B". The "C" series of resins was made in the customary way except that they were washed with benzene in a separatory funnel before the final dehydration was carried out (76). The "D" resins were made from pure
These results seem to indicate that future investigation should be centered on the two-stage test and it's phenol

The crude phenol used in the preliminary experiments were, however, much better than the products obtained from
phenol products (series w) or to commercial benzine. They were, however, much better than the products obtained from
phenol products (series w) or to commercial benzine. The crude phenol products was comparable to the pure
saturation because of the low water absorption. None of

The one-stage "nano" plastic was perfect, the most
the "nano" plastic were the best of all the various phenol
was much better in strength but had a high water absorption.
out of the mold badly and had low strength. The "nano"
the "nano" plastic were the best in strength but had a high water absorption.
they can

The one-stage "nano" plastic shows the extent of reaction of the mold. Since
the weight of the powder used was about 10 grams
the weight of the powder used was about 10 grams.

The one-stage "nano" plastic, however, did not
absorption test. This was also true of the two-stage "nano"
red a tendency to distillate and became pitted during the water
in color and had a smooth surface. The "nano" and "nano" plastic
cases, most of the molded products were dark brown to black
phenol for comparison. Solid resins were obtained in all

127
### TABLE XXVI

Plastics from Crude Lignin Phenols

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>Process</th>
<th>Time (hours)</th>
<th>Phenols (gms.)</th>
<th>Water Absorption</th>
<th>Resin molded (inches)</th>
<th>Strength (Basis Sample on drop) (Basis Plastic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>two-stage</td>
<td>4</td>
<td>64</td>
<td>6.9</td>
<td>4</td>
<td>--</td>
</tr>
<tr>
<td>A-2</td>
<td>two-stage</td>
<td>6</td>
<td>68</td>
<td>9.0</td>
<td>2.5</td>
<td>--</td>
</tr>
<tr>
<td>A-3</td>
<td>two-stage</td>
<td>8</td>
<td>84</td>
<td>8.6</td>
<td>6</td>
<td>0.84</td>
</tr>
<tr>
<td>B-1</td>
<td>one-stage</td>
<td>2.5</td>
<td>44</td>
<td>10.9</td>
<td>11</td>
<td>2.22</td>
</tr>
<tr>
<td>C-1</td>
<td>one-stage</td>
<td>2.5</td>
<td>32</td>
<td>8.7</td>
<td>9</td>
<td>0.30</td>
</tr>
<tr>
<td>C-2</td>
<td>two-stage</td>
<td>3.5</td>
<td>52</td>
<td>8.9</td>
<td>8</td>
<td>3.33</td>
</tr>
<tr>
<td>C-2</td>
<td>two-stage</td>
<td>3.5</td>
<td>52</td>
<td>10.2</td>
<td>15</td>
<td>3.05</td>
</tr>
<tr>
<td>D-1</td>
<td>one-stage</td>
<td>2</td>
<td>--</td>
<td>9.9</td>
<td>23</td>
<td>0.17</td>
</tr>
<tr>
<td>D-1</td>
<td>one-stage</td>
<td>2</td>
<td>--</td>
<td>10.2</td>
<td>19</td>
<td>0.09</td>
</tr>
<tr>
<td>D-2</td>
<td>two-stage</td>
<td>4</td>
<td>--</td>
<td>10.6</td>
<td>10</td>
<td>----</td>
</tr>
<tr>
<td>D-2</td>
<td>two-stage</td>
<td>4</td>
<td>--</td>
<td>10.0</td>
<td>5</td>
<td>0.45</td>
</tr>
<tr>
<td>Bakelite</td>
<td>--------</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>23</td>
<td>----</td>
</tr>
</tbody>
</table>
with a one-stage reaction and with some method for removing the unreacted phenols from the resin. While the products developed in the preceding investigation would be satisfactory for many purposes, they can undoubtedly be improved. Such products should be quite cheap in comparison with plastics made from phenol and cresylic acid because no involved separation and purification of the phenols are necessary.

2. Alkali lignin plastics

Since no work has been recorded in the literature on the preparation of plastics from alkali lignin, an investigation of this was begun. A few attempts were made to prepare plastics of the lignin-aniline and lignin-furfural type from alkali lignin. While these were not very satisfactory, it was found by Mr. J. A. Johnston of this laboratory that a good molding composition could be produced by reacting alkali lignin with furfural and urea. A study of this type of plastic was made by G. L. Wheelock (112) under the joint direction of Mr. Johnston and the author. His results will be summarized briefly.

The resins were made by thoroughly mixing alkali lignin, urea, slaked lime, and, in some cases, carbon black in the proper proportions. To the solid mixture furfural was added and the whole mass heated for two hours in an oil bath at a temperature of 110-115°C with occasional mixing. The products were hard, brittle resins. These were dried at
50°C for 24 hours and then ground to pass through a 60 mesh screen. Molding powders were made by mixing these resins in a ball mill with wood flour, in amount equal to the weight of the lignin in the resin. Samples were molded in the Carver press at a pressure of 5000 lb./in² and at a temperature of about 195°C. The mold was cooled before the plastics were removed; The tests were made on the products as described previously.

Table XXVII shows the composition and properties of some of the best plastics obtained. Their strength is fair and they would be satisfactory for many purposes. Their water absorption is rather high and this would probably limit their application to articles used in dry places. The plastics had good appearance and took a good polish. They were dark brown in color; those to which carbon black had been added were black. The best plastics retained their good appearance after the water absorption test.

These results, although of a preliminary nature, indicate that the alkali lignin-furfural-urea plastics have promise. With further research they could undoubtedly be improved. All the raw materials are cheap and the plastic could probably be made much cheaper than the widely-used phenol-formaldehyde plastics.
**TABLE XXVII**

Lignin-Furfural-Urea Plastics

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>Lignin (gms.)</th>
<th>Furfural (gms.)</th>
<th>Urea (gms.)</th>
<th>Ca(OH)₂ (gms.)</th>
<th>Black (gms.)</th>
<th>Strength (inches)</th>
<th>Absorption (gms.)</th>
<th>Carbon (gms.)</th>
<th>Drop (gms.)</th>
<th>Sample (gms.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFU6.4</td>
<td>24</td>
<td>12</td>
<td>8</td>
<td>2.4</td>
<td>0</td>
<td>18</td>
<td>9.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFU8.4</td>
<td>24</td>
<td>16</td>
<td>8</td>
<td>2.4</td>
<td>0</td>
<td>8</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFU12.6</td>
<td>24</td>
<td>24</td>
<td>12</td>
<td>2.4</td>
<td>0</td>
<td>8</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFU7.4</td>
<td>24</td>
<td>14</td>
<td>8</td>
<td>2.4</td>
<td>2.4</td>
<td>4</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFU6.4</td>
<td>24</td>
<td>12</td>
<td>6</td>
<td>2.4</td>
<td>2.3</td>
<td>10</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
VI. DISCUSSION OF RESULTS

The extent of application of the three processes for the production of lignin will depend on the characteristics of the methods and upon the demand for their products.

The first two methods, namely; precipitation of lignin with strong acids and with carbon dioxide, are especially useful in recovering lignin from soda liquors which are at present wastes from pulp and paper mills. They would thus have a better chance for immediate use, because the problem of waste soda liquor disposal is a pressing one at the present time. It is likely to become an even more serious problem since legislation prohibiting dumping the raw liquor into streams is becoming more widespread. Of these first two methods, the carbon dioxide precipitation process should be the cheaper in the long run but it would involve greater initial outlay for equipment. Since both lignin and pentosans are recovered by this method, the profits from the sale of these materials should be greater than those from the acid process. For future research on the carbon dioxide process it is suggested that studies be made on the causticization of the effluent liquor and on uses for the pentosan material.

The production of lignin and cellulose by butanol-water extraction is much simpler than any of the present-day
pulping processes, but its wide application on a commercial scale may be slow in developing because of the large amount of capital invested in the sulfite, sulfate, and soda pulping plants. It is probably the cheapest of any of the processes studied and it permits separation of the cellulose, lignin, and pentosans. Future research should include studies on the aqueous layer of the cook liquors and methods for the recovery of the pentosans therein.

The destructive distillation studies show only one of a large number of potential uses for lignin. The products from the destructive distillation of lignin should find a ready market because they are all in considerable demand. The economical feasibility of this utilization of lignin would, of course, depend on the cost of the lignin. Some idea of the value of the products may be had from the following estimate which is based on 100 pounds of alkali lignin:

<table>
<thead>
<tr>
<th>Product</th>
<th>Quantity</th>
<th>Price</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>50 lb.</td>
<td>$0.10</td>
<td>$5.00</td>
</tr>
<tr>
<td>Phenol</td>
<td>1 lb.</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Cresylic acid</td>
<td>3 lb.</td>
<td>0.11</td>
<td>0.33</td>
</tr>
<tr>
<td>Other phenols</td>
<td>6 lb.</td>
<td>0.10</td>
<td>0.60</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.8 lb.</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>$6.12</strong></td>
</tr>
</tbody>
</table>

In addition to these products, the acids and neutral oils should have some value. In view of these figures, it is likely that the estimated cost of the alkali lignin prepared by the sulfuric acid precipitation process ($5.80 per 100 lbs.)
For the demonstration on methods of producing "I" theory and on uses
much promised, future research should be carried out
promising new materials for the chemical industries offering
and from waste some tie more to a
The results of this study show that the nitrogen from
metallurgical materials are extremely low
which other types of processes since the cost of the raw
a direct use of the nitrogen and should be able to compete
processes of the alkali nitrogen-reducing type offer
could be made having a large variety of properties and uses.
advantage extended methods of refining the tar. The processes
the use of alkali nitrogen tar for making plastics seems
the use of alkali nitrogen tar for making plastics should prove practical.
the process using these tigurins should prove practical
$1 or $2 per 100 pounds would not be too high, however, and
or different nitrogen, which could probably be brought down to
distillation new materials. The cost of certain different nitrogen
would be prohibitive for use of the nitrogen as a destructive
VII. CONCLUSIONS

(1) Alkali lignin may be recovered from the soda cook liquor of cornstalks by adding a sufficient excess of strong mineral acid and heating. The excess concentration necessary for good lignin precipitation depends on the kind of acid used and the time of heating.

(2) Alkali lignin prepared from cornstalks by precipitation with mineral acids may be fractionated into a phenolic fraction and an acidic fraction by successive treatment of its alkaline solution with carbon dioxide and hydrochloric acid.

(3) The phenolic alkali lignin fraction may be precipitated from cornstalk soda liquor by treating it with carbon dioxide. In order to obtain good filtration of this lignin, the pentosans should be precipitated from the liquor by adding alcohol prior to the carbon dioxide treatment.

(4) The mineral acid and carbon dioxide precipitation processes may be used to recover lignin from waste soda liquors. The carbon dioxide process is the more economical of the two.

(5) Lignin and pentosans may be extracted from cornstalks by cooking them with butanol-water solutions at high temperatures and high pressures. The lignin can be quantitatively
recovered by distilling off the alcohol from the alcoholic layer of the coack liquor. The pentosans are segregated in the aqueous layer.

(6) The butanol-water extraction process is the cheapest of all the processes studied and it gives the highest yield of lignin.

(7) In order to obtain the maximum yield of distillates from the destructive distillation of cornstalk alkali lignin, it should be heated to at least 400°C.

(8) The maximum yield of tar was obtained at a distillation pressure of 5.5 inches of mercury.

(9) The maximum yield of phenols was obtained at a distillation pressure of 2.2 inches of mercury but still lower pressures would probably give higher yields.

(10) The method of heating and the rate of heating had little effect on the yields of the distillation products.

(11) More than half of the lignin tar can be fractionally distilled. The distillable portion was practically all phenolic and it boiled over the range 180-250°C.

(12) Many of the constituent phenols may be isolated from the lignin tar by efficient fractional distillation. Those identified were phenol, o-cresol, p-cresol, guaiacol,
3,5-xylenol, and creosol.

(13) The aqueous distillate contained 0.8 per cent methanol; it contained very little if any acetone and acetic acid.

(14) The carbonized residue can be activated by the air and zinc chloride methods, the latter method giving the better products. The decolorizing capacity of some of the activated carbons obtained compared favorably with commercial activated carbon.

(15) Plastics of the phenol-formaldehyde type may be prepared from lignin tar or from fractions thereof. The products from purified fractions were the best but those from the crude tar and crude phenols were suitable for many purposes.

(16) Plastics may be prepared from alkali-lignin, furfural, and urea. These plastics had fair strength but their resistance to water was not especially good. They have the advantage of cheapness and ease of preparation.
VIII. SUMMARY

The production of lignin from cornstalks by (1) precipitation of alkali lignin from soda liquor with strong mineral acids, (2) precipitation of alkali lignin from soda liquor with carbon dioxide, and (3) extraction of cornstalks with butanol-water solutions has been studied. The first two processes are adaptable to the recovery of lignin from waste pulp and paper mill liquors and of the two, the carbon dioxide process is much the cheaper. The third process is less expensive than either of the first two and it gives a much higher yield of lignin.

The utilization of lignin has been studied from the points of view of destructive distillation and preparation of plastics. The optimum conditions for the production of phenols from cornstalk alkali lignin by destructive distillation are a temperature of at least 400°C and as high a vacuum as is practical to attain. The lignin tar and separated lignin phenols were carefully fractionally distilled in an efficient column and phenol, o-cresol, p-cresol, guaiacol, 3,5-xylenol, and cresol were identified in the fractions. The fractions boiling in the range 180-250°C are practically wholly phenolic. The aqueous distillate was found to contain 0.84 per cent of methanol (basis lignin) and only traces
of acetone and acetic acid.

Plastics of the phenol-formaldehyde type were prepared from the lignin tar and from fractions of it. Products as good as commercial plastics were obtained from a carefully purified phenolic fraction of the tar and products which were poorer, but satisfactory for many purposes, were obtained from the crude lignin tar and crude lignin phenols.

Plastics of the lignin-furfural-urea type have good strength and fair water resistance. They are much cheaper than phenol-formaldehyde plastics and could be substituted for them in many cases.
IX. LITERATURE CITED


More than 70 per cent of lignin can be converted into four known alcohols and glycols by a hydrogenation process using copper-chromium oxide as a catalyst. The products consist of 28 per cent of methanol and 50 per cent of an alcohol and two glycols which are derivatives of propylcyclohexane.


Of a large number of hydroxyl compounds studied, butyl and amyl alcohols are the best for pulping aspen wood. They have the advantage of being completely miscible with water at the pulping temperatures but immiscible at room temperature.


Alcoholic nitric acid gives higher pulp yields than aqueous nitric acid. The decomposition products are removed by heating the pulp with aqueous alkali.


A solution of sodium lignosulfonate is acidified with acetic acid to give a tanning compound.


Alkali lignin was prepared from straw by (1) precipitation of soda liquor with 2.5 per cent excess of hydrochloric acid (2) separation of pentosans from the liquor with alcohol followed by acid precipitation of lignin and (3) extraction of the straw with alcohol-alkali solutions.

Lignin was extracted from winter rye straw with methanol-caustic solutions and its physico-chemical properties, such as molecular weight and conductivity, were studied.


Derivatives of alkali lignin were made. The preparation of phenols from lignin by caustic fusion was discussed. Protocatechuic acid and catechol were obtained from the caustic fusion.


Saccharification plants in Germany are described and problems in the industrial use of concentrated hydrochloric acid are discussed.


Resinates are separated from soda liquors, treated with sulfuric acid and then with turpentine, first in the cold and then in the hot. The turpentine solution is vacuum distilled and the resin is left in the residue.


Soda liquor was treated with nitre cake to precipitate organic matter and then causticized with lime.


Soda liquor is sprayed into a heated atmosphere containing CO₂ or SO₂ to concentrate and precipitate organic matter. The solution is then causticized.

Soda liquor is treated with a basic aluminum compound and CO₂. A precipitate forms which is destructively distilled to give an intimate mixture of carbon and Al₂O₃. The effluent liquor may be causticized.


Glycol lignin, methanol lignin, and Freudenberg lignin all seem to be identical when purified. The compositions of lignins prepared by various investigators are surveyed critically.


Crude lignin, obtained by precipitation from warm black liquors with acids, is carbonized, treated with soda ash solution and finally with acids.


Lignin or sawdust is reacted with phenol with HCl as a catalyst at 180°C. The product is washed free from phenol and purified by solution in ethanol and precipitation with water.


Soda liquor from cornstalks is dried and carbonized at 300°C. A better process is to precipitate the organic matter with acids before drying, and then carbonize.

Cellulosic material is pulped by treating it with chlorine water and then with caustic solutions.


Extractive-free spruce wood was digested with 4% NaOH solution at 8 atmospheres pressure. The precipitate obtained from the liquor with HCl had a molecular weight of only 356. It agreed in composition with the lignin of Klason.


Soda liquors are treated with CO₂ and heated. The resulting precipitate is used as a raw material for fermentation to produce alcohol or as an animal food.


Soda liquor is heated under pressure, treated with CO₂, and the lignin is filtered off. The filtrate is concentrated and treated with lime to obtain a dry mixture which is aggregated with CO₂ and moisture. This moisture is heated to 160-200°C and leached with a small amount of cold water to remove sodium acetate.


Resins and lacquers were made by reacting low temperature coal tar fractions with formaldehyde.


Soda liquor from grasses is treated with acids, CO₂, or SO₂ to precipitate organic matter.


A number of packing materials was tested and the most efficient type was 1 and 2 turn helices made of either wire or glass.

Lignin gave higher yields of liquid and gaseous products than did cellulose or coal.


Willstatter lignin yielded 13.2% aqueous distillate, 12.5% oil, 57.2% carbon, and 17.0% gas.


Lignin was dissolved in soda ash solution and oxidized with air at 200°C and 55 atmospheres. The yield of aliphatic acids obtained was 8.26% and the yield of benzene-carboxylic acids was 5.12%.


Lignin is impregnated with a phenol and molded under heat and pressure. Fillers may be added.


Plastic molding materials were made from sawdust by (1) hydrolysis, (2) esterification, (3) chlorination, and (4) acid hydrolysis.


A structural formula for lignin was proposed.


Low temperature coal tar and its fractions were treated with formaldehyde and with benzaldehyde. Solid resins were obtained.

Soda liquors are treated with acids in the presence of hydrocarbon solvents. Resins are liberated which dissolve in the solvents.


The preparation of vanillin from wood was described.


Willstatter lignin from pine was destructively distilled.


Lignin was extracted from wood with methanol containing HCl as a catalyst.


Sulfite liquor is treated with NH₃ under pressure at 110-120°C. A pitch is obtained which is suitable as a dye dispersing agent and as a tanning agent.

40. Harris, W. D. Plastics from high-pentosan cellulose material. Iowa State Coll. J. Sci. 9, 159-61 (1934).

Plastics were made by reacting cellulose, pentosans, and lignin with phenol.


A very readable survey of the constitution, reactions, and physico-chemical properties of lignin.

Willstatter lignin from pine and aspen was destructively distilled and compared with cellulose and xylan.


Acid lignin was hydrolyzed with water, alkalis, and acids. The highest yield of methanol, 14.3%, was obtained with dilute HCl at 150-160°C and 5-6 atmospheres.


Willstatter lignin was destructively distilled. The gas contained 9.6% CO₂, 50.9% CO, 37.5% CH₄, and 2.0% C₆H₆.


Lignin was nitratred and the product was reduced and diazotized. When coupled with amines and phenols, it gave pink and brown dyes.


Extracted spruce meal was digested with 8-10 parts of ethylene glycol and 0.2% I₂ for 6-8 hours at 110°C. The lignin was precipitated by pouring the liquor into a large amount of water. It was purified by dissolving in NaOH solution and precipitating with CO₂.


Sulfate black liquor was treated with mineral acids, acetic acid, and CO₂ to precipitate lignin. No difference in the lignins precipitated by the different acids was noted. The lignin was fractionated into an alcohol-soluble fraction (γ) and an alcohol-insoluble fraction (α).

Alkali lignin was prepared from sulfate liquor by acid precipitation. Previous work on alkali lignin was summarized.


Lignin or lignosulfonic acid is treated with chlorine in the presence of water without applying heat. Methanol is separated from the product by steam distillation.


Acid lignin is swelled in alkaline solutions and then mixed with synthetic resins or casein as a binding agent.


Organic materials in soda liquors are precipitated with acids and then destructively distilled.


Sulfite liquor is treated in 4 steps with a lime reagent in an apparatus consisting of 4 reaction vessels and 4 settling tanks in series. The sludge from the first tank is CaHSO₃ which is used in reboiling and the sludges from the other three tanks are lignosulfonates. The carbohydrates remain in the effluent and the oxygen demand of the liquor is reduced by one-sixth.


The lignosulfonate precipitate from the Howard process (53) is cooked with lime under direct steam pressure. A solid is obtained which is suitable for use as a pigment and in rubber or paper products.


The lignosulfonate precipitate (53) is heated and evaporated, nearly all the free SO₂ being removed. The product is diluted with water to produce a gel which is
useful as a bonding agent.


Lignosulfonates are treated with Ca(HSO₄)₂ in the presence of water to produce dispersions suitable as tanning agents, mordants, dispersing agents, wood-preserving agents, and insecticides.


The phenols in the tar are resinified by sulfuric acid or formaldehyde and the neutral and unreactive compounds are removed by vacuum or steam distillation.


Lignin was precipitated from soda liquor and purified by chloroform extraction.


Lignin was isolated from spruce wood by treating it with 72% H₂SO₄ at room temperature and then with 3% H₂SO₄ at a boiling temperature.


Sulfate black liquor was treated with CO₂ and a lignin precipitate was obtained. Treatment of the filtrate with H₂SO₄ gave a further precipitate which seemed identical with the first precipitate.

A review of the chemistry of lignin with particular emphasis on the condensation and polymerization products of lignin.

64. Kuster, W. and Daur, R. Uber die Einwirkung von aromatischen Diazokorpern auf Lignin und Cellulose. Cellulosechem. 11, 4-6 (1930).

Lignin was nitrated, reduced, diazotized, and coupled with amines, phenols, and with lignin itself.


Oak and beech woods were heated with 4-5 parts of alkali and an equal weight of water to 185° C. The liquor was acidified to obtain a lignin which was partially soluble in alcohol.


No strain of bacteria could be found which would appreciably attack lignin or produce a gas from it.


The apparent molecular weight of methanol lignin is between 4,000 and 10,000, as determined by viscosity, osmotic pressure, boiling point raising, diffusion, and spreading measurements.


Lignin is almost insoluble in 40% NaOH solution at 160°C, but is removed from spruce by more dilute solutions.


The effect of sodium hydroxide concentration, temperature, and pressure on the removal of lignin from wood by alkaline extraction was investigated.


Lignin containing 75% moisture and much H₂SO₄ was hydrogenated at 400-450°C, 50-70 atmospheres, and with Mo₅ as a catalyst. The yield of tar was very small but with phenol or lignin tar as a solvent, lignin was completely transformed into liquid (44%) and gaseous (products). The tar was aromatic in nature.


Phenols were separated from phenate-soluble compounds by extraction with a brine-caustic reagent or by precipitation with chloroform.


Phenolic fractions of the tar were reacted with formaldehyde to obtain either hardening or non-hardening resins. These were used in electrical insulation work and as binders for laminated boards.


Pine lignin was distilled, yielding 57% carbon, 6.5% tar, 13.5% aqueous distillate, and 23% gas and loss.


Lignin obtained by the incomplete hydrolysis of lignocellulose with acids is mixed with 6-10% of plasticizer, such as latex or benzylcellulose.


Carbonized lignin residue from soda liquors is activated by the air or steam method. Sodium fluoride may be added to volatilize silicon compounds. The carbon is treated with HCl, washed and dried.


Soda liquor is treated with CO₂ and then with Na₂ZnO₂. The lignin is filtered off and the effluent liquor treated with O₂ or O₃ and then with lime. No evaporation is necessary in the process.


Bagasse was treated with dilute HNO₃ and then with dilute NaOH, which dissolves the lignin. By acidification of the alkaline liquor, more or less nitrated lignin is precipitated. Good yields of high α-cellulose pulp are obtained.


Lignin was prepared from corn cobs by alkaline extraction and acid precipitation. Its chemical and physical properties were studied.

Corn cobs were extracted successively with cold alcoholic NaOH, hot alcoholic NaOH, aqueous NaOH at 100°, and aqueous NaOH under pressure. The lignin fractions obtained in each step had different methoxyl contents.


Lignin was prepared from corn cobs by the Klassen, Willstatter, and alkali methods and compared as to destructive distillation products.


A very complete review.


Alkali lignin from corn cobs was distilled at 25 mm. pressure. A yield of tar of 28% was obtained; this tar was investigated and several phenols identified therein.


Waste sulfite liquor was treated with aqueous ammonia at high temperatures and pressures. The product had fertilizer value, but was not as good as some commercial fertilizers.


Alkali lignin was condensed with aromatic amines and furfural to obtain resins which were used as stains and as binders for compressed boards. Most of the resins were of the soluble, fusible type.

Willstatter lignin was distilled at 5-25 mm. pressure. Eugenol was identified in the phenolic portion of the tar and several hydrocarbons isolated from the neutral oils.


Cellulosic materials are treated with gaseous chlorine and the lignin is then removed by treatment with aqueous alkalies.


Flax was cooked with 10% NaOH solution at 130°C. The resulting liquor was acidified with HCl while still hot, and the lignin was filtered off. A yield of 20-22% was obtained. Acetyl, methyl, chloro, bromo, and nitro derivatives were prepared.


Alkali lignin was prepared from seven different woods. The hypothesis was advanced that all lignins are related to a parent substance, "lignol".


Alkali lignin was precipitated from soda liquor with HCl. It contained 5% pentosans.


Soda liquors are treated with mineral acids at low temperatures and heated slowly to obtain a precipitate in a grainy form.


Carbon dioxide precipitates the lignin and one-third of the "humic substances" from soda liquors, while
\( \text{H}_2\text{SO}_4 \) precipitates the "humic acids".

   Soda liquor is treated with CO\(_2\) to precipitate humus substances, which are then dried and destructively distilled.

   The hydrolysis of cellulose by \( 72\% \text{H}_2\text{SO}_4 \) should be carried out at 20\(^\circ\)C for two hours, instead of at higher temperatures and longer times.


   Lange's process (55) for preparing alkali lignin was applied to pine wood.


   Only 8-10\% of the original methoxy in the lignin could be accounted for in the distillates.

   Wood was digested with 30-50 parts of 10\% NaOH solution. Hemicelluloses were precipitated from the sook liquor by addition of 2 volumes of alcohol.

Willstatter lignin was subjected to destructive distillation.


Spruce Willstatter lignin was distilled under 1-12 mm. pressure and 450°C. The greater part of the tar was soluble in either Na₂CO₃ or NaOH solutions, but only a very small amount of it was soluble in NaHCO₃ solution.


Southern pine soda liquor was treated with CO₂ at room temperature and pressure, then at 19 lb./in² and 100°C, cooled, and filtered. About one-half of the organic matter was removed by this treatment.


Lignin was isolated from wood by treating the wood with fuming HCl, which treatment hydrolyzed the cellulose quantitatively.

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