

COAL-TAR, the black, viscous, sometimes semi-solid, fluid of peculiar smell, which is condensed together with aqueous "gas liquor" when the volatile products of the destructive distillation of coal are cooled down. It is also called "gas-tar," because it was formerly exclusively, and even now is mostly, obtained as a by-product in the manufacture of coal-gas, but the tar obtained from the modern coke-ovens, although not entirely identical with gas-tar, resembles it to such an extent that it is worked up with the latter, without making any distinction in practice between the two kinds. Some descriptions of gas-tar indeed differ very much more than coke-oven tar from pure coal-tar, viz. those which are formed when bituminous shale or other materials, considerably deviating in their nature from coal, are mixed with the latter for the purpose of obtaining gas of higher illuminating power.

It may be generally said that for the purpose of tar-distillers the tar is all the more valuable the less other materials than real coal have been used by the gas-maker. All these materials—bog-head shale, bituminous lignite and so forth—by destructive distillation yield more or less paraffinoid oils, which render the purification of the benzols very difficult and sometimes nearly impossible for the purposes of the manufacturer of coal-tar colours.

Neither too high nor too low a temperature should have been observed in gas-making in order to obtain a good quality of tar. Since in recent times most gas retorts have been provided with heating arrangements based on the production of gaseous fuel from coke, which produce higher temperatures than direct firing and have proved a great economy in the process of gas-making itself, the tar has become of decidedly inferior quality for the purposes of the tar-distillers, and in particular yields much less benzol than formerly.

Entirely different from gas-tar is the tar obtained as a by-product from those (Scottish) blast furnaces which are worked with splint-coal. This tar contains very little aromatic hydrocarbons, and the phenols are of quite a different character from those obtained in the working of gas-tar. The same holds good of oil-gas tars and similar substances. These should not be worked up like gas-tars.

The ordinary yield of tar in the manufacture of coal-gas is between 4 and 5% of the weight of the coal. Rather more is obtained when passing the gas through the apparatus of E. Pelouze and P. Audouin, where it is exposed to several shocks against solid surfaces, or by carrying on the process at the lowest possible temperature, as proposed by H. J. Davis, but this "carbonizing process" can only pay under special circumstances, and is probably no longer in practical use.

All coal-tars have a specific gravity above that of water, in most cases between 1.12 and 1.20, but exceptionally up to 1.25. The heavier tars contain less benzol than the lighter tars, and more "fixed carbon," which remains behind when the tars are exhausted of benzol and is a decidedly objectionable constituent. All tars also mechanically retain a certain quantity of water (or rather gas-liquor), say, 4% on the average, which is very obnoxious during the process of distillation, as it leads to "bumping," and therefore ought to be previously removed by prolonged settling, preferably at a slightly elevated temperature, which makes the tar more fluid. The water then rises to the top, and is removed in the ordinary way or by special "separators."

The tar itself is a mixture of exceedingly complex character. The great bulk of its constituents belongs to the class of "aromatic" hydrocarbons, of very different composition and degrees

of volatility, beginning with the simplest and most volatile, benzene (C_6H_6), and ending with an entirely indistinguishable mass of non-volatile bodies, which compose the pitch left behind in the tar-stills. The hydrocarbons mostly belong to the benzene series C_nH_{2n-6} , the naphthalene series C_nH_{2n-12} , and the anthracene and phenanthrene series C_nH_{2n-18} . Small quantities of "fatty" ("aliphatic") hydrocarbons are never absent, even in pure tars, and are found in considerable quantities when shales and similar matters have been mixed with the coal in the gas-retorts. They belong mostly to the paraffins C_nH_{2n+2} , and the olefines C_nH_{2n} . The "asphalt" or soluble part of the pitch is also a mixture of hydrocarbons, of the formula C_nH_{2n} ; even the "carbon," left behind after treating the pitch with all possible solvents is never pure carbon, but contains a certain quantity of hydrogen, although less than any of the volatile and soluble constituents of the tar.

Besides the hydrocarbons, coal-tar contains about 2% of the simpler phenols $C_nH_{2n-7}OH$, the best known and most valuable of which is the first of the series, carbolic acid (*q.v.*) C_6H_5OH , besides another interesting oxygenized substance, cumarone C_9H_6O . The phenols, especially the carbolic acid, are among the more valuable constituents of coal-tar. Numerous sulphur compounds also occur in coal-tar, some of which impart to it their peculiar nauseous smell, but they are of no technical importance or value.

Still more numerous are the nitrogenated compounds contained in coal-tar. Most of these are of a basic character, and belong to the pyridine and the quinoline series. Among these we find a somewhat considerable quantity of aniline, which, however, is never obtained from the tar for commercial purposes, as its isolation in the pure state is too difficult. The pyridines are now mostly recovered from coal-tar, but only in the shape of a mixture of all members of the series which is principally employed for denaturing alcohol. Some of these nitrogenated compounds possess considerable antiseptic properties, but on the whole they are only considered as a contamination of the tar-oils.

Applications of Coal-Tar in the Crude State.—Large quantities of coal-tar are employed for various purposes without submitting it to the process of distillation. It is mostly advisable to dehydrate the tar as much as possible for any one of its applications, and in some cases it is previously boiled in order to remove its more volatile constituents.

No preparation whatever is needed if the tar is to be used as *fuel*, either for heating the gas-retorts or for other purposes. Its heating-value is equal to the same weight of best coal, but it is very difficult to burn it completely without producing a great deal of evil-smelling smoke. This drawback has been overcome by employing the same means as have been found suitable for the combustion of the heavy petroleum residues, called "masut," viz. converting the tar into a fine spray by means of steam or compressed air. When the gas-maker cannot conveniently or profitably dispose of his tar for other purposes, he burns it by the above means under his retorts.

Several processes have also been patented for producing *illuminating gas* from tar, the most notable of which is the Dinsmore process. This process has been adversely criticized by very competent gas-makers, and no great success can be expected in this line.

Coal-tar is very much employed for painting wood, iron, brick-work, or stone, as a preventive against the influence of weather or the far more potent action of corrosive chemicals. This, of course, can be done only where appearance is no object, for instance in chemical works, where all kinds of erections and apparatus are protected by this cheap kind of paint. Coal-tar should not be used for tarring the woodwork and ropes of ships, a purpose for which only wood-tar has been found suitable.

One of the most considerable outlets for crude tar is in the manufacture of *roofing-felt*. This industry was introduced in Germany upwards of a hundred years ago, even before coal-tar was available, and has reached a very large extension both in that country and in the United States, where most of the gas-tar seems to be devoted to this purpose. In the United Kingdom

it is much less extensive. For this manufacture a special fabric is made from pure woollen fibre, on rolls of about 3 ft. width and of considerable length. The tar must be previously dehydrated, and is preferably deprived of its more volatile portions by heating in a still. It is heated in an iron pan to about 90° or 100° C.; the fabric is drawn through it by means of rollers which at the same time squeeze out the excess of tar; on coming out of these, the tarred felt is covered with a layer of sand on both sides by means of a self-acting apparatus; and is ultimately wound round wooden rolls, in which state it is sent out into the trade. This roofing-felt is used as a cheap covering, both by itself and as a grounding for tiles or slates. In the former case it must be kept in repair by repainting with tar from time to time, a top covering of sand or small gravel being put on after every coat of paint.

Coal-tar is also employed for the manufacture of *lamp-black*. This is done by burning the tar in ovens, connected with brick-chambers in which the large quantity of soot, formed in this process, deposits before the gases escape through the chimney. Numerous patents have been taken out for more efficiently collecting this soot. Most of it is employed without further manipulation for the manufacture of electric carbons, printing inks, shoe-blackening, patent leather and so forth. A finer quality of lamp-black, free from oily and empyreumatic parts, is obtained by calcining the soot in closed iron pots at a red heat.

Distillation of Coal-Tar.—Much more important than all applications of crude coal-tar is the industry of separating its constituents from it in a more or less pure form by fractional distillation, mostly followed by purifying processes. Most naturally this industry took its rise in Great Britain, where coal-gas was invented and made on a large scale before any other nation took it up, and up to this day both the manufacture of coal-gas and the distillation of the tar, obtained as a by-product thereof, are carried out on a much larger scale in that than in any other country. The first attempts in this line were made in 1815 by F. C. Accum, and in 1822 by Dr G. D. Longstaff and Dr Dalston. At first the aim was simply to obtain "naphtha," used in the manufacture of india-rubber goods, for burning in open lamps and for some descriptions of varnish; the great bulk of the tar remained behind and was used as fuel or burned for the purpose of obtaining lamp-black.

It is not quite certain who first discovered in the coal-naphtha the presence of benzene (*q.v.*), which had been isolated from oil-gas by M. Faraday as far back as 1825. John Leigh claims to have shown coal-tar benzene and nitro-benzene made from it at the British Association meeting held at Manchester in 1842, but the report of the meeting says nothing about it, and the world in general learned the presence of benzene in coal-tar only from the independent discovery of A. W. Hofmann, published in 1845. And it was most assuredly in Hofmann's London laboratory that Charles Mansfield worked out that method of fractional distillation of the coal-tar and of isolating the single hydrocarbons which laid the foundation of that industry. His patent, numbered 11,960 and dated November 11th, 1847, is the classical land-mark of it. About the same time, in 1846, Brönner, at Frankfort, brought his "grease-remover" into the trade, which consisted of the most volatile coal-tar oils, of course not separated into the pure hydrocarbons; he also sold water-white "creosote" and heavy tar-oils for pickling railway timbers, and used the remainder of the tar for the manufacture of roofing-felt. The employment of heavy oils for pickling timber had already been patented in 1838 by John Bethell, and from this time onward the distillation of coal-tar seems to have been developed in Great Britain on a larger scale, but the utilization of the light oils in the present manner naturally took place only after Sir W. H. Perkin, in 1856, discovered the first aniline colour which suddenly created a demand for benzene and its homologues. The isolation of carbolic acid from the heavier oils followed soon after; that of naphthalene, which takes place almost automatically, went on simultaneously, although the uses of this hydrocarbon for a long time remained much behind the quantities which are producible from coal-tar, until the

manufacture of synthetic indigo opened out a wide field for it. The last of the great discoveries in that line was the preparation of alizarine from anthracene by C. Graebe and C. T. Liebermann, in 1868, soon followed by patents for its practical manufacture by Sir W. H. Perkin in England, and by Graebe, Liebermann and H. Caro in Germany.

The present extension of the industry of coal-tar distilling can be only very roughly estimated from the quantity of coal-tar produced in various countries. Decidedly at the head is Great Britain, where about 700,000 tons are produced per annum, most of which probably finds its way into the tar-distilleries, whilst in Germany and the United States much less gas-tar is produced and a very large proportion of it is used for roofing-felt and other purposes.

We shall now give an outline of the processes used in the distillation of tar.

Dehydration.—The first operation in coal-tar distilling is the removal of the mechanically enclosed water. Some water is chemically combined with the bases, phenols, &c., and this, of course, cannot be removed by mechanical means, but splits off only during the distillation itself, when a certain temperature has been reached. The water mechanically present in the tar is separated by long repose in large reservoirs. Very thick viscous tars are best mixed with thinner tars, and the whole is gently heated by coils of pipes through which the heated water from the oil-condensers is made to flow. Sometimes special "tar-separators" are employed, working on the centrifugal principle. The water rises to the top and is worked up like ordinary gas-liquor. More water is again separated during the heating-up of the tar in the still itself, and can be removed there by a special overflow.

Tar-Stills.—The tar is now pumped into the tar-still, fig. 1. This is usually, as shown, an upright wrought-iron cylinder, with an arched top, and with a bottom equally vaulted upwards for the purpose of increasing the heating surface and of raising the level of the pitch remaining at the end of the operation above the fire-flues. The fuel is consumed on the fire-grate *a*, and, after having

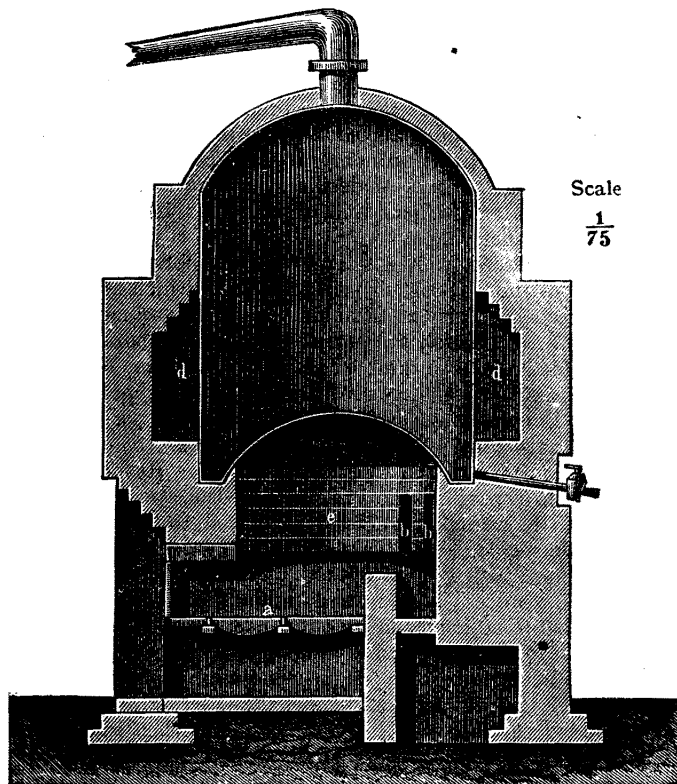


FIG. 1.—Tar-Still (sectional elevation).¹

traversed the holes *bb* in the annular wall *e* built below the still, the furnace gases are led around the still by means of the flue *d*, whence they pass to the chimney. Cast-iron necks are provided in the top for the outlet of the vapours, for a man-hole, supply-pipe, thermometer-pipe, safety valve, and for air and steam-pipes reaching down to the bottom and branching out into a number of distributing

¹ The illustrations in this article are from Prof. G. Lunge's *Coal Tar and Ammonia*, by permission of Friedrich Vieweg u. Sohn.

arms. Near the top there is an overflow pipe which comes into action on filling the still. In the lowest part of the bottom there is a running-off valve or tap. In some cases (but only exceptionally) a perpendicular shaft is provided, with horizontal arms, and chains hanging down from these drag along the bottom for the purpose of keeping it clean and of facilitating the escape of the vapours. This arrangement is quite unnecessary where the removal of the vapours is promoted by the injection of steam, but this steam must be carefully dried beforehand, or, better, slightly superheated, in order to prevent explosions, which might be caused by the entry of liquid water into the tar during the later stages of the work, when the temperature has arisen far above the boiling-point of water. The steam acts both by stirring up the tar and by rapidly carrying off the vapours formed in distillation. The latter object is even more thoroughly attained by the application of a vacuum, especially during the later stage of distillation. For this purpose the receivers, in which the liquids condensed in the cooler are collected, are connected with an air pump or an ejector, by which a vacuum of about 4 in., say $\frac{1}{3}$ atmosphere, is made which lowers the boiling process by about 80° C.; this not merely hastens the process, but also produces an improvement of the quality and yield of the products, especially of the anthracene, and, moreover, lessens or altogether prevents the formation of coke on the still-bottom, which is otherwise very troublesome.

Most manufacturers employ ordinary stills as described. A few of them have introduced continuously acting stills, of which that constructed by Frederic Lennard has probably found a wider application than any of the others. They all work on the principle of gradually heating the tar in several compartments, following one after the other. The fresh tar is run in at one end and the pitch is run out from the other. The vapours formed in the various compartments are separately carried away and condensed, yielding at one and the same time those products which are obtained in the ordinary stills at the different periods of the distillation. Although in theory this continuous process has great advantages over the ordinary style of working, the complication of the apparatus and practical difficulties arising in the manipulation have deterred most manufacturers from introducing it.

The tar-stills are set in brickwork in such a manner that there is no over-heating of their contents. For this purpose the fire-grate is placed at a good distance from the bottom or even covered by a brick arch so that the flame does not touch the still-bottom at all and acts only indirectly, but the sides of the still are always directly heated. The fire-flue must not be carried up to a greater height than is necessary to provide against the overheating of any part of the still not protected inside by liquid tar, or, at the end of the operation, by liquid pitch. The outlet pipe is equally protected against overheating and also against any stoppage by pitch solidifying therein. The capacity of tar-stills ranges from 5 to 50 tons. They hold usually about 10 tons, in which case they can be worked off during one day.

The vapours coming from the still are condensed in coolers of various shapes, one of which is shown in figs. 2 and 3. The cooling-pipes are best made of cast-iron, say 4 in. wide inside and laid so as to have a continuous fall towards the bottom. A steam-pipe (b) is provided for heating the cooling water, which is necessary during the later part of the operation to prevent the stopping up of the pipes by the solidification of the distillates. A cock (a) allows

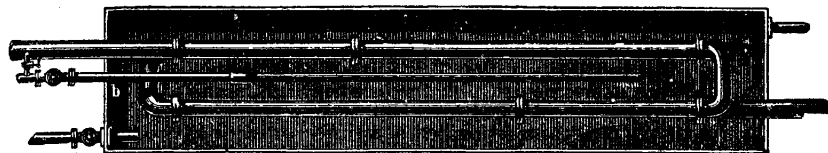


FIG. 2.—Condensing Worm (Plan), scale $\frac{1}{16}$.

steam to be injected into the condensing worm in order to clear any obstruction.

The cooling-pipe is at its lower end connected with receivers for the various distillates in such a manner that by the turning of a cock the flow of the distillates into the receivers can be changed at will. In a suitable place provision is made for watching the colour, the specific gravity, and the general appearance of the distillates. At the end of the train of apparatus, and behind the vacuum pump or ejector, when one is provided, there is sometimes a purifier for the gases which remain after condensation; or these gases are carried back into the fire, in which case a water-trap must be interposed to prevent explosions.

Distillation of the Tar.—The number of fractions taken during the distillation varies from four to six. Sometimes a first fraction is taken as "first runnings," up to a temperature of 105° C. in the still,

and a second fraction as "light oil," up to 210° C., but more usually these two are not separated in the first distillation, and the first or "light oil" fraction then embraces everything which comes over until the drops no longer float on, but show the same specific gravity as water. The specific gravity of this fraction varies from 0.91 to 0.94. The next fraction is the "middle oil" or "carbolic oil," of specific gravity 1.01, boiling up to 240° C.; it contains most of the carbolic acid and naphthalene. The next fraction is the "heavy oil" or "creosote oil," of specific gravity 1.04. Where the nature of the coals distilled for gas is such that the tar contains too little anthracene to be economically recovered, the creosote-oil fraction is carried right to the end; but otherwise, that is in most cases, a last fraction

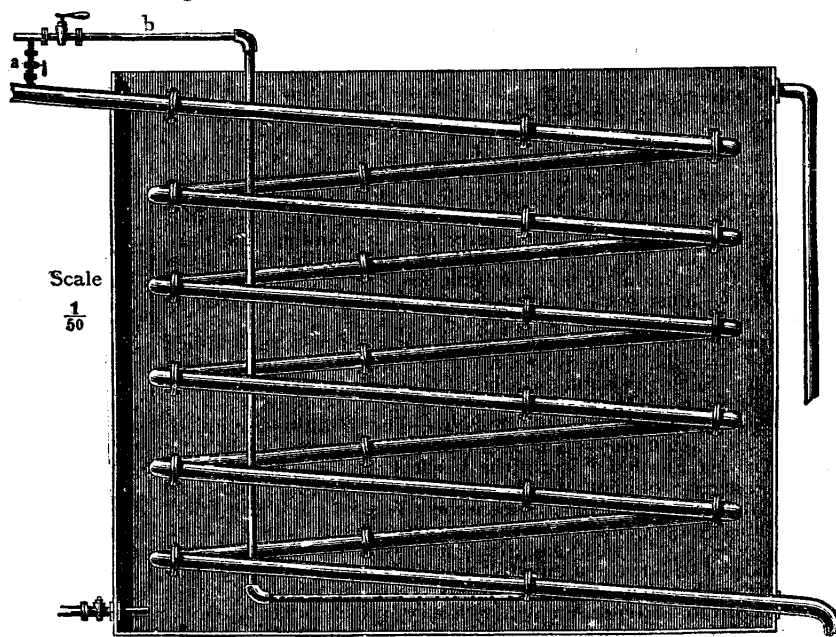


FIG. 3.—Condensing Worm (side elevation).

is made at about the temperature 270° C., above which the "anthracene oil" or "green oil" is obtained up to the finish of the distillation.

During the light-oil period the firing must be performed very cautiously, especially where the water has not been well removed, to prevent bumping and boiling over. It has been observed that, apart from the water, those tars incline most to boiling over which contain an unusual quantity of "fixed carbon." During this period cold water must be kept running through the cooler. The distillate at once separates into water (gas-liquor) and light oil, floating at the top. Towards the end of this fraction the distillation seems to cease, in spite of increasing the fires, and a rattling noise is heard in the still. This is caused by the combined water splitting off from the bases and phenols and causing slight explosions in the tar.

As soon as the specific gravity approaches 1.0, the supply of cold water to the cooler is at least partly cut off, so that the temperature of the water rises up to 40° C. This is necessary because otherwise some naphthalene would crystallize out and plug up the pipes. If a little steam is injected into the still during this period no stoppage of the pipes need be feared in any case, but this must be done cautiously.

When the carbolic oil has passed over and the temperature in the still has risen to about 240° C., the distillate can be run freely by always keeping the temperature in the cooler at least up to 40° C. The "creosote oil" which now comes over often separates a good deal of solid naphthalene on cooling.

The last fraction is made, either when the thermometer indicates 270° C., or when "green grease" appears in the distillate, or simply by judging from the quantity of the distillate. What comes over now is the "anthracene oil." The firing may cease towards the end as the steam (with the vacuum) will finish the work by itself. The water in the cooler should now approach the boiling-point.

The point of finishing the distillation is different in various places and for various objects. It depends upon the fact whether *soft* or *hard* pitch is wanted. The latter must be made where it has to be sold at a distance, as soft pitch cannot be easily carried during the warmer season in railway trucks and not at all in ships, where it would run into a single lump. Hard pitch is also always made where as much anthracene as possible is to be obtained. For hard pitch the distillation is carried on as far as practicable without causing the residue in the still to "coke." The end cannot be judged by the thermometer, but by the appearance and quantity of the distillate

and its specific gravity. If carried too far, not merely is coke formed, but the pitch is porous and almost useless, and the anthracene oil is contaminated with high-boiling hydrocarbons which may render it almost worthless as well. Hard pitch proper should soften at 100°C ., or little above.

Where the distillation is to stop at soft pitch it is, of course, not carried up to the same point, but wherever the pitch can be disposed of during the colder season or without a long carriage, even the hard pitch is preferably softened within the still by pumping back a sufficient quantity of heavy oil, previously deprived of anthracene. This makes it much easier to discharge the still. When the contents consist of soft pitch they are run off without much trouble, but hard pitch not merely emits extremely pungent vapours, but is mostly at so high a temperature that it takes fire in the air. Hard pitch must, therefore, always be run into an iron or brick cooler where it cools down out of contact with air, until it can be drawn out into the open pots where its solidification is completed.

Most of the pitch is used for the manufacture of "briquettes" ("patent fuel"), for which purpose it should soften between 55° and 80°C . according to the requirements of the buyer. In Germany upwards of 50,000 tons are used annually in that industry; much of it is imported from the United Kingdom, whence also France and Belgium are provided. Apart from the softening point the pitch is all the more valued the more constituents it contains which are soluble in xylene. The portion insoluble in this is denoted as "fixed carbon." If the briquette manufacturer has bought the pitch in the hard state he must himself bring it down to the proper softening point by re-melting it with heavy coal-tar oils.

We now come to the treatment of the various fractions obtained from the tar-stills. These operations are frequently not carried out at the smaller tar-works, which sell their oils in the crude state to the larger tar-distillers.

Working up of the Light-Oil Fraction.—The greatest portion of the light-oil fraction consists of aromatic hydrocarbons, about one-fifth being naphthalene, four-fifths benzene and its homologues, in the proportion of about 100 benzene, 30 toluene, 15 xylenes, 10 trimethylbenzenes, 1 tetramethylbenzene. Besides these the light-oil contains 5-15% phenols, 1-3% bases, 0.1 sulphuretted compounds, 0.2-0.3% nitriles, &c. It is usually first submitted to a preliminary distillation in directly fired stills, similar to the tar-stills, but with a dephlegmating head. Here we obtain (1) first runnings (up to 0.89 spec. grav.), (2) heavy benzols (up to 0.95), (3) carbolic oil (up to 1.00). The residue remaining in the still (chiefly naphthalene) goes to the middle-oil fraction.

The "first runnings" are now "washed" in various ways, of which we shall describe one of the best. The oil is mixed with dilute caustic soda solution, and the solution of phenols thus obtained is worked up with that obtained from the next fractions. After this follows a treatment with dilute sulphuric acid (spec. grav. 1.3), to extract the pyridine bases, and lastly with concentrated sulphuric acid (1.84), which removes some of the aliphatic hydrocarbons and "unsaturated" compounds. After this the crude benzol is thoroughly washed with water and dilute caustic soda solution, until its reaction is neutral. The mixing of the basic, acid and aqueous washing-liquids with the oils is performed by compressed air, or more suitably by mechanical stirrers, arranged on a perpendicular, or better, a horizontal shaft. Precisely the same treatment takes place with the next fraction, the "heavy benzols," and the oils left behind after the washing operations now go to the steam-stills. The heaviest hydrocarbons are sometimes twice subjected to the operation of washing.

The washed crude benzols are now further fractionated by distillation with steam. The *steam-stills* are in nearly all details on the principle of the "column apparatus" employed in the distillation of alcoholic liquids, as represented in fig. 4. They are usually made of cast iron. The still itself is either an upright or a horizontal cylinder, heated by a steam-coil, of a capacity of from 1000 to 2000 gallons. The superposed columns contain from 20 to 50 compartments of a width of $2\frac{1}{2}$ or 3 ft. The vapours pass into a cooler, and from this the distillate runs through an apparatus, where the liquor can be seen and tested, into the receivers. The latter are so arranged that the water passing over at the same time is automatically removed. This is especially necessary, because the last fraction is distilled by means of pure steam.

The fractions made in the steam distillation vary at different works. In some places the pure hydrocarbons are not extracted and here only the articles called: "90 per cent. benzol," "50 per cent. benzol," "solvent naphtha," "burning naphtha" are made, or any other commercial articles as they are ordered. The expression "per cent." in this case does not signify the percentage of real benzene, but that portion which distils over up to the temperature of 100°C ., when a certain quantity of the article is heated in glass retorts of a definite shape, with the thermometer inserted in the liquid itself. By the application of well-constructed rectifying-columns and with proper care it is, however, possible to obtain in this operation nearly pure benzene, toluene, xylene, and cumene (in the two last cases a mixture of the various isomeric hydrocarbons). These hydrocarbons contain only a slight proportion of thiophene and its isomers, which can be removed only by a treatment with fuming sulphuric acid, but this is only exceptionally done.

Sometimes the *pyridine bases* are recovered from the tarry acid which is obtained in the treatment of the light oil with sulphuric acid, and which contains from 10 to 30% of bases, chiefly pyridine and its homologues with a little aniline, together with resinous substances. The latter are best removed by a partial precipitation with ammonia, either in the shape of gas or of concentrated ammoniacal liquor. This reagent is added until the acid reaction has just disappeared and a faint smell of pyridine is perceived. The mixture is allowed to settle, and it then separates into two layers. The upper layer, containing the impurities, is run off; the lower layer, containing the sulphates of ammonia and of the pyridine bases, is treated with ammonia in excess, where it separates into a lower aqueous layer of ammonium sulphate solution and an oil, consisting of crude pyridine. This is purified by fractionation in iron stills and distillation over caustic soda. Most of it is used for denaturing spirit of wine in Germany, for which purpose it is required to contain 90% of bases boiling up to 140°C . (see ALCOHOL).

Working up of the Middle-Oil Fraction (Carbolic Oil Fraction).—Owing to its great percentage of naphthalene (about 40%) this fraction is solid or semi-solid at ordinary temperatures. Its specific gravity is about 1.2; its colour may vary from light yellow to dark brown or black. In the latter case it must be re-distilled before further treatment. On cooling down, about four-fifths of the naphthalene crystallizes out on standing from three to ten days. The crystals are freed from the mother oils by draining and cold or hot pressing; they are then washed at 100°C . with concentrated sulphuric acid, afterwards with water and re-distilled or sublimed. About 10,000 tons of naphthalene are used annually in Germany, mostly for the manufacture of many azo-colours and of synthetic indigo.

The oils drained from the crude naphthalene are re-distilled and worked for carbolic acid and its isomers. For this purpose the oil is washed with a solution of caustic soda, of specific gravity 1.1; the solution thus obtained is treated with sulphuric acid or with carbon dioxide, and the crude phenols now separated are fractionated in a similar manner as is done in the case of crude benzol. The pure phenol crystallizes out and is again distilled in iron stills with a silver head and cooling worm; the remaining oils, consisting mainly of cresols, are sold as "liquid carbolic acid" or under other names.

Most of the oil which passes as the "creosote-oil fraction" is sold in the crude state for the purpose of pickling timber. It is at the ordinary temperature a semi-solid mixture of about 20% crystallized hydrocarbons (chiefly naphthalene), and 80% of a dark brown, nauseous smelling oil, of 1.04 spec. grav., and boiling between 200° and 300°C . The liquid portion contains phenols, bases, and a great number of hydrocarbons. Sometimes it is redistilled, when most of the naphthalene passes over in the first fraction, between 180° and 230°C ., and crystallizes out in a nearly pure state. The oily portion remaining behind, about 60% of this distillate, contains about 30% phenols and 3% bases. It has highly disinfectant properties and is frequently converted into special disinfectants, e.g. by mixing it with four times its volume of slaked lime, which yields "disinfectant powder" for stables, railway cars, &c. Mixtures

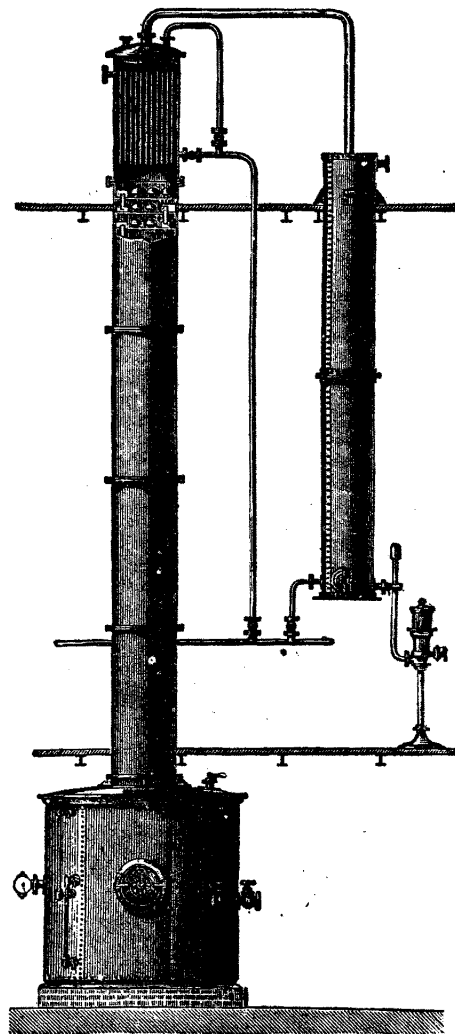


FIG. 4.—Benzol Still (elevation), scale $\frac{1}{16}$.

of potash soaps (soft soaps) with this oil have the property of yielding with water emulsions which do not settle for a long time and are found in the trade as "creolin," "sapocarbol," "lysol," &c.

That description of creosote oil which is sold for the purpose of pickling railway sleepers, telegraph posts, timber for the erection of wharves and so forth, must satisfy special requirements which are laid down in the specifications for tenders to public bodies. These vary to a considerable extent. They always stipulate (1) a certain specific gravity (*e.g.* not below 1.035 and not above 1.065); (2) certain limits of boiling points (*e.g.* to yield at most 3% up to 150°, at most 30% between 150° and 255°, and at least 85% between 150° and 355°); (3) a certain percentage of phenols, as shown by extraction with caustic soda solution, say 8 to 10%.

Much of this creosote oil is obtained by mixing that which has resulted in the direct distillation of the tar with the liquid portion of the anthracene oils after separating the crude anthracene (see below). It is frequently stipulated that the oil should remain clear at the ordinary temperature, say 15° C., which means that no naphthalene should crystallize out.

Working up the Anthracene Oil Fraction.—The crude oil boils between 280° and 400° C. It is liquid at 60° C., but on cooling about 6 to 10% of crude anthracene separates as greenish-yellow, sandy crystals, containing about 30% of real anthracene, together with a large percentage of carbazol and phenanthrene. This crystallization takes about a week. The crude anthracene is separated from the mother oils by filter presses, followed by centrifugals or by hot hydraulic presses. The liquid oils are redistilled, in order to obtain more anthracene, and the last oils go back to the creosote oil, or are employed for softening the hard pitch (*vide supra*). The crude anthracene is brought up to 50 or 60, sometimes to 80%, by washing with solvent naphtha, or more efficiently with the higher boiling portion of the pyridine bases. The naphtha removes mostly only the phenanthrene, but the carbazol can be removed only by pyridine, or by subliming or distilling the anthracene over caustic potash. The whole of the anthracene is sold for the manufacture of artificial alizarine.

BIBLIOGRAPHY.—The principal work on Coal-tar is G. Lunge's *Coal-tar and Ammonia* (3rd ed., 1900). Consult also G. P. Sadtler, *Handbook of Industrial Organic Chemistry* (1891), and the article "Steinkohlentheer," Kraemer and Spreker, in *Encyklopädisches Handbuch der technischen Chemie* (4th ed., 1905, viii. 1). (G. L.)