The major portion of wood distillation products in the United States is obtained from forest and mill residues, chiefly beech, birch, maple, oak, and ash. Marketing of the natural byproducts recovered has been concerned traditionally with outlets for acetic acid, methanol, and charcoal. Large and lower cost production of acetic acid and methanol from other sources has severely curtailed markets formerly available to the distillation industry, and has in turn created operational conditions generally unfavorable to many of the smaller and more marginal plants. Increased demand for charcoal, which is recovered in the largest amount as a plant product, now provides a compensating factor for more favorable plant operation.

The present hardwood-distillation industry includes six byproduct-recovery plants. With the exception of one smaller plant manufacturing primarily a specialty product, all have modern facilities for direct byproduct recovery. Changing economic conditions during the past 25 years, including such factors as progressively increasing raw material, equipment, and labor costs, and lack of adequate markets for methanol and acetic acid, have caused the number of plants to be reduced from about 50 in the mid-thirties to the 6 now operating. In addition to this group, a few oven plants formerly practicing full recovery have retained the carbonizing equipment and produce only charcoal.

Other countries reportedly producing substantial quantities of distillation products in recent years are Albania, Austria, Canada, Germany, and Sweden. There have been distillation operations likewise in Belgium, Chile, England, France, India, Mexico, and Japan. Bolivia and Peru have indicated industrial interest also in this field. The extent of current production abroad is not known. The heavy hardwood stands of the tropical countries would provide potentially high production areas of raw material for industrial carbonization.

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1 This is a revision of an earlier Forest Products Laboratory report of the same title, by L. F. Hawley.

2 Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
Hardwood-Distillation Products and Uses

The products of hardwood distillation have a number of important industrial uses. The markets for acetic acid and methanol have been reduced, however, by the increased production of these compounds by other processes. Other carbon materials have also limited the diversification of uses for charcoal. Because of its heating properties, however, charcoal is in excellent demand for recreational purposes. The following are the principal products of the industry and their uses:

Charcoal.--Charcoal has been an important raw material for many years. As lumps, sized screenings, powder, briquets, or in activated form, it is used chiefly as domestic or specialized fuel. It is also used in substantial quantities in metallurgical and chemical processes. The following lists show items, products, and industries that utilize charcoal in some way.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Metallurgical</th>
<th>Chemical</th>
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<tbody>
<tr>
<td>citrus growers</td>
<td>aluminum metal</td>
<td>activated carbon</td>
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<tr>
<td>recreational</td>
<td>armor plate</td>
<td>black powder</td>
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<tr>
<td>household</td>
<td>casehardening</td>
<td>brake linings</td>
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<tr>
<td>foundry</td>
<td>copper, brass, and bronze</td>
<td>carbon disulfide</td>
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<tr>
<td>incinerator</td>
<td>electromanganese</td>
<td>carbon monoxide</td>
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<tr>
<td>laundry</td>
<td>foundry molds</td>
<td>catalyst reactor</td>
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<tr>
<td>meat and fish curing</td>
<td>magnesium metal</td>
<td>fertilizers</td>
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<td>mining</td>
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<td>shipyard</td>
<td>nickel</td>
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<td>tinning and plumbing</td>
<td>pig iron</td>
<td>glass</td>
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<td>rubber</td>
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<td>sodium cyanide</td>
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Acetic acid.--Acetic acid is used in the chemical industry in the preparation of various inorganic acetates and white lead pigment. It is also used widely in the manufacture of cellulose acetate for lacquers, plastics, rayon, and photographic films, and in the preparation of various other organic acetates, such as methyl, ethyl, and amyl acetate, for use as solvents. Acetic acid also is an intermediate in the manufacture of
various synthetic organic chemicals. It serves as a reagent in textile dyeing processes and as a coagulating medium for rubber.

Acetone.—Acetone is no longer an important wood-distillation product. Since about 1920, decreasing amounts have been produced by conversion of acetate of lime. There has been none produced in this manner for a number of years because acetone may be produced more cheaply by other methods.

Methanol.—Methanol, like acetone, is now being produced more cheaply and extensively by other means. Heavy industrial demands for methanol assure large production by distillation for some time to come, however. Important uses for methanol are as an industrial solvent, an ethanol-denaturing agent, and anti-freeze. Other major uses in manufacturing are the following:

- dry-cleaning compounds
- formaldehyde
- fuel
- heating and illuminating compositions
- organic syntheses
- paint and varnish removers
- paints, varnishes, and lacquers
- perfumes
- polishing and cleaning compounds
- smokeless powder
- soaps
- methyl acetone

Methyl acetone.—This product is essentially a mixture of methanol, acetone, and methyl acetate recovered in the refining of the methanol. The composition of the material varies somewhat with processing methods at different plants. The plant products have similar market use as solvent materials.

Wood tar.—The settled and "dissolved" or "soluble" tars are becoming increasingly valuable to the wood-distillation plant as chemical raw materials. The recovery of a number of marketable products from them has been developed. Further research and pilot-scale developments indicate that additional specialized products will be obtained.

Commercial Methods of Wood Distillation

Charcoal has been made for centuries by simple charring methods in earth pits or mounds, and subsequently in masonry kilns. The heat required for the carbonization is furnished by partial combustion of the charge controlled through a regulated input of air. Early industrial charcoal production was carried out in large masonry kilns.

In the United States, two lines were followed from the early kiln charcoal industry toward the establishment of the conventional oven-distillation operations in which chemical byproducts together with charcoal are of chief importance. One operational method used the brick byproduct kiln,
in which heating was accomplished by retarded combustion and the volatile products of combustion and distillation were condensed and recovered. The yield of chemicals from the byproduct kilns was about one-half that obtained by the distillation of wood in externally heated ovens. Byproduct kilns located in areas requiring large quantities of charcoal for iron furnaces continued to operate for many years.

A further change from the initial kiln production methods to the oven operations involved the use of the cylindrical retort. These retorts were about 5 feet in diameter and 9 feet in length with pairs set horizontally over a single firebox. They were manually charged and discharged.

Improved ovens have entirely replaced the former types and have been considered standard oven carbonizing equipment since about 1932. The later ovens were developed mainly to decrease the amount of labor required, since with their design wood may be charged directly into the ovens on cars and the charcoal may be removed in the same manner without further handling. More efficient operation was obtained by this method, with yields of byproducts per cord of wood equal to those formerly obtained from recovery-type commercial carbonization equipment.

One disadvantage in conventional oven carbonization is the excessive oven surface temperature necessary to maintain the proper distillation temperature at the center of the charge. This condition promotes oven deterioration, especially when the oven is fired improperly. Similar rapid deterioration occurs with forced firing for the distillation of unseasoned wood.

**Drying the Wood**

The wood should be air-dried for 12 to 18 months before distillation. The use of unseasoned wood not only requires more fuel and a longer distillation cycle but the amount of crude liquor is increased with moisture from the wood. Such practice is costly, since both additional refining equipment and power are needed for processing.

There is lack of agreement regarding the effect of various amounts of moisture in wood on the yields of methanol and acetic acid. If yields are increased by moisture, as has been reported in some instances, it is questionable if the increase is sufficient to overcome the increased costs of carbonization and refining.

The cost of air-drying adequate supplies of wood is an important plant item. Interest on the investment in a suitable wood inventory amounts to a considerable sum. Piling and loading charges both before and after the wood is dried are also significant. The use of predriers avoids excessive labor costs for yard handling and eliminates the usual carrying charges of interest, insurance, and taxes.
Accelerated methods for drying wood are applied at a number of the distillation plants. The pre-driers generally employed are of brick or tile tunnel-like construction, and hold from 1 to 3 days' supply of wood in oven distillation cars. The wood is dried by contact with the forced circulation of flue gases from the oven stacks. The dual use of flue spark arresters and moderate gas temperatures in the driers reduces the fire hazard.

The drying of wood takes place more rapidly endwise with the grain than radially. Because shorter lengths dry faster, some plants reduce the usual 4-foot cord lengths of wood to block size and load the blocks into cars from hoppers without further handling after they are sawed. Short blocks of wood fed into a car from a hopper reportedly provide more weight to the load than hand-piled 4-foot cordwood.

Relationship Between
Wood Composition and Its Distillation Products

The two main constituents of wood, cellulose and lignin, yield different wood-distillation products. Cellulose when distilled produces no methanol, but gives a comparatively high yield of acetic acid (14). Lignin apparently is the only source of methanol in wood.

The chemical composition of wood is usually expressed in terms of certain groups of substances that have distinctive solubilities or give certain reactions. For example, "methoxy group," "acetic acid by hydrolysis," "alkali soluble," "water soluble," and "ether soluble" are common terms used in reporting a wood analysis.

The methoxy group is the one of particular interest in wood distillation. Its determination is not a direct measure of the amount of methanol that can be obtained by destructive distillation of the wood. In general, however, larger yields of methanol are obtained from the woods that show higher methoxy values. The ratio between the percentage of methoxy groups and the percentage of methanol obtained by distillation is approximately 3 to 1, which indicates that somewhat higher yields of methanol might be obtained by modifying the distillation.

The amount of acetic acid obtained by hydrolysis varies with different species of wood and does not bear direct relation to the amount obtained by destructive distillation. The amount of acetic acid obtained by hydrolysis is less than that obtained by distillation. It has been possible, however, to employ decomposition methods providing larger yields of acetic acid than have been obtained by destructive distillation. As

\[ \text{figures in parentheses refer to Literature Cited at the end of the report.} \]
one example, wood mixed with relatively large proportions of caustic soda at a sustained temperature of about 200° C. may be expected to yield as high as 15 percent of acetic acid (17). The composition of the wood therefore would appear to offer no obstacle in obtaining considerably increased yields of both methanol and acetic acid by suitable modification of the distillation process.

Other constituents of wood, such as "water solubles," "ether solubles," and the like, are of no great importance in wood distillation, since they occur on the average in but small amounts. In softwood material containing comparatively large amounts of resin, as the old stumpwood of longleaf and slash pines, the resinous fraction becomes important in itself and provides the basis for a special distillation industry.

Relation between Temperature and Decomposition of Wood Substance

One of the most important factors in wood distillation is the temperature at which wood begins to distill. Probably the first correct figures published concerning this temperature with relation to the decomposition of wood substance were by Chorley and Ramsay (5). Their data indicated that only slight decomposition occurred below a temperature of about 270° C. At this temperature it was shown further that the decomposition was very rapid, with the reaction subsequently becoming exothermic. In 1907, Klason (13, 14) and his coworkers repeated the experiments more accurately and in greater detail. The results obtained were similar to those of Chorley and Ramsay and included, furthermore, a computation of the amount of heat given off by the exothermic reaction.

As previously shown by Violette (30), experiments in distilling wood in a vacuum have shown that no apparent exothermic heat is obtained. Heating in a rapid current of superheated steam has the same effect as a vacuum distillation insofar as the rapid removal of the products from the retort is concerned. No exothermic reaction should be expected therefore under these conditions.

The decomposition of wood below a temperature of 270° C. takes place slowly and yields mostly carbon dioxide and water. The exothermic reaction begins at about 270° C. The decomposition of wood with formation of the ordinary distillation products proceeds to completion without further addition of heat. The residual charcoal, when heated to higher temperatures, progressively approaches pure carbon. The volatile products given off during the heating periods are mostly tar and gases with traces of methanol and acetic acid.

Klason made the initial measurements of the heat of the exothermic reaction, and provided the first partial explanation of the heat generated (12).
It was found possible, moreover, to conduct wood distillation to completion under very low pressure and regulated temperature without an exothermic reaction. The products formed by this slow decomposition varied from those obtained under normal distillation conditions. A transparent red oil accounted for more than 40 percent of the weight of the products from the low-pressure decomposition, and it was associated with below-average amounts of gas and charcoal. The red oil, when heated to about 275°C, decomposed exothermically, and formed considerable quantities of gas, water, a black tar similar to ordinary hardwood tar, and coke. This experiment indicates that the first decomposition of wood by heat is not exothermic, but rather that some of the primary products of the early distillation decompose exothermically when heated to a higher temperature. In ordinary processing, this distinction between primary and secondary reactions becomes meaningless, and it may be considered that commercial wood distillation is an exothermic reaction.

Temperature Control

Temperature control, as a means of increasing the yields of methanol and acetic acid, has been a subject of interest in the wood-distillation industry. Many years ago, Senfft (29) published information showing the effect of charging the wood into a very hot retort compared to charging into a cold retort. In nearly all cases, the distillation conducted in the very hot retort resulted in a higher yield of gas and lower yields of charcoal, tar, and acids. Methanol determinations were not made in his study. There has been some general opinion expressed among recovery-plant operators that higher methanol yields can be obtained by a slow distillation of 36 hours rather than by the conventional 24-hour cycle.

Palmer's experimental work on temperature control (23) showed that it is possible to increase the yields of acetic acid and methanol by modifying retort firing with relation to the retort vapor temperatures and the periodic composition of the distillate. It was found that, by firing heavily at the start of the distillation and then substantially less, the temperature was not carried excessively high by the exothermic reaction. Under these same conditions, he found it was possible also to complete the distillation in the usual 24-hour period with increased yields. The results of this work indicate strongly that slow distillations give higher yields and fast distillations give lower yields.

Such conclusions are probably correct under conditions of large-scale distillations with the accompanying superheating of the walls of the oven. It has been shown by Klason in the article previously mentioned, however, that these conclusions do not necessarily follow in connection with small-scale distillations. Klason distilled wood in a small glass apparatus under conditions varying from a 3-hour period at the highest possible vacuum to a 14-day distillation at ordinary pressures. From the results of this series of distillations it was possible to decide with considerable
accuracy which products were primary from initial decomposition of the wood by heat and which were secondary products obtained by decomposition or interaction of the primary products. It was shown that methanol and acetic acid were both primary products, and that the amounts formed did not vary appreciably with different conditions of distillation.

A fast small-scale distillation may be conducted without excessive superheating of the walls of the containing vessel or in such a manner that the walls of the vessel may be only 5° to 10° C. higher than the reaction temperature. This elevation of wall temperature is not considered sufficient to produce secondary reactions. In commercial practice, on the other hand, the cross section of the distillation unit is very large. In order to complete a distillation in 24 hours, it is necessary that the walls of the retort be heated 100° or 200° C. higher than the reaction temperature during much of the distillation. In commercial oven equipment, it would appear that the high speed of distillation is obtained only by the greatly increased temperature of the walls, and with sufficient superheating to produce secondary reactions.

**Influence of the Speed of Distillation on Yields**

Klason found that slow distillation produced more secondary reactions because the vapors remained in the retort for a longer period than during rapid distillation. In this case, the application of additional heat to the containing vessel for more rapid distillation did not have so much effect on the secondary reactions of the vapors as did the time the vapors were retained in the retort. Klason also showed that, within certain limits and conditions of distillation, it is not possible to vary the yields of methanol and acetic acid appreciably by variation of the speed of the reaction or the pressure at which it is carried on. This does not suggest, however, that it is impossible to increase yields in commercial oven practice by temperature control, since commercial plants obtain, on the average, about two-thirds of the acetic acid that can be obtained in similar small-scale equipment. Carefully managed plants obtain the apparent full yields of methanol. Temperature control thus appears of little importance in methanol recovery.

**Crude Products of the Destructive Distillation of Wood**

The foregoing discussion suggests that the complexity of the composition of wood and the character of its decomposition by heat might involve also a chemical reaction equally complex, with the formation of a variety of products. This is true with relation to the various chemical constituents of the products, but the less refined product fractions described in terms of the industry are limited in number. These crude products are charcoal, vapors (pyroligneous acid and tar), and gases.
Charcoal

The charcoal or impure carbon remaining as a residue in the oven is generally regarded as a finished commercial product, but without any precise classification of its chemical composition. It may be considered a very complex hydrocarbon that varies in composition between that of wood and pure carbon, depending upon the temperature to which the wood has been subjected. The commercial product generally contains 15 to 25 percent volatile matter. Klason considers ordinary charcoal as chiefly a primary charcoal with a secondary deposit of tar coke.

Charcoal designated as a marketable material requires only cooling prior to plant storage or shipment. In commercial practice, it is generally cooled for 48 hours in steel coolers with a subsequent conditioning period of 24 hours in the open or in open sheds.

Regardless of this cooling and air seasoning, spontaneous combustion may occur. It is unlikely that this combustion effect is caused by incomplete cooling or by sparks or brands remaining in the coal. It would seem most probably due to the heat generated when freshly made charcoal is in contact with the air. Under suitable conditions, the absorption of air by large amounts of charcoal would probably be sufficiently high to promote combustion. The possibility of combustion from heat formed by such contact would be remote, however, if the heat were rapidly dissipated. In large piles of charcoal through which circulation is difficult, this heat would have a chance to accumulate and increase the possibility for combustion.

Primary Vapors (Pyroligneous Acid and Tar)

The chemically valuable products of wood distillation are contained in the crude vapors. The condensed vapors separate on standing into a lower layer of heavier tar and an upper layer of crude pyroligneous acid. Density and insolubility are not sufficient, however, for the complete separation of these two products. Similar constituents are present in both the tar and the pyroligneous acid fractions. Practically complete separation can be made by fractional and other distillation procedures.

The crude pyroligneous acid is mainly water, methanol, acetic acid, and "dissolved tars." A more precise designation for "dissolved tars" would be "dissolved tar-forming materials," since in tar form they are insoluble in the liquor. Upon fractional distillation, a part of the liquor is separated from the higher boiling constituents and from the residue that is formed largely by the combination of the tarry compounds at higher temperatures. The soluble tar in pyroligneous acid is dissimilar in composition to that of the "settled" or insoluble tar, and consists chiefly of pitch and a small amount of oil.
Many other wood-distillation products have been reported present in small amounts in the pyroligneous acid. Several lists of such products have been reported \((4, 7, 10, 20, 27)\). The following list does not include products found mainly in the tars. An extensive compilation of distillation products occurring in both the pyroligneous acid and tar fractions from hardwoods and resinous woods shows well over two hundred products \((21)\).

- formic acid
- acetic acid
- propionic acid
- butyric acid
- valeric acid
- caproic acid
- crotonic acid
- angelic acid
- methylamine
- isoamyl alcohol
- \(\alpha\)-methyl \(\beta\)-keto-pentamethylene
- pyromucic acid
- methanol
- allyl alcohol
- acetaldehyde
- furfural
- methyl furfural
- acetone
- pyroxanthene
- methyl formate
- methyl propyl ketone
- pyridine
- methyl ethyl ketone
- ethyl propyl ketone
- dimethyl acetal
- methylol
- valero lactone
- methyl acetate
- pyrocatechin
- ammonia
- isobutyl alcohol
- ketopentamethylene
- methyl pyridine

The presence of some of these products may be recognized at times by the effect of the refining process on them. In the old acetate-recovery process, for example, when the pyroligneous acid is distilled in order to free it of dissolved tar, the acid is obtained as a straw-colored liquid and can contain only volatile products. However, when the distilled pyroligneous acid is neutralized with lime and evaporated, considerable amounts of nonvolatile tarry material remain with the residual acetate of lime. This tarry impurity could well be formed in part from some volatile constituents of the pyroligneous acid by decomposition and polymerization in the presence of lime.

Small quantities of oils also remain dissolved in the pyroligneous acid until it is neutralized and distilled. These oils have been separated from the distillate, and at some plants are known as primary oils or lime-lee oils. They are a source of raw material from which beechwood creosote may be produced.

The tar obtained in the distillation of hardwood was formerly used as fuel only. Later industrial practice included its treatment with steam to remove acetic acid and methanol \((10)\). The value of the tar at the present time is determined to greater extent by its use as a chemical raw material.

**Wood Gas**

The amounts of noncondensible gas formed during wood distillation vary. About 7,000 cubic feet per dry cord are produced on the average. The gas has a heating value of about 300 British thermal units per cubic foot.
and may be used as supplementary plant fuel. The gas fraction contains large quantities of carbon dioxide, which accounts for its relatively low heating value. Carbon monoxide and methane are its main combustible constituents. It is probable that smaller amounts of hydrogen and ethylene gases are obtained only as secondary products when the temperature of distillation is quite high.

Valuable products are lost with the gases passing through the condenser. An initial loss is in the mechanical carry-over of liquid in the form of fog or mist. Incomplete plant cooling cannot be the cause of the carry-over, since the fog persists even though condensers are cool and the vapors are presumably well chilled. Product losses are not readily avoided with heavy quantities of gas passing through the condensers.

Another source of loss in the gases is the vaporization of the low-boiling constituents of the distillate despite low condenser temperatures. The most volatile constituents are lost in greatest proportions. Because they are among the most valuable products of wood distillation, the lack of plant return from this source is substantial. Methanol, methyl acetate, and acetone are the chief products not fully recovered since they not only have low boiling points but also form constant-boiling mixtures that have lower boiling points than the pure products.

The loss due to drops of liquid mechanically carried over as fog can be reduced by scrubbers in which the gas is subjected to a countercurrent flow of wash water. More efficient recovery of products has been obtained by means of electrical precipitation. Some previous experiments with electrical precipitation in the gas line beyond the condenser gave evidence of fog dissipation and recovery of products otherwise lost. The material precipitated amounted to approximately 1.7 percent of the total distillate obtained at the condenser. The proportion of valuable products in the precipitator liquid is slightly different from that in the condensate. The proportion of tar to pyroligneous acid is about the same, but with somewhat less methanol in the pyroligneous acid from the precipitator than from the condenser.

Use of Scrubbers for the Recovery of the Low-Boiling Constituents Carried Off by the Gas

The loss of the vapors of low-boiling constituents entrained in the gas can be controlled to some extent by maintaining a lower condenser-water temperature. Another method is to treat the gas with a liquid in which the volatile products are soluble and have a lower vapor pressure. Water is a satisfactory scrubbing agent, since it is readily available and is a good solvent for the volatile products.
The amount of products recoverable by water scrubbing depends upon the amount of water and the efficiency with which it is used. With complete contact between large amounts of water moving countercurrent to the gas, it is possible to make added recovery of the vaporized products in the gas. There is a limit to economical recovery amounts, however, because water would be required in amounts so large that the cost of recovery from the water would be prohibitive.

In the operation of the early kiln plants, the residual nitrogen of the air and the volatile products of combustion were included with the normal amounts of gases and vapors given off from the distillation of the wood. Most of these kiln plants had gas-scrubbing apparatus in which pyroligneous acid was frequently used for the scrubbing material rather than water. This practice was inefficient, since the gas was being washed by a liquid of the kind with which it was already in equilibrium. In order that more efficient scrubbing might be conducted, the first fraction of liquor from the condensing system, which held smaller amounts of the low-boiling constituents, was used for the scrubber.

Interesting applications of the scrubbing principle may be noted from the old kiln-plant installations. Special scrubbing towers using fresh water as an extracting agent obtained increases in yields of methanol amounting to as much as 3 gallons per cord. In view of these increased yields obtained with a gas scrubber at a kiln plant, it would seem that a somewhat proportional increase could be obtained at the oven plants. Although the volume of gases is greater from the kiln plant, the concentration of the more volatile products is higher in the liquor from the oven plant. On this basis, it can be assumed that the product loss in the oven gas may be as great as in the kiln gas.

Several methods have been suggested for removal of the tars from the primary condenser liquid and gases at later steps in the processing. These methods include: the use of tar separators (11), in which the vapors from the retort are washed with liquid tar; a related scheme of tar extraction by wood oils (2), whereby the retort vapors are partly condensed and the tar-oil condensate is fed countercurrent to fresh vapors to wash them free of tar; heat treatment under pressure (21) to promote polymerization of the tarry constituents and precipitation of the polymerized tars from solution; and the more recent method of tar elimination from the pyroligneous acid by polymerization and condensation through addition of small amounts of sulfuric acid (22). However, the commercial methods most commonly employed are distillation of the raw liquor from the higher boiling tars, as already indicated, and demethanolization of this total condensate with subsequent treatment in evaporators for recovery of the tars.

Methods practiced by industry for the recovery of commercial products from the mixtures of wood distillates generally include only those for the production of acetic acid directly or indirectly as acetate of lime, for the production of methanol from the pyroligneous acid, and for separation of the different oils contained in the tar.
It has been indicated that distilling wood gives the two crude products, pyroligneous acid and tar; that density and insolubility are not sufficient for the complete separation of these products; that some constituents of each are found in the other; and that complete separation can be accomplished only by extraction or distillation. Initial plant operations vary, and may provide for either demethanolization of the total crude liquor or for the separation of the tarry material from the pyroligneous acid and the subsequent separation of the methanol and acetic acid from the pyroligneous acid and the settled tar.

Earlier equipment used in refining the mixtures of wood distillates were fired stills heated directly from a firebox beneath them. This type of still is now steam-heated, is much easier to regulate, and provides better results due to less superheating of the product.

**Products Obtained by Wood-tar Distillation**

Wood tars subjected to fractional distillation and other processes may be separated into various products that have distinctive chemical and physical properties. In the initial distillate from settled tar, the light oils with boiling points up to about 200°C have specific gravities less than 1.0 and contain practically no phenols. These light oils are very complex, and were the subject of early investigation by G. S. Fraps (7). He found that these oils contained groupings of aldehydes, ketones, and acids of the formaldehyde, acetone, and acetic acid series, with acids occurring mostly in the form of methyl esters. No exact quantitative determinations of the light oils were made, and the compounds identified probably constituted only a small proportion of the total oil.

The heavier oils have been studied in some detail also, with major attention given to their phenolic fraction. Numerous phenolic bodies have been detected, and the phenolic compounds appear to be either the straight phenols or methyl ethers of phenols. The results of later studies (31) provide fuller classification of the more important compounds occurring in the crude tar.

Considerable progress has been made over a period of years on the isolation and on the development of methods for the isolation of compounds from the so-called "soluble tar" portion obtained from pyroligneous acid. The investigators (8) report practical separation procedures for 15 compounds occurring both in this tar and in the acetic oil stripped from the acid-refining stills. These and other compounds have been reported, and in some cases identified, as present in some part of the heterogeneous water mixture from oven distillation.

Less extensive chemical studies have been conducted on the residual pitch. Its general properties, however, would indicate it to be very complex.
chemically. A hard or soft pitch can be obtained corresponding to the amount of heavy oils remaining undistilled in the pitch.

When wood tars are distilled with steam, a product known in the market as "wood oil" is obtained. This oil will vary in composition with the amount of steam and the temperature used in the distillation. It usually contains the light oils previously mentioned and also considerable quantities of the heavy oils with boiling points above 200° C.

Uses for Tar Products of Wood Distillation

Soluble and settled tars are obtained in relatively large amounts from wood distillation, and both are potentially valuable chemical base materials. As already noted, chemical products are commercially recoverable from the soluble tar. Settled tar, in addition to its use as a plant fuel, has several fairly good outlets. Commercial processing produces a creosote fraction, gasoline gum inhibitor, flotation oil, and various grades of pitch. Investigations have been made regarding its use as a natural-rubber softening compound. Fractionation of the tar oils yields light oils that have good solvent properties, and the heavier oils have been used as stains and disinfectants. Tar pitch has been reportedly used in rubber and phonograph-record manufacturing and as a waterproofing and insulating material.

Recovery of Acetic Acid

The method for the recovery of acetic acid is indirect, and provides gray acetate or acetate of lime as the plant product. This method, in association with refining steps developed for the recovery of methanol, has been traditional with the industry. Only one in the present operating group of recovery plants maintains facilities for the procedure, and it produces partially refined, directly marketable sodium acetate.

In conventional acetate of lime processing, the tar-free pyroligneous acid is neutralized with lime in order to form the nonvolatile salt, from which methanol is separated completely by distillation. The impure solution of acetate of lime that remains is evaporated and the salt residue is dried to the commercial product called "gray acetate of lime."

At first, this method was used on crude pyroligneous acid rather than on tar-free acid. After lime neutralization, evaporation, and drying, a product containing tarry impurities or "brown acetate of lime" resulted. Calcium acetate is more soluble in cold water than in hot, and it is not possible to crystallize this salt by the usual methods. Impurities also prevent the formation of good crystals when the solution is evaporated.
The finished material therefore is a gray granular powder without crystalline form.

Many factors in the neutralization of the distilled pyroligneous acid with lime have not been carefully studied. In practice, the neutralization was usually carried to a point that gave the most satisfactory acetate of lime. If the neutralization was incomplete or carried past the proper end point, difficulty was encountered in forming a granular acetate. A tendency resulted then for the material to separate out in a hard crust on the bottom of the evaporating pan instead of forming the usual granular crust on the surface of the liquid.

Since the pyroligneous liquor contains both acetic acid and methanol, it must also contain methyl acetate in an amount determined by the equilibrium between the quantities of water, methanol, and acid present. When pyroligneous acid is neutralized with lime, the methyl acetate is hydrolyzed to methanol and acetic acid. The acetic acid combines with the calcium in the lime to form acetate of lime in addition to that formed from the free acetic acid. This reaction takes place slowly. In most cases, there are considerable amounts of methyl acetate still undecomposed in the distillate. Slightly higher yields of methanol and acetic acid might be possible, therefore, if the hydrolysis went to completion before distillation of the neutralized liquor.

**Crude-Acid Refining**

**Removal of Soluble Tar**

A fairly common removal of the constituents forming soluble tar from the pyroligneous acid was by primary-tar still separation. In other plants, the same purpose was accomplished by using multiple-effect evaporators. The more efficient multiple-effect evaporators were applied generally at the larger plants, while the copper still, which was simpler and less expensive to operate, found use chiefly in the smaller operations. A common objection to the use of the evaporator was based on a tarry deposition on the tubes that probably resulted from the condensation of tar-forming constituents originally in the vapor state.

**Separation of the Methanol**

In earlier practice, the separation of the methanol from the neutralized pyroligneous acid was carried out by continued redistillation in a series of ordinary pot stills without a fractionating column. The first fractionating device applied to this type of operation was the so-called Burcey pans, by which a certain amount of fractional condensation was obtained. Little difficulty is encountered in producing crude 82 percent
methanol by this refining method. Column stills are now used where quality of product and larger production are important factors.

In the application of triple-effect evaporators, the neutralized pyroli-
neous acid is fed into a continuous column still for removal of the crude methanol, and the remaining acetate liquor is subsequently moved through the evaporators to recover the acetate of lime. Concentration of the methanol solution in continuous stills provided a more efficient procedure than crude distillation from the neutral acetate liquor in a lime-lee still followed by further concentration.

The first refined methanols were of poor quality and had both color and an off odor. This product was used largely as a solvent, which made it unnecessary to prepare an alcohol of high purity. While the color and odor were gradually improved, quantities of acetone still remained in the refined product. Methanol and acetone form a constant-boiling mixture that cannot be easily separated except by fractional-distillation methods. This constant-boiling mixture has such a high proportion of acetone, however, that it is possible to obtain very pure methanol by commercial distillation, although the acetone separated from it contains some methanol. Methyl acetate forms similar constant-boiling mixtures with both methanol and acetone. At the present time, natural methanol with only slight traces of acetone is produced in the industry.

Acetate of Lime -- Evaporation and Drying

Ordinarily, when distilled pyroli-
neous acid is neutralized with lime, a quantity of insoluble material settles out from the liquor. This sludge contains insoluble impurities from the lime and also insoluble organic bodies precipitated or polymerized by the neutralization of the liquid. This sludge was commonly discarded, but later methods employed mechanical filtration for removal of the acetate liquor it contained.

The methanol-free liquor from the lime-lee stills contained about 15 per-
cent by weight of calcium acetate. Some form of evaporation was first used, after which the concentrated liquor was run to a steam-heated drum drier for the formation of acetate sludge. The sludge was further heat-
treated in a Huillard-type drier to form granular particles.

The methods for the recovery of acetic acid and methanol outlined in the foregoing paragraphs have been largely replaced by modern and more efficient processing procedures. A description of these older operational methods here maintains intact a general account of the industrial processing formerly applied, and with it the opportunity of recording information of historical interest.
Destructive-Distillation Processes Using Sawdust and Similar Wood Waste

Many publications on wood distillation have described in some detail commercial methods for the destructive distillation of sawdust. None of the processes has, however, been commercially successful. Wood is a poor conductor of heat. Sawdust is quite possibly worse, since a mass of sawdust may contain many more closed air spaces that are less efficient conductors. A stationary mass of sawdust is, therefore, very difficult to distill conventionally because of retarded heat flow. It is essential for distillation that sawdust be put in motion, either by rotating a retort or by agitation within a stationary retort. Either type of mechanism requires a gas-tight sealer between the moving and fixed members.

Comparatively recent investigations (28) in the development of a continuous process for the carbonization of sawdust have been conducted with encouraging results. Extension of the results obtained would indicate the possibility of commercial production of at least 50 tons of charcoal briquets per day. The small-scale retort developed and applied in this work rotates horizontally with heat supplied internally.

Other current carbonization studies (6, 18) on the utilization of wood-waste "fines" involve processes in which the wood particles are held in fluidized suspension while subjected to heat.

Other Wood Carbonization Processes and Their Commercial Application

Briquetting Process

A number of years ago, one company avoided some of the difficulties of sawdust distillation by forming the sawdust into compressed masses for processing. Sufficient pressure applied to softwood sawdust gives a compact briquet without the use of binding material. Hardwood sawdust yields less firm briquets that readily disintegrate during distillation. With slight mechanical pressure applied during the distillation, the hardwood briquets remained fairly firm and satisfactory charcoal was produced.

Further development of this process included the formation of a larger briquet of about 4 inches in cross section. The units were fed from an automatic loader into tubular retorts approximately 20 feet long. Each of the tubes was provided with a piston exerting a continuous pressure of 8 or 10 pounds per square inch on the column of briquets during distillation. The small diameter of the tubes allowed each to act as a single retort, and the distillation cycle was completed in about 3 hours. The cost of raw-material preparation and specialized equipment, together
with limited capacity, was somewhat compensated for by higher yields and a shorter carbonization cycle. A small-scale commercial operation was conducted at a western location some years ago. No further operations have since been undertaken.

Sawtelle Process

The early Sawtelle process avoided some of the complications of sawdust distillation by combining the distillation of the wood with the production of producer gas from the charcoal. The operation was carried out by using an up-draft gas producer with the wood as fuel. In operation, the sawdust and fine chips form a cone-shaped pile in the gas producer, with the upper part of the mass in the drying stage, the next lower part undergoing destructive distillation, and the bottom charcoal layer in the process of being converted to producer gas. The heat required for distillation and drying is supplied by the hot gases. This process was reportedly successful at one time in a small-scale commercial gas producer. Additional details regarding this manner of processing are generally unavailable.

Stafford Process

This process utilizes essentially the smaller blocks and hogged or chipped forms of forest wood and mill waste, and makes full use of the reaction heat developed in wood distillation. The carbonization is conducted in large, well-insulated vertical tubes into which dry, warm wood is introduced at the top continuously. The heat of decomposition of the wood is sufficient to establish distillation conditions for an equal quantity of dry, warm wood without the addition of external heat. A substantial bed of charcoal is maintained at the bottom of the retort where partial cooling is accomplished prior to withdrawal continuously or at intervals. A large plant employing this type of processing was established in 1924 and has since maintained continuous production. Methanol and charcoal are the chief products being recovered at present. The latter product is of comparatively small particle size and requires little grinding preparatory to briquet manufacture. The entire charcoal output of this plant is used for the production of briquets.

Seaman Process

The Seaman process was developed and demonstrated in a commercial-size unit many years ago. The distillation equipment consisted of a rotating, inclined retort about 30 feet long and 3 feet in diameter. The hot, dry sawdust was charged at the upper end, and the charcoal was removed continuously from the lower end. The average yields of acetic acid were reportedly quite high and those of methanol somewhat low. There are no commercial operations employing this process at the present time.
Direct Acid-Recovery Methods

The heavier production levels of cheaper methanol and acetic acid from fermentation processing were largely responsible for drastic changes in the refining procedures of the wood-distillation industry. Because of the creation of less desirable markets for the wood-distillation products due to competition with increased production from other sources, it became necessary that more efficient refining methods be introduced for economical production at some of the larger plants. A procedure for direct recovery of acetic acid became, therefore, a logical step from the more costly and cumbersome lime-fixation method. Only the stronger plants were in a position to convert to the direct-recovery methods. Many plants less favorably situated were abandoned.

Several direct methods for recovering the acetic acid have been developed. All these processes begin with the pyroligneous acid and have in common the basic principle of solvent extraction applied to either the vapor or liquid form of the crude liquor. A few of the better known methods would include (a) the Albin-Suida process (1), in which a high-boiling, wood-oil solvent extracts the acetic acid from the vapors formed by distilling the liquor, and the solvent and the acetic acid are then separated by vacuum distillation; (b) the Brewster process (3), which makes use of a low-boiling solvent like ether to remove the acid by a liquid-liquid extraction; and (c) the Othmer process (20), which removes the water by distillation of a constant-boiling mixture formed by the acid with an appropriate organic compound such as butyl acetate or butyl alcohol.

Wood Carbonization -- Circulation of Heated Inert Gases

As early as 1921, Pearce (24) obtained a patent for carbonizing green wood by circulating heated, inert gases through the charge. Modifications and improvements of this type of processing were subsequently made by Reichert (16, 27) in Germany, Lambiotte (15) in Belgium, and by Pieters (25) in France. The processes of Pearce and Reichert have been commercially applied in Europe for some time, and provide operating techniques well in advance of the conventional oven processing commonly applied. A modified carbonization unit employing the principles of inert-gas recirculation has been operated on a semicommercial basis in this country for several years.

In general, these methods are similar and vary only in the direction of the heated gases through the retort and whether the retorts are continuously or discontinuously operated. In all cases, the inert gases are suitably supplied from the decomposition of the wood itself. In these operations, part of the wood gases, after leaving the retort, condensers, and scrubbers, are led to a burner furnace for combustion and tubular
heating of the remaining gases circulating through the retort. The heated gases move continuously to the wood charge as the circulating and heating medium. Because of the heat of reaction within the retort and the controlled heat of the circulating gases, additional fuel is not required to maintain unit carbonization in groups of several retorts.

Increased yields of acetic acid and methanol are reportedly obtained by use of these general methods. A factor of additional interest is the possibility of selective control of the charcoal volatiles by regulation of the retort and gas temperatures.

Since operations of this kind may be continuous and are assumed to be lower in both overhead and labor costs, it might reasonably be predicted that further developments of the industry might well be along these lines. The results of fluidized-bed and rotary-tube carbonization process developments already carried out on wood fines would indicate also an encouraging outlook for commercial carbonization and utilization in the wood-waste field.
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