Wood Distillation.

Part I, General

by H. E. Watson and J. J. Sudborough.

I. *Introduction.*

The manufacture of charcoal from wood appears to be one of the earliest chemical operations carried out by prehistoric man. In all probability the process was found out shortly after the discovery of metallic iron, as although the earliest iron appears to have been made by heating a mixture of wood with iron ore, yet specimens made at a slightly later date bear evidence of the use of charcoal in their manufacture.* In this connection it is interesting to note that the chief sources of such iron were Central and Southern India, so that there is good reason to believe that India was the first country to produce charcoal in any considerable quantities.

At a somewhat later period the art of wood distillation had made considerable progress, for it is on record that the Egyptians produced wood vinegar and tar and used them for embalming their dead.†

Coming to more modern times, the charcoal burner plays a considerable part in the myths and legends of all European countries, and, as far as can be ascertained, his method of carbonizing wood has persisted practically unaltered for centuries.

In this process the wood is built up into a stack, usually in the forest where it is felled. The exact design of the stack naturally differs from place to place, but the principle is the same in all cases. Generally speaking, the wood is carefully arranged in the form of a hemisphere or a paraboloid round a central core consisting of several vertical billets. The wood is packed tightly except for a few air passages, and when the stack is complete the central core is removed, forming a chimney, and the rest of the wood is covered with a layer of leaves or moss, and finally with a covering of turf or mud. The combustion is started by throwing several small pieces of burning wood into the chimney. As soon

* W. H Schoff, J. Amer. Oriental Soc , 1915, *35*, iii, 224.

† O. Vogel. Chem. Zeit., 1907, No. 82.

as the stack proper begins to burn, the top of the chimney is blocked up and the supply of air is very carefully regulated by removing portions of the outer covering. The air enters at the bottom, and the products of combustion are allowed to escape, first near the top of the stack and then lower down, until the whole mass is thoroughly charred. The progress of the combustion can be ascertained by noting the colour of the smoke. When carbonisation is completed, all openings in the stack are tightly closed with moist earth, and the whole is left to cool for several days. The stack is then opened up, and the charcoal collected.

In this process, the temperature attained in the stack is considerable, being frequently as much as 700°C, and the charcoal produced is of a high grade, possessing the following properties :—

a. Great density and hardness,
b. High calorific value,
c. High carbon content and very little volatile matter,
d. Is not easily ignited and burns with practically no flame.

On the other hand, the yield is small, being only about 20% on the weight of the wood charred, compared with some 30% obtained by the more modern closed retort processes. In the latter, however, a certain quantity of extra wood is required for fuel which reduces the nett amount, but even when allowance is made for this there is still a considerable balance in favour of the closed retorts.

The stack process is very convenient for producing charcoal to meet small local demands for domestic use or minor metallurgical operations. It requires no extensive organisation for the supply of wood or the disposal of products, a fair quantity of charcoal can be manufactured with a minimum amount of labour, and no capital is necessary, so that work can be carried on intermittently or to suit the season.

For these reasons the process is admirably suited to India and particularly to South India, where, owing to the lack of coal, charcoal is required in every village; consequently the number of charcoal burners is very large.

In modern processes of wood distillation the valuable by-products, which in the old stack process were usually allowed to pass into the air in the form of vapour, are collected and sold in the crude form or worked up into marketable derivatives.

To effect this, the wood is heated in closed iron retorts or occasionally in masonry containers. In nearly all cases the heating is external and the vapours and gases are led from the retorts by suitable outlet pipes into cooling coils or tubes made of copper, in which the greater portion of the vapours condense forming a dark coloured liquid. The uncondensed gas consists mainly of carbon dioxide (about 59%) and carbon monoxide (33%) with smaller amounts of hydrogen and various hydrocarbons. This gas has a nett calorific value of about 850 Cals. per cubic meter, and is usually burnt under the retorts, since it effects a saving of about one-third of the fuel required for the actual distillation. It may also be even more profitably used for the production of power by means of gas engines.

The most important by-product is the liquid collected from the condensers. If this is allowed to stand it separates into two, or under certain circumstances, three layers. One of these, the brown watery liquid, is known as pyroligneous acid, while the residue constitutes wood tar. The pyroligneous acid contains a certain amount of tar in solution, but consists mainly of an aqueous solution of acetic acid and methyl alcohol, together with a little acetone. More than 20 other substances are also commonly present, but in small quantities only, and are of very slight importance.

The tar is a complicated mixture, and differs very considerably in its composition according to the type of wood from which it is made. Tar from hard woods is heavier than water, and on an average not more than 35%, including 15% of water and acetic acid, is volatile at temperatures below 230°C; and 10 to 15% of the volatile oil boiling below 230° consists of cresote and guaiacol. On the other hand, tar from resinous woods such as fir is lighter than water, and about 60% is volatile below 230°, and this volatile portion consists largely of turpentine and resin oils.

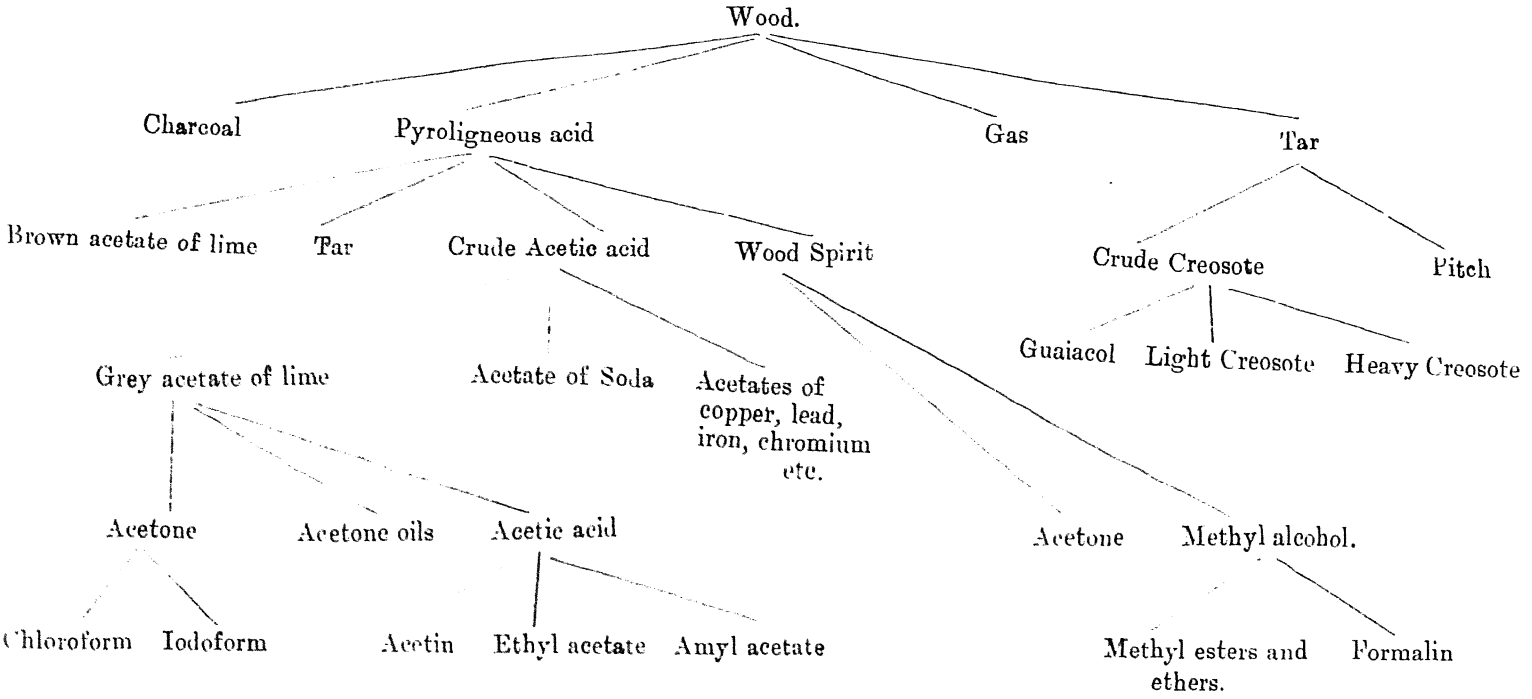
From whatever type of wood the tar is obtained it is separated into two portions, (a) the tar which settles out from the pyroligneous acid, and (b) the tar which is soluble in the pyroligneous acid. The latter is of little value, and is usually burnt under the retorts after removal of the acetic acid.

Diagram No. 1 shows the various products mentioned above, and also indicates some of the more important derivatives which can be manufactured from these primary substances.

The distillation of wood with recovery of by-products, although of comparatively recent origin, has now developed into an industry of enormous dimensions. The first factories to be

DIAGRAM No. I.

The Principal Products of Wood Distillation.



established contented themselves with the production of a crude acetic acid and acetates, in addition to the charcoal, as no use had been found for the wood spirit or tar, but now four main primary products are made *viz.*, charcoal, grey acetate of lime, wood spirit and tar. In many cases plant for the production of pure acetic acid and acetone is installed at the distillery, and other products derived from the primary ones are manufactured on an ever increasing scale.

It is estimated that about three million tons of wood are distilled every year throughout the world for the sake of the by-products, producing approximately 1,50,000 tons of acetic acid, and 35,000 tons of wood spirit. In the United States, whole forests are cut down, and the production in that country is about half that of the total. The industry has also assumed large proportions in Canada where half the remainder is distilled, while the remaining quarter is treated in Europe, mainly in Germany and Austria.

The greater portion of the acetate of lime is converted into acetic acid which is used in dye making, for edible purposes, and for the production of salts and other secondary products such as esters for which there is a large demand. Many of the salts are used in the dyeing industry, while the esters may be used for flavouring and perfumery purposes or in the synthesis of more complicated chemicals. Another most important product, obtained by the distillation of the grey acetate, is acetone which is largely used as a solvent, particularly in the manufacture of cordite, as well as being employed in the manufacture of chloroform and iodoform.

Within the last few years it has been found possible to make acetone from the starchy material of cereals by a fermentation process, and this has been largely developed owing to war conditions ; it is, however, difficult to say which of the two methods will survive in normal times.

Wood spirit is used in a partly refined form for the denaturing of alcohol, and for the preparation of varnishes, and enormous quantities are consumed in this way. Many thousands of gallons are carefully purified giving methyl alcohol, which is essential for the manufacture of many important dyes, and is the material from which formalin is made.

From the tar, drugs such as creosote and guaiacol can be separated and even the charcoal dust is now worked up into briquettes to be used as fuel.

Hence it will be seen that wood distillation, although not comparable with the distillation of coal, gives rise nevertheless to an extraordinary variety of products which are used in industries of all kinds. Many of these products must be regarded as indispensable for the manufacture of other articles, and it is certainly no exaggeration to apply to this important operation the term "key industry".

II. *Raw Materials.*

Any material of a woody nature will give on distillation charcoal and pyroligneous acid, but in practice only certain classes of wood are usually treated. These are (1) jungle trees which are useless for timber, (2) the branches, roots, and other waste portions of timber trees, (3) refuse from saw mills (4) waste products such as palm kernels, the outer portions of the coffee bean, and particularly the residues left after expression of the oil from olives.

With regard to size, finely divided matter such as sawdust, or the waste products just mentioned must be treated in special retorts, while very small branches of an inch in diameter or less, are usually used as fuel, as the charcoal is of little value. The maximum size on the other hand, depends on the time taken by the distillation. In the large American stacks, logs as large as 15 inches in diameter become completely carbonised. For the ordinary large sized retort in which the distillation takes about 20 hours, it is not advisable to use wood of greater diameter than 7 to 8 inches and anything larger than this must be split.

The length of the pieces of wood used is usually adjusted so that an integral number of lengths will fit into the retort or truck when placed end to end. A convenient length is about 2 to 4 feet, but longer lengths than this may be used when the wood is straight and uniform.

The quantity of moisture in the wood is of very great importance, and exercises a considerable effect upon the yield of by-products.

When freshly felled, wood contains much moisture and the amount varies with the kind of wood and the season at which it is felled, but on the average the quantity for the harder kinds of wood is about 40%. If wood containing this quantity of water is distilled, a very large amount of fuel is required, both for the original distillation, and for the subsequent redistillation and evaporation of the resulting pyroligneous acid. This extra fuel is about 55% of the amount required for the distillation of wood

containing only 20% of moisture. At the same time a retort designed for treating dry wood can only be used for a much smaller quantity of abnormally wet wood, as more time is required for distillation of the excess water and the time period for each charge is increased. Attempts to shorten the time by appreciably increasing the heat of the furnace result in damage to the retorts. Owing to this fact, the output of a factory may be very much diminished by the use of wet wood, while the working expenses remain the same, and it has been estimated that, for a given outturn, these expenses may be easily increased by 50% through using improperly dried wood.

A third disadvantage of wet wood is due to the fact that such wood gives a proportionately smaller quantity of acetic acid on distillation. Thus 167 lbs. of wood with 40% of moisture will give considerably less acetic acid than 125 lbs. with 20% of moisture, although the amount of perfectly dry wood is the same (100 lbs.) in both cases. The yield of charcoal is little altered, while actually a little more wood spirit is obtained, although this increase is not nearly sufficient to compensate for the loss of the acetic acid.*

It will thus be seen how necessary it is for economic working to make sure that the wood used is not unduly wet. On the other hand, it must not be too dry. If wood containing only 2% or 3% of moisture is heated in a retort, at a certain temperature a most violent reaction, almost approximating to an explosion, will set in, and even if the condensing plant is sufficient to cope with the sudden rush of gas which results, the temperature inside the retort will rise so high that there will be much decomposition, and the yield of products will be greatly reduced.

In practice it is found that wood with a moisture content of 15 to 20% is best for distillation in order to ensure a moderately quiet run. This quantity is practically the amount which is found in "air dried" wood, that is to say wood which has been cut and exposed to the atmosphere for a considerable period. In Europe and America the time usually allowed for drying is at least a year, but in India it would be less owing to the higher temperature.

The chief objection to the air drying of wood is the amount of capital necessary to stock a whole year's supply, and attempts have been made to dry the wood artificially. It has been found that this can be done in three days, but apart from the great danger of fire, the cost is so high that ordinarily

* See footnote p. 117.

the quick process of drying cannot compete with the other method. Suggestions have been made to utilise the waste heat from the retorts and other plant for drying purposes, but calculation shows that even if the whole of such heat could be utilised it would not suffice to reduce the moisture content from 40% to 20%. The most that can be done with practical success is to heat the air dried wood to about 100°C. by means of the waste flue gases before running it into the retort. In this way about 5% of the total fuel can be saved.

III. *The Chemistry of Wood Distillation.*

Very little is known about the actual chemical change which takes place during the distillation of woody tissues, a few facts, however, have been established.

The chief chemical constituents of woody tissues are the lignocelluloses and water. The lignocelluloses consist of lignin and cellulose in varying quantities, and it is from these two substances that the various by-products are derived.

Lignin is less stable than cellulose and in the estimation of cellulose in tissues is usually decomposed by chlorine, bromine or hydrogen peroxide. The actual products present in the distillate are probably not the primary products of decomposition of the cellulose and lignin molecules and it is impossible definitely to state the manner in which such simple substances as methyl alcohol and acetic acid are obtained from the complex molecules of cellulose and lignin.

P. Klason, Heidenstam and Norlin* appear to have established the fact that if wood, represented by the formula $C_{42}H_{66}O_{28}$ is heated to 400°C, the reaction up to 275° is endothermic and heat is absorbed, at 275° the reaction becomes exothermic and heat is evolved. The complete distillation is exothermic, the heat evolved being about 6% of the total heat of combustion of the wood distilled. The cellulose gives acetic acid and no methyl alcohol, while the lignin gives both, so that the proportion of these two substances in the distillate varies considerably with the variety of wood distilled. The charcoal formed at this temperature, excluding the ash, has the empyrical formula $C_{16}H_{10}O_2$, that is to say, it contains only 82% of carbon. In addition there is a large amount of decomposition into water, carbon monoxide and carbon dioxide.

* Ark. Kemi Min. u Geol., 1908 3, 9.

In the ordinary closed retort the highest temperature reached is usually about 400° and the reaction may be divided into three stages :—

1. Up to 170°. The evaporation of the water in the wood by means of external heat.

2 From 170° to 275°. Further heating of the wood combined with some decomposition, and evolution of carbon monoxide and dioxide. Acetic acid is formed, but very little methyl alcohol or tar.

3. Above 275°. The exothermic reaction. The temperature may rise to 400° or even higher. Large quantities of gaseous hydrocarbons are evolved together with much acetic acid, methyl alcohol and tar.

In some cases, for instance if the wood is very moist, it is necessary to supply more heat at the end of the third period to bring the charcoal to a sufficiently high temperature, otherwise the carbon content will be low. Charcoal which has been heated to 330° is not properly black, and contains only 73% of carbon. At 350° this figure rises to 76·5%, and at 400°, as already mentioned it is about 82%.

When the wood is allowed to cool in the retorts, a fourth stage may be added to the above, namely the adsorption of the gaseous hydrocarbons by the charcoal, followed apparently by decomposition when so absorbed. In this way the carbon content of the charcoal may be quite appreciably increased.

It will be observed, that in the third period, the greatest amount of gas of high calorific power is given off, and it is just at this stage that external heat is not essential, consequently it is fundamentally wrong to burn the gas under the retort from which it is being evolved. It should be used for heating another retort at a different stage, or for power producing purposes.

The following description given by Juon* applies to a large Ottelinska kiln (class 1 p. 90) in which the hot gases from an external furnace pass through the kiln, and illustrates the fact that the distillation proceeds quite differently when the type of retort or kiln is altered. At temperatures below 200°C the liquid which distils over is mostly water, and the gases, the volume of which is relatively small, consist of carbon dioxide (68%), carbon monoxide (30%) and hydrocarbons (2%). At temperatures between 200° and 280° acetic acid vapour accompanies the steam, and the gas, the volume of which in still small, has much the same composition as before. Between 280° and

* E. Juon. Stahl u. Eisen 1907, 733.

380° the volume of gas is large, the percentage of hydrocarbons is about equal to that of the carbon dioxide (35 –36%) and the calorific value of the gas increases appreciably; wood spirit and light tars also pass over with the water and acetic acid. At temperatures between 380° and 500° heavy tar appears in the distillate and the percentage of hydrocarbons in the gas increases further (49%), if the temperature is increased to 700° the gas becomes rich in hydrogen and large quantities of tar and paraffin are obtained in the distillate.

The substances mentioned among the primary products undergo considerable decomposition before leaving the still, and one of the chief problems in wood distillation at present is to increase the yield of valuable products by reducing to a minimum their decomposition in the still to more or less valueless substances.

Acectic acid is comparatively stable, but it appears probable that at temperatures in the neighbourhood of 300°, and especially when it is in the nascent state, i. e. just being produced, it is acted upon to some extent by steam. This reaction would certainly be accelerated by contact with a substance presenting a very large surface, such as charcoal. It is quite possible in commercial working for the three stages of the decomposition mentioned above, to take place concurrently. If for example, a large moist log is rapidly heated, the surface may have reached the exothermic stage, before the interior is dry. Under these conditions much steam will be evolved, and will come in contact with the hot, newly formed acetic acid and decompose it. The result is a greatly increased yield of gas, and a decreased yield of acid. This is commonly found in practice when the wood is too moist and the firing too rapid. Consequently an attempt should be made to complete the first stage of the reaction before the third one starts. In addition to the steam given off in the first stage, a certain amount is evolved in the second stage, but this does not appear to have such an adverse effect upon the yield of acid, possibly because of its dilution with other gases.

In contrast to acetic acid, methyl alcohol does not appear to be decomposed by an excess of superheated steam, but unregulated heating of the contents of the retort has an enormous influence on the yield, and if the wood is very slowly dried, so that the subsequent exothermic reaction is so violent that temperatures much above 400° are attained, the quantity of methyl alcohol given off is very small. By carefully controlling the

violence of the exothermic reaction, however, a much higher yield may be obtained. For example, R. C. Palmer,* by careful regulation of the temperature in a retort of the ordinary commercial size, was able to obtain 30% more methyl alcohol and about 6—10% more acetic acid than is usual with the same woods distilled in the ordinary way.

The primary products, as they make their way through the hot still and outlet pipe into the condenser, undergo secondary decompositions. This is shown by deposits of carbonaceous matter on the walls of the still and in the pipe. This deposit is a source of considerable trouble, and even the largest outlets require frequent cleaning to prevent their becoming completely blocked. In large retorts it is now customary to provide two outlet tubes one near each end so that the gases have to traverse a comparatively short length of heated surface. The result is a considerably increased yield of by-products. In some installations an exhaust fan is fitted with the object of removing the gases in the retort as rapidly as possible, the pressure in the retort being kept a little below that of the atmosphere. This system appears to be based on a fallacy, as the gases do not move appreciably faster and it has the disadvantage that if there is any leak in the retort, air can enter and cause local combustion.

In addition to losses of alcohol and acetic acid, a too rapid heating may cause a diminution in the quantity of charcoal. E. Juon† has shown that in large masonry ovens in which the temperature may reach 700° or more, a large proportion of the gas evolved above 500° is hydrogen, while the quantity of carbon monoxide also increases, indicating a certain amount of decomposition of the charcoal by steam. This reaction probably takes place to a smaller extent in lower temperature distillations especially when local overheating occurs.

It is clear that there is still need for further research, especially in the direction of the reactions which take place in the retorts, and it is probable that further investigation will result in an increase in the efficiency of this important part of the operation.

Although much of what has been stated in this section may appear to be of little or no interest to the practical wood distiller, in reality many of the points mentioned are of vital importance. The facts prove beyond doubt that, for the purposes of recovery of high yields of wood spirit and acetic acid it is essential

* J. Indus. & Eng. Chem., 1915, *7*, 663.

† Stahl u. Eisen, 1907, 733, 771.

that the distillation should take place *slowly and that high temperatures during the course of the distillation should be avoided.* This may be accepted as one of the most important conditions which the distiller must keep in mind. It is necessary to remove a considerable portion of the water present in the wood before raising the temperature to 275° and when this temperature has been reached, the firing of the retort must be carefully regulated by means of the dampers, so that less external heating takes place during the stage when heat is developed by the decomposition of the wood itself.

IV. Modern Retorts.

The retorts used at present for distilling wood may be divided into five classes:—

1. Kilns of large capacity, worked intermittently.
2. Small fixed retorts discharged by hand.
3. Small portable retorts.
4. Large retorts or ovens with separate coolers, and mechanical handling of the wood in trucks.
5. Continuous mechanical plant.

1. The first class of retort is usually constructed of masonry in the form of a truncated cone or dome, and may be as much as 24 feet in diameter and 18 feet high, holding 150 tons of wood. The heating is effected by the combustion of a portion of the wood, just as in the old fashioned stacks, the only difference being that the by-products are collected. The large American or Meiler ovens are of this type, and are stated to be economical to erect and to work. As in this process an appreciable portion of the wood in the kiln is lost by the process of combustion, it has become customary in certain districts to burn low grade material, such as sawdust or twigs, in an external furnace adjoining the kiln and to admit the hot products of combustion to the bottom of the kiln. The Schwarz oven and its modifications, *e. g.*, the Ottelinska, which are extensively used in Sweden, are examples of this type. In such ovens it is essential that the hot gases shall be evenly distributed through the wood. This is usually accomplished by admitting the gases into the kilns through a branching system of channels with openings at the bottom of the kiln and erecting several chimneys attached to the periphery of the kiln.

Enormous retorts of this class have actually been constructed of sheet iron, heated externally by flues and internally by

pipes through which hat gases pass ; their cost however, is very high.

Kilns of the dimensions indicated have usually been erected where immense quantities of charcoal are required for the production of iron or for other metallurgical operations and the yield of by-products is unimportant, but they appear to be falling into disuse because of their inefficiency and the difficulty of controlling the distillation.

2. The second class of retort consists of a sheet iron cylinder, usually horizontal with a door at one end, and an outlet pipe at the other. It holds from 1 to 2 tons of wood, and two or more such stills are generally set in a system of flues from an external furnace.

Distillation occupies about 12 hours, and soon after the flow of distillate has ceased, the door of the retort is opened and the charcoal raked out rapidly into an airtight iron box which is immediately closed.

Most of the German, Austrian and Russian, as well as the older British installations are on this system. As opposed to the last (No. 1) it is characterised by being nearly continuous in operation, as the retorts after discharging are at once refilled without cooling.

3. The third class of retort is made of iron and is similar to the last, but it is suspended by a flange vertically in the furnace. It is attached to the condenser by an easily broken joint, and when the distillation is finished the condenser is disconnected, the whole retort lifted bodily from the furnace by means of a crane and carried away to the cooling house, and a fresh retort previously filled with wood is immediately put into the place it formerly occupied. When the retort is cool, the lid is taken off, the charcoal removed and fresh wood introduced.

This retort is chiefly used in France, Belgium and Italy. It usually contains about 2 tons of wood, since larger sizes are difficult to manipulate owing to their increased weights. The chief advantage which this type possesses is that the charging, owing to its being carried out cold, can be more carefully controlled than in a hot retort, and consequently very little space need be wasted. On the other hand, the continual movement, and sudden changes of temperature greatly shorten the life of the retort and the furnace, and thus materially increase the renewal charges of the factory.

On the Pacific Coast of America this type of retort is modified by having an openwork iron basket fitting into the retort. This basket is filled with wood, lowered into the hot retort and the retort cover bolted on. After distillation the basket containing the charcoal is lifted into a cooler and a fresh basket introduced into the retort. It is claimed that by this means considerable saving in wear and tear of retorts and furnace and also a saving in fuel are brought about.

4. The fourth kind of retort is being largely used in modern installations as it is the most economical, and gives the highest yield of by-products, as well as charcoal of very good quality. The retort proper is a horizontal iron cylinder made of stout boiler plates well rivetted, is about 45 feet long and 6 feet in diameter, and holds about 12 tons of wood. This is set in a furnace, fitted at the ends with doors which are closed by means of nuts and bolts. The escaping gases are carried off by means of wide exit tubes at the top. Along the bottom of the retort run rails which carry the four trucks upon which the wood is loaded.

Opposite the retort proper stands another similar iron cylinder which is used for cooling purposes. As soon as the distillation is completed, the door of the retort is opened and the trucks, carrying the charcoal, are drawn out of the retort and into the cooler by means of an electric motor or other mechanical contrivance. The door of the cooler is shut, and a fresh charge of wood, ready loaded on another set of four trucks, is run into the retort. With proper care the whole of this operation can be carried out in half an hour, and as it is usual to arrange for the distillation to occupy the remainder of 24 hours, it will be seen that the process is practically continuous. The loss of charcoal by combustion while passing from the retort to the cooler is quite negligible owing to the very short time (a few seconds) required for the transference.

The trucks consist of an iron frame-work which fits fairly closely into the still and runs on small wheels. The openwork structure allows of the escape of the gaseous products from all sides and a close fit is necessary in order that space may not be lost.

In some factories the loaded trucks are placed in a preheater before being run into the retort. This heater is also an iron cylinder and is heated by the waste flue gases. This preheating serves the purpose of removing a small amount of moisture and at the same time heats the wood before entering the retort proper, and both these mean a slight saving in fuel costs.

The cooler may be either left to cool slowly in the air or may be cooled by allowing cold water to run over it.

5. The last type of retort is one in which the operation of distillation is continuous. Such retorts are generally only used for the treatment of special classes of materials such as sawdust, chippings, waste from dye wood or tan wood extraction factories, and the residue from olive oil presses and are consequently not of wide application. The general principle is that the wood is carried through the furnace on a mechanical conveyor and distilled during its progress. Many different means of effecting this have been devised, but it is not proposed to describe them in detail. The retorts are all complicated, wear out rapidly and the yield of by-products from the class of wood dealt with is very low. Continuous retorts for dealing with cord wood have also been invented, but the same remarks apply to them.

Whichever type of iron retort is used, considerable care is required in setting it in its furnace so that the best results can be obtained. It is essential that the arrangements are such that the wood in the retort is heated as uniformly as possible and it is also necessary that no portion of the retort should be directly heated by the flames from the furnace, as this produces over heating and a burning out of a number of plates and necessitates continual repairs or even complete replacement of the retorts. The heating is always carried out by hot gases and so arranged, whether the retort is of the vertical or horizontal type, that the gases come first in contact with the bottom of the retort. As this necessarily means that the lower part of the retort gets worn out first, horizontal retorts are so set that after a time they can be moved round with readjustment of exit pipe so that the top becomes the bottom.

Various devices for the even distribution of the hot gases around the retort have been adopted and although the description of these may appear simple, the actual accomplishment of an even heating, upon which the success of the distillation largely depends, is always difficult to attain. Spiral shaped flues have been used but do not appear to be very efficient. A method highly recommended is to carry the hot gases along a fire brick channel just below the retort and allow them to escape through numerous small holes in the roof of the channel so that the retort becomes heated at a number of different points at the same time.

In setting a retort in a furnace it is advisable to keep all the weight off the brick work. This is accomplished either by hanging the retort by means of rods from I beams or by using

lugs on the retort and placing iron pipes or posts under the lugs, in all cases allowing for the expansion of the retort. As the masonry around the retort shows great tendency to crack, the walls should be tied through and through with long rods.

The chief factor which decides the capacity of the retort to be used is the length of time which is to be taken for completly charring the charge. This can vary from twelve hours for a small retort to twenty days for big kilns. Before deciding the relative dimensions of the retort several points have to be considered. It is obvious that the wood in a long, narrow cylinder would be much more uniformly heated that in a short, broad cylinder, as in the latter case the wood in the interior would be only just warm when that close to the walls was already well charred. The long, narrow retort, on the other hand, has the disadvantage that the products of distillation have to traverse a considerable length of heated surface before leaving the retort and hence the amount of decomposition of the acetic acid would be high. To minimise this decomposition numerous exit tubes would have to be attached to the retort. The tendency on the whole has been to increase the ratio length / diameter and to provide at least two exit tubes. At one time a common dimension for a retort was 9 feet x 4 feet, whereas now stills 45 feet x 6 feet are frequently used.

Attention has already been drawn (p 89) to the deposit of hard carbonaceous matter in the outlet pipes and retorts. The deposit has to be removed from the outlet pipes as otherwise their capacity for carrying off the vapours becomes less and they may ultimately become completely choked. The interior of the retort must also be scraped down periodically, otherwise the incrustation becomes thick, especially at the botttom, and as carbon is a bad conductor of heat, the retorts lose in efficiency and the risk of burning out increases.

In section III attention has been drawn to the great need of temperature regulation during the course of the distillation. In some large retorts temperature readings are made regularly at one or two points in the retort by means of thermocouples. The retort is provided with iron tubes reaching to the middle of the retort and closed at their inner ends, and in these the thermocouples are inserted.

V. Methods of Working up the Primary Products.

The actual products obtained from the retorts by the distillation are: —

1. Charcoal. 2. Wood tar. 3. Pyroligneous acid and 4. Wood gas. The gas is used directly for heating purposes

and the charcoal when removed from the coolers is in a marketable form.

The tar and pyroligneous acid, on the other hand, require further treatment before they can be regarded as saleable articles. The working up of these two products is carried out in the distillery as the freight charges on the crude pyroligneous acid would be too high to admit of its removal to a refinery at any distance from the distillery.

The methods of refining have now reached such a state of efficiency that in certain factories the conversion of the crude product into the pure material entails a loss of only one per cent. Improvements in the refining plant have also led to the reduction of the fuel consumption to about a third of its value when working with cruder plant. Such results are only to be obtained at the largest establishments, working with the most modern plant, a description of which is beyond the scope of the present paper. It is only proposed here to give a brief account of the plant necessary for producing grey acetate of lime, acetate of soda, acetic acid, and wood spirit at the distillery.

The vapours, on leaving the still, are led through short wide pipes into the condenser. In factories where one condenser is used for several retorts the wide exit pipes from each retort lead into a main channel and in order to prevent the vapours from one retort passing into another, each exit pipe dips under a layer of distillate in the main channel. All pipes should be made of copper or cast iron and should be sufficiently wide to be easily cleaned.

The types of condenser which have been adopted are the worm, the box and the tubular. The worm condenser has to be fairly wide in order to take the large volume of vapour and is somewhat inefficient as in a wide tube the gases not in contact with the walls of the tube take an appreciable time to cool and hence a considerable length of worm is required. The worm suffers from the further disadvantage that it is very difficult to clean. The box type does not suffer from this defect, as the wide condensing tube is bent on itself several times ; the straight lengths of pipe are enclosed in a box through which the cooling water passes, but each return bend is outside the box and is fitted by a flange joint to the straight lengths and is thus easily removable for purposes of cleaning. As the vapours condense, the volume of gas passing through the condensing tube diminishes and hence the diameter of the tube can be gradually lessened in both this type of condenser and also in the worm condenser. A modification of this form of condenser consists in surrounding the copper

condensing tube with a wider iron cooling tube and passing a current of cold water between the two tubes and in a counter direction to the hot gases. In this modification also the return ends of the condenser tube are not cooled and are attached by flange joints to the straight tubes. The connection between the different lengths of cooling tube is by means of short connecting pieces.

In the tubular condenser the tubes are of much smaller diameter and a number are attached to a dome shaped top into which the vapours from the retort pass, and to a box at the bottom in which the condensed liquid collects and passes into a separator. The whole of the interior part is made of copper and is placed in an iron or wooden vessel through which cold water is passed from the bottom to the top. The dome must be sufficiently large to distribute the vapours, as they enter, without producing a back pressure.

The outlet tube from the condenser is attached to a separator in which the condensed liquid collects and can be run off automatically whilst the uncondensed gases are led away by a pipe.

Condensers should be carefully designed in order that they may work efficiently with the vapours from the particular retort to which they are to be attached, a point too frequently neglected.

It is very important that the condenser should cool the liquors thoroughly, otherwise an appreciable quantity of acetic acid, and even larger amounts of methyl alcohol are carried away with the permanent gases. For instance, it has been shown * that, if during the violent exothermic reaction, the liquors are only cooled to 38°C (100°F) a temperature which is frequently the minimum obtainable in some parts of this country, about 5 % of the acetic acid and 45 % of the alcohol remain uncondensed. It is therefore, absolutely essential in India, to pass the gases which leave the condenser through a scrubber, or tower filled with coke or stones, down which water or weak pyroligneous acid is running. With an efficient scrubber of this type nearly all the acid and alcohol can be recovered.

The condensed liquor is run into a series of vats in which it is allowed to settle. In Europe these vats are usually of wood and as the weight of distillate is roughly 50 per cent of the weight of the charge of the retort, their capacity should be

* J. C. Lawrence, J Soc. Chem. Ind., 1918, *37*, 137.

not *less* than about 350 gallons for every ton of wood distilled daily in order to allow for three days' storage. A seven days' storage is sometimes recommended.

After standing two or more days, the clear pyroligneous acid is run into a copper still heated by a steam coil and provided with a small fractionating column. On warming, practically all the methyl alcohol, together with some acetic acid pass over first and are collected separately. Acetic acid and water distil next, while a residue of tar is left in the still. The latter is usually run into another still where steam is blown through it until all the acetic acid is removed. The final residue is of a nature different from the tar insoluble in the pyroligneous acid, and is usually burnt. The crude methyl alcohol is neutralised with lime or sodium carbonate and redistilled in a still with a fractionating column. The distillate is commercial wood spirit, while a solution of calcium or sodium acetate remains behind.

This solution is added to the bulk of the redistilled acid, and the whole neutralised. Usually the solution is set aside for several days in wooden vats to clarify and is then concentrated. For this purpose, the simplest type of plant is a large steam jacketted pan in which the solution is boiled down until it becomes semi solid. The pasty mass is then removed and the drying completed either on iron plates heated by the furnace gases, in special steam pans fitted with a stirrer, or by means of a revolving steam heated drum. In the case of acetate of lime the drying temperature must not exceed 150° as decomposition takes place at higher temperatures. The product is finally ground and forms the commercial grey acetate of lime. In the case of the sodium salt, the simplest method of obtaining a pure product is to stop the first evaporation just before the solution begins to get solid, and run the liquor into a cast iron pan fitted with a mechanical agitator, and heated over a free fire. The acetate first dries and then melts. If the temperature is raised to about 280° all the tarry matters are decomposed and charred, and the resulting mass when treated with water gives a nearly colourless solution with solid matter in suspension. The latter can be easily removed, and the solution allowed to crystallise.

According to the method just outlined, the crude pyroligneous acid is first redistilled, and then evaporated. This requires a considerable amount of fuel, in fact, if the fuel used is wood with a calorific value of 3500 calories working at 50 % efficiency, the following amounts of fuel would be required for each 1000 lbs of wood distilled :—

Original distillation	150 lbs.
Redistillation of crude pyroligneous acid...	154 lbs.
Concentration of acetate of lime to pasty consistence	112 lbs,

making a total of say 420 lbs in addition to the combustible gases from the retorts.

Great economy would be effected if the original condensation could be conducted so as to produce a clear distillate free from tar, as the manufacture of grey acetate of lime would then consist of a simple neutralisation followed by evaporation, but so far there is no process for doing this which is altogether free from objection.

The methods described above are comparatively simple, and in England a plant operating in this way would be placed in charge of a foreman. Directly attempts are made to economise fuel, the plant becomes more complicated, and more expert supervision is required. It is probable that in this country the extra charges for establisment, interest on capital, depreciation, and patent licenses would far more than out-weigh the saving in fuel.

Acetic acid in a comparatively pure form, is not, generally speaking, one of the substances turned out in situ in a wood distillation factory, but rather a product of the refinery. It is proposed, however, to give a brief outline of its preparation, owing to its importance in the east for use in the rubber industry, and also, in order to show that the process is by no means a simple one.

Acetic acid attacks all the commoner metals when exposed to the air, but copper is not affected in absence of air, hence it is usual to make all vessels in which acetic acid is to be treated of thick copper. For the purest kinds of edible acid, silver outlet pipes and condensers are necessary, so that the outlay on plant is considerable, and the depreciation of the copper vessels if not in continual use, is very heavy.

The simplest and oldest way of making acetic acid is by treating acetate of soda with sulphuric acid. If the crystals are used and the whole distillate collected together, the product is an acid of about 50 per cent. strength. A more concentrated acid can be produced by using fused sodium acetate. The acid is finally redistilled in a steam heated copper still to remove impurities. This method is never used now except for making edible acetic acid, owing to its high cost as compared with other methods.

Ordinarily, grey acetate of lime is used as the starting material for making acetic acid. There are two main methods of treatment, (a) with hydrochloric acid, and (b) with sulphuric acid. In the first case the acetate is mixed with the acid in wooden vats or masonry pits and allowed to stand for twelve hours. The liquid is then run into a copper still, and heated either by a free fire or by steam coils. The liquid which distils contains 40 to 45 per cent. of acid, and contains chloride, while an appreciable amount of acetic acid remains behind in the still. This method would probably be impracticable in India for the present owing to the high price of hydrochloric acid.

The sulphuric acid process, which is now the most largely used, requires more expensive plant owing to the fact that calcium sulphate is insoluble, and when acetate of lime is treated with sulphuric acid a pasty mass is formed. Consequently mechanical stirrers are necessary and these require a considerable amount of power to drive them. A cast iron pan, fitted with such a stirrer and heated by free fire is used, and the acetate mixed with concentrated sulphuric acid. The acetic acid which distills contains about 75 per cent. of acid, but it is also contaminated by considerable amounts of oily matter and sulphur dioxide, which result from the reaction of the tarry matter in the acetate of lime with the sulphuric acid. This decomposition involves the use of about 15 per cent. excess of sulphuric acid over the theoretical quantity.

A great improvement in the sulphuric acid process has been effected by the use of a vacuum still which may be heated by steam. Owing to the lower temperature of the reaction, very little decomposition of tarry matter takes place, the product is much purer, and less sulphuric acid is required.

Another interesting method is that of Behrens. This consists in dissolving the acetate of lime in acetic acid, and then treating with sulphuric acid and filtering off the calcium sulphate. This has the advantage of dispensing with the rather complicated vacuum apparatus, but the stages of the operation are more numerous. Both these methods give a fairly pure 80 per cent. acid.

The acid obtained by any of the above processes is ordinarily rectified by distillation in a still with a fractionating column. The latter is frequently constructed partially of porcelain, although in view of the brittleness of this substance, its use is of questionable advantage as compared with copper. Theoretically, acetic acid and water can be completely separated by fractional distillation, but in practice this is not the case. It is almost impossible by fractionation to obtain concentrated acetic acid from

a solution containing 10 per cent. or less of acid even with very great expenditure of fuel; consequently it is usual to put the acid on the market in two forms (1) 98 % "Glacial Acetic Acid". (2) 30 % "Commercial Acetic Acid." 100 lbs. of 80 % crude acid will give about 68 lbs. of the former and 27 lbs. of the latter, whereas 45 % acid will give 21 lbs. and 76 lbs. respectively. The great superiority of the sulphuric acid process over the hydrochloric acid method, when glacial acetic acid is the product chiefly required, is thus evident. By another rectification each 100 lbs. of the 30 % acid may be separated into 20 lbs. of 90 % acid and 80 lbs. of 15% but this is seldom done owing to the small demand for the latter strength of acid.

Finally the glacial acid is frequently redistilled to remove impurities, and slightly increase the strength.

It is evident that all these operations require a considerable amount of fuel. The quantity naturally varies very greatly with the exact type of plant used, but a rough estimate for a factory working the sulphuric acid process without a vacuum is about 5 cwt. of good coal for each ton of acetate of lime treated.

VI. Wood Distillation in India.

India's immense forests and her comparatively cheap labour would, at first sight, give the impression that the country is an ideal one for wood distillation on an enormous scale.

Before such a conclusion can be justifiably drawn the industry must be carefully studied in all its aspects.

Dealing with the question of materials most suited for the wood distiller there is no doubt but that ideal sites for distilleries would be :—

1. In or near plantations where high grade timber is felled. An example of such a plantation is the teak plantation in Nilambur, S. Malabar.

The large trees are felled and all sound timber sold as such. At present the greater proportion of the loppings etc. are left on the ground to rot. The only cost in such a case would be the sawing of such waste into pieces of suitable size for the retorts and the cost of carting to the actual factory.

In such plantations the wood removed in the course of thinning would also be available.

The cost of such wood should be appreciably lower than that of jungle trees cut for the purpose of wood distillation only.

2. Plantations of special types of timber grown for the purpose of wood distillation, These should be species which grow quickly and give a good charcoal in addition to fair yields of by-products. Species suited for S. India appear to be casurina and for higher altitudes blue gum. In the case of different species of blue gum the recovery of the essential oil from the leaves could be carried out side by side with the distillation of the wood.

3. In large virgin forests. In working such a jungle for obtaining material suitable for wood distillation, attempts should always be made to dispose of as much of the big valuable trees for timber purposes as possible and to use the loppings of such trees and all materials unsaleable as timber for the retorts, otherwise the whole cost of felling and sawing large trees would have to be borne by the factory. Materials too small for the retorts can always be burnt in the furnace for heating the retorts. All the sawdust and waste can also be burnt for the same purpose in a specially constructed furnace.

It should be borne in mind that when only one species of wood is used in a factory then the charcoal obtained is all of the same grade. Teak and casurina give excellent charcoal. Certain jungle woods, on the other hand, produce a soft, light charcoal of inferior quality.

In all cases the transport charges would be one of the chief factors controlling the cost of the wood. To reduce transport costs a system of light tramways for carting the wood from the forest to the factory would probably be necessary.

The following figures will give some idea of the gross receipts which could be realised by a factory distilling 6000 tons of wood a year. The saleable products turned out by such a factory would be (a) charcoal (b) grey acetate of lime (c) wood spirit and (d) tar.

The London pre-war prices for grey acetate of lime and wood spirit were respectively Rs. 135 per ton and Rs. 1/12/– per gallon. The prices we have taken are :—charcoal Rs. 20 per ton, grey acetate of lime Rs. 135 per ton, wood spirit Rs. 1 per gallon and wood tar Rs. 30 per ton. All these materials fetch far higher prices at the present time *e, g.* grey acetate is Rs. 675 per ton and wood spirit Rs. 12/8/–per gallon, but prices will undoubtedly fall after the war. It is extremely difficult to draw definite conclusions regarding the post-war prices of many chemicals. It is obvious that numerous very large factories now entirely employed in turning out materials required for war purposes will

then be occupied in manufacturing products for peace purposes. When it is borne in mind that the number of chemical factories, including wood distilleries, in Britain, France, America the British Colonies and Japan has been increased considerably during the last 4 years, it is clear that the few years after the conclusion of peace will be years of the keenest competition. This is already recognised in England ; the Departmental Committee on Sulphuric Acid and Fertiliser Industries appointed by the Minister of Munitions recommend the scrapping of a certain proportion of the plant, especially such as is inefficient, and the compensation from public funds for such compulsory scrapping.*

A somewhat similar state of affairs may hold good in the case of wood distillation products, the quantities turned out may be rather more than the countries under peace conditions can utilise. This necessarily means an appreciable fall in prices of articles such as acetate of lime and wood spirit. On the other hand, it is highly probable that labour charges in Europe and America will never fall again to what they were in pre-war times. This has also been realised in England and the suggestion has been made that to compensate for higher wages a greater efficiency of machinery should be aimed at by running all machinery and plant for the full 24 hours by means of 3 shifts of labour. In the case of a wood distillation factory this latter factor does not come into force, as big retorts are worked practically continuously. It is largely a question then of the effects of large supplies tending to reduce and higher wages tending to keep up the prices.

In part II the yields of acetic acid and of wood spirit from some typical S. Indian woods are given and the values we have taken for purposes of calculation are 3·3 tons of acetic acid and 1·4 tons of wood spirit for every 100 tons of wood.

For each 100 tons of wood the following amounts would be realised :—

				Rs.
23	tons	of charcoal at Rs 20	...	560
5·8	do	grey acetate of lime at Rs. 135	...	783
1·5	do	wood spirit (80 %) at Rs. 1 per gallon	...	420
6	do	tar at Rs. 30	...	180
			Total Rs.	1943

* Chem. Trade J., 1918, *62*, 203.

As 500 tons are distilled each month, the gross receipts would be Rs. 9715 per mensem.

On the outgoing side the chief items would be the cost of wood and depreciation charges on the plant.

It is difficult to assign a uniform value for the wood as this must undoubtedly vary with the locality and with the type of wood used. Even in the case of wood felled for the purpose of distillation the cost should not exceed Rs. 5 per ton and allowing 42 tons of fuel for each 100 tons of wood distilled, the monthly expenditure on wood comes to Rs. 3550.

The cost of a plant for distilling 500 tons of wood a month may be taken as £. 8000 to 9000 in England or £. 10,000 to £. 11,000 delivered and erected *i. e.* Rs. 1,50,000 to 1,65,000.

The life of a retort is comparatively short, while copper condensers and stills do not last much longer. The depreciation would thus be relatively high and a charge of 20 to 25 per cent. per annum on the cost of the whole plant should be made. Taking the value of the plant at Rs. 1,65,000 and the mean depreciation charge as 22·5 per cent. this would give an annual charge of Rs. 37,125 or a monthly charge of say Rs. 3,100.

These figures leave a balance of Rs. 9,715 less Rs. 3,550 less Rs. 3,100=Rs. 3,065 per mensem to meet other charges: such charges include:—rent, interest on capital, supervision, office and labour charges, chemicals, water, repairs, etc. The sum should be sufficient to meet all these items of expenditure and to yield a profit in addition to the interest on capital. Any reduction in the cost of the wood or rise in the price of the products would increase these profits.

The calculations just given assume that the products obtained can all be sold at the prices given.

This aspect of the question deservs a little further study.

It is true that the Indian forests are immense, but it is also true that the most important ones, those of the Western Ghauts the Himalayas and Assam are, generally speaking, in mountainous and inaccessible country. Apart from the fact that this means increased difficulty in felling and bringing the wood to the factory, it also involves the finished products being carted long distances and then being sent still further by rail.

To deal with the products individually; the one offering the most difficulty is charcoal. If the distillation is carried out

primarily for making charcoal for iron smelting or other industrial purposes, as is proposed in Mysore, this difficulty does not arise, but in normal cases where it is a question of utilising wood waste to the best advantage, the disposal of the charcoal will not be easy. A small distillery would have no difficulty in finding a local market, but as the distillery grows in size, the difficulty of selling the charcoal will be increased far more than proportionately. Charcoal is light and carries badly, so that briquetting would be necessary if it were to be sent any distance. Consequently the question resolves itself into one of freight, as far as South India and Bombay are concerned, while in Bengal, there would be the additional difficulty of cheap coal as a competitor for many purposes.

With regard to acetates, there is a certain demand for these substances in the country in cotton mills and dyeing establishments, while a considerable quantity could be converted into acetic acid. One of the chief use for grey acetate of lime was for the manufacture of acetone, but, as already stated, acetone can now be obtained by the fermentation of cereals and the question is largely one of the relative costs of the two methods.

Wood spirit, although used in enormous quantities in Europe for denaturing alcohol is not utilised for this purpose in India, probably owing to its scarcity. It is possible that a demand for it for this purpose might arise if a steady supply could be assured, while, in any case, considerable amounts would probably be absorbed for making varnishes.

The disposal of wood tar is always a matter of some difficulty. A limited amount might be used for disinfecting purposes, although greatly inferior to coal tar, and another possible use appears to be for the tarring of roads, as a few small scale experiments have shown that it as good as, or even superior to, coal tar for this purpose. Failing these uses, a certain quantity could be used in briquetting the charcoal and the residue would have to be utilised as fuel.

With regard to acetic acid, there is undoubtedly a large demand for this in the East for rubber coagulation, but the product used almost exclusively at present owing to costs of transportation is the glacial acid (98 %) and consequently it would be difficult to dispose of the dilute acid which is always produced along with the concentrated (cf. p. 100). It would probably be necessary to convert this dilute acid into salts. such as iron and lead acetates which could then be exported.

Considering this question of the disposal of the products as a whole, it seems probable that a few small factories would be able to sell the whole of their output without difficulty, but any overdevelopment of the industry might only end in disaster.

The following figures taken from the Bulletin of the Imperial Institute (1916, *14*, 567) give the average imports, for the years 1913-15, of wood distillation products into Britain.

Acetate of lime	4750 tons
Acetic acid	4280 ,,
Acetone	3490 ,,
Wood spirit	589210 galls.
Wood tar	13160 tons

In the case of tar about 8 per cent was re-exported, but practically all the other products were consumed in the United Kingdom.

It is clear that the forest resources of the British Isles would be inadequate to meet these demands, even if the industry were increased to its full extent This means that there will always be a market in Britain for most of the products. Canada and the United States supply the great bulk of the acetate of lime, acetic acid and wood spirit, and Russia and Sweden most of the wood tar. In 1913 Austria supplied large quantities of acetone but in 1915 the great bulk was imported from America.

The chief problem for the wood distiller in India is, can he turn out his products at prices that will enable him to compete with the American and European distiller? To compensate for the high freight charges between India and England he will have to manufacture his products at a cost rather below the average American or European cost.

This necessarily means extremely careful selection of sites for factories and the provision of cheap raw materials, including wood, lime and sulphuric acid. The factory must be near a cheap supply of wood of suitable quality, it should be near a market for all the charcoal made, and proximity to a port is desirable in order to reduce to a minimum the freight charges on all products exported.

VII. *Softwood Distillation.*

The whole of the preceding sections have dealt with the process known generally as "Hardwood Distillation" and in

Europe and America it is the method adopted for different types of deciduous trees rich in ligno-cellulose material.

Another important branch of the wood distillation industry is the one known as "Softwood Distillation" or coniferous wood distillation; and deals with woods containing resinous materials and oils in addition to water and ligno-celluloses. Softwoods of this type, for example pine, fir and spruce, yield large quantities of crude tar and only small quantities of acetic acid and wood spirit in comparison with the amounts produced from hardwoods.

In N. America and Scandinavia the distillation of soft woods has developed into a very large industry and includes the production of resin, pine oils, turpentine, and resin spirits At the present time this industry does not appear to be so adapted to the needs of India as the hardwood distillation industry and we do not propose dealing with it in detail.

The methods of distillation are not the same as those in the hardwood distilleries and the products and the methods of refining them are also different.

Distillation with superheated steam and extraction with a solvent are frequently used as well as the older method of distilling from fire-heated retorts. A brief account of some of these methods will be found in Lawrence's paper in the Journal of the Society of Chemical Industry (1918, 37, 51) and an account of suitable plant in W. B. Harper's "Utilisation of Wood Waste by Distillation" (1907).

A full account of the method of tapping species of pine for the oleoresin and the manufacture of resin and turpentine from the oleoresin will be found in the Indian Forest Bulletin No. 26, 1914 by E. A. Smythies.