Kirk-Othmer Encyclopedia of Chemical Technology.

TAR AND PITCH

Most organic substances, other than those of simple structure and low boiling point, when pyrolyzed, ie, heated in the absence of air, yield dark-colored, generally viscous liquids termed tar or pitch. The differentiation between these terms is not precise. When the by-product is a liquid of fairly low viscosity at ordinary temperature, it is regarded as a tar; if of very viscous, semisolid, or solid consistency, it is designated as a pitch. Thus, in preparative organic chemistry, a tar or pitch is frequently the distillation residue. Some thermal decomposition always accompanies the distillation of vegetable and animal fats and oils, resulting in the production of small amounts of vegetable-oil pitch, wool-grease pitch, stearin pitch, and so on. Such products, of poorly defined composition and properties, have little industrial importance and are mainly burned as fuel.

Large amounts of tar or pitch by-products are produced by industrial processes. The distillation of crude petroleum (qv) yields a pitch-like residue termed bitumen or asphalt (qv). In the United States, these terms are interchangeable, but in Europe the term asphalt is generally restricted to naturally occurring rock or lake asphalt, whereas the residual product of crude-oil distillation is termed bitumen. Although these are important industrial materials produced in millions of metric tons annually, they are not included herein (see Asphalt; Petroleum, products).

With regard to coal-derived tar and pitch, the following definitions are appropriate to distinguish them from ostensibly similar materials from other sources and from crude oil in particular.

Coal tar is the condensation product obtained by cooling to approximately ambient temperature, the gas evolved in the destructive distillation of coal. It is a black viscous liquid denser than water and composed primarily of a complex mixture of condensed ring aromatic hydrocarbons. It may contain phenolic compounds, aromatic nitrogen bases and their alkyl derivatives, and paraffinic and olefinic hydrocarbons. Coal-tar pitch is the residue from the distillation of coal tar. It is a black solid having a softening point of 30–180°C (86–359°F).

In the processing of crude oil eventually bitumen or vacuum residues arise, ie, asphalt, obtained as a nonvolatile residue from the distillation of crude oil and contains a high proportion of hydrocarbons having carbon numbers predominantly greater than C_{25} and high carbon-to-hydrogen ratios; and residues petroleum vacuum, a complex residue from the vacuum distillation of the residuum from atmospheric distillation of crude oil, consisting of hydrocarbons having carbon numbers predominantly greater than C_{34} and boiling point of approximately 495°C (923°F). However, to complicate matters, Ashland (United States) also markets a material known as petroleum pitch, although technically it should be called bitumen.

1. Wood Tar

The pyrolysis or carbonization of hardwoods, eg, beech, birch, or ash, in the manufacture of charcoal yields, in addition to gaseous and lighter liquid products, a by-product tar in ca 10 wt % yield. Dry distillation of softwoods, eg, pine species, for the production of the so-called DD (destructively distilled) turpentine yields pine tar as a by-product in about the same amount. Pine tar, also called Stockholm tar or Archangel tar, was at one time imported from the Baltic by European maritime countries for the treatment of cordage and ship hulls;

it was an important article of commerce from the seventeenth to the nineteenth century. The small amount produced in the late twentieth century is burned as a crude fuel. Charcoal production from hardwoods, on the other hand, has increased in the 1990s years.

1.1. Composition, Processing, and Uses

There are no statistics available for the amount of wood tar processed, but almost all of it is burned. The commercial by-products from wood carbonization are limited to methanol, denatured methanol, methyl acetate, and acetic acid. These products are derived from the aqueous phase of the condensed products, the so-called pyroligneous acid. On distillation, pyroligneous acid yields wood spirit, acetic acid having small amounts of propionic and butyric acids, and soluble tar. The wood spirit, on refining, yields methanol as well as methyl acetate and acetone. The aqueous acid fraction is neutralized with milk of lime to give gray acetate of lime, 82–84% $(CH_3COO)_2Ca$, which is neutralized to give acetic acid or pyrolyzed to give acetone. The soluble tars are mainly condensation products of aldehydes and phenols; they are burned as fuel.

Small amounts of the sedimentation tar, ie, the separated organic layer from the condensed wood-carbonization vapors, are distilled, first at atmospheric pressure to give wood spirit, crude acetic acid, and light wood oils. The first two of these fractions are added to similar fractions from the pyroligneous acid for further processing. The light wood oil is treated with permanganate and sulfuric acid and used as a solvent or for giving a wood smoke or tar note to perfumes, soaps, and shampoos. Further distillation under reduced pressure yields wood creosote, which is used for the preservation of cordage, timber, and Hessian sacks, and as a disinfectant, component of wood stains, and froth-flotation agent.

Chemically, wood tar is a complex mixture that contains at least 200 individual compounds, among which the following have been isolated (1): 2-methoxyphenol, 2-methoxy-4-ethylphenol, 5-methyl-2-methoxyphenol, 2,6-xylenol, butyric acid, crotonic acid, 1-hydroxy-2-propanone, butyrolactone, 2-methyl-3-hydroxy-4*H*-pyran-4-one, 2-methyl-2-propenal, methyl ethyl ketone, methyl isopropyl ketone, methyl furyl ketone, and 2-hydroxy-3-methyl-2-cyclopenten-1-one.

2. Coal Tar

By far the largest source of tar and pitch is the pyrolysis or carbonization of coal (qv). Generally, the terms tar and pitch are synonymous with coal tar and the residue obtained by its distillation (see Coal-conversion processes, carbonization). The importance of coal tar as an industrial raw material dates back to the first half of the eighteenth century, when the carbonization of coal and the by-product production of tar were expanding rapidly in the United Kingdom. Initially, the crude tar was subjected to a simple flash distillation in pot stills to yield a solvent naphtha, creosote for timber preservation, and a residue of pitch that found an outlet as a binder for coal briquettes. Later, coal tar was the main source of aromatic hydrocarbons, phenols, and pyridine bases needed by the rapidly expanding dyestuffs, pharmaceuticals, and explosives industries. The development of by-product coke ovens and crude-benzene recovery at both coke ovens and gasworks greatly increased the supplies of crude tar and tar distillates for the recovery of tar chemicals, ie, benzene, toluene, xylenes, phenol, cresols and cresylic acids, pyridine and methylpyridines, and naphthalene and anthracene, in addition to the so-called bulk products, eg, creosote, tar paints, road tars, and pitch binders (2–4).

Until the end of World War II, coal tar was the main source of these aromatic chemicals. However, the enormously increased demands by the rapidly expanding plastics and synthetic-fiber industries have greatly outstripped the potential supply from coal carbonization. This situation was exacerbated by the cessation of the manufacture in Europe of town gas from coal in the early 1970s, a process carried out preponderantly in the continuous vertical retorts (CVRs), which has led to production from petroleum. Over 90% of the world production of aromatic chemicals in the 1990s is derived from the petrochemical industry, whereas coal tar is chiefly a source of anticorrosion coatings, wood preservatives, feedstocks for carbon-black manufacture, and binders for road surfacings and electrodes.

Apart from the presence of a few percent (usually below 5%) of aqueous liquor containing inorganic salts and a percent or so of coal-char-coke dust arising from carryover of particles in the carbonization process, coal-tar consists essentially of two parts. The first, which at atmospheric pressure distills up to about 400°C, is primarily a complex mixture of mono- and polycyclic aromatic hydrocarbons, a proportion of which are substituted with alkyl, hydroxyl as well as amine and/or hydro sulfide groups, and to a lesser extent their sulfur-, nitrogen-, and oxygen-containing analogues and, for those tars produced at the lower coal carbonization temperatures, they contain in addition hydroaromatics, alkanes, and alkenes. The second part is the residue from the distillation, amounting to at least 50% of the coal-tar products by high temperature carbonization and consisting of a continuation of the sequence of polynuclear aromatic, aromatic, and heterocyclic compounds, but reaching molecules containing 20 to 30 rings.

2.1. Manufacture and Processing

The largest volume of coal is carbonized in batch coke ovens to produce a hard coke suitable for blast furnaces for the reduction of iron ore. Oven temperatures, as measured in the flues, are between 1250 and 1350° and residence time varies between 17 and 30 h. The gas made in this process is mainly used as fuel and other applications in the steel works (see Fuels, synthetic).

Until 1960–1970, in countries where natural gas was not available, large amounts of coal were carbonized for the production of town gas, as well as a grade of coke which, although unsuitable for metallurgical use, was satisfactory as a domestic fuel in closed stoves. The early cast-iron and silica horizontal retorts used at gasworks were replaced by continuous vertical retorts. These operated at flue temperatures of 1000–1100°C. The volatile products were rapidly swept from the retort by the introduction of steam at 10–20% by weight of the coal carbonized.

The passing of the Clean Air Act in the United Kingdom in 1956 resulted in a revival of interest in low temperature carbonization to produce a very reactive coke suitable for open fires. In the Coalite process, the coal is heated at 600–650°C for 4 h in small retorts each holding 6–7 metric tons (5). The Rexco process employed large internally heated retorts in which charges of 34 metric tons were heated to 700–750°C for 6 h, but is no longer in operation in the United Kingdom (6).

In the future, crude, low temperature tar may be supplied as by-products of synthetic natural gas (SNG) and syncrude from coal substitute. A number of the more advanced SNG processes such as Lurgi, Bi-Gas, and Cogas employ low temperature pyrolysis of coal and yield a by-product tar. The tar obtained from the Lurgi process appears to be similar to Coalite tar. Lurgi gasifiers were chosen for five large U.S. plants for the conversion of western lignite and subbituminous coals to SGN. In full operation, these plants were expected to produce 2×10^6 metric tones of by-product tar per year. Lurgi gasifiers are also employed to produce synthesis gas for South Africa's three Fischer-Tropsch plants, which yield ca 250,000 metric tons of tar.

2.1.1. Primary Distillation

As produced, crude coal tar is of value only as a fuel. Although formerly large amounts were burned, the practice has largely been abandoned. In the 1990s, 99% of the tar produced in the United Kingdom and Germany and 75% of U.S. production is distilled. Most of the crude tar regarded as being burned in the United States is first topped in simple continuous stills to recover a chemical oil, ie, a fraction distilling to 235°C that contains the bulk of naphthalene and phenols.

Although 10–30-t mild-steel or wrought-iron pot stills, equipped with fractionating columns, are still in use at one tar works in Spain, continuous stills that have daily capacities of 100–700 t are preferred and used exclusively in the rest of the world.

The various designs of continuous tar stills are basically similar. The crude tar is filtered to remove large-sized solid particles, dehydrated by heat exchange and passage through a waste heat coil, then heated under pressure to ca 360°C, and flashed to separate volatile oils from the involatile pitch. The volatile oils are separated into a series of fractions of increasing boiling range by fractional condensation in a side-stream column or a series of columns. The various designs differ in the extent to which heat exchange is used, in the plan of the pipe-still furnace, in the distillation pressure, and in whether recycle of pitch or base tar is involved.

The Abderhalden design, employed at some French distilleries and used in the United Kingdom for distilling tar to a base-tar residue, is probably the simplest single-pass, atmospheric-pressure design (7). After straining and the addition of alkali as a corrosion inhibitor, the crude tar is heat-exchanged with the distillation side-streams and the hot pitch and then passed through an economizer coil in the convection section of the furnace. This furnace is essentially a rectangular chamber lined with refractory brick divided into two sections by a curtain wall, which has apertures to enable the hot flue gases to pass from one compartment to the other. The first section serves as the combustion and radiant-heating section in which coke-oven gas, fuel oil, or creosote-pitch fuel is burned at specially designed nozzles projecting into the chamber. The products of combustion are drawn by a fan from the combustion chamber into the second, or convection, chamber before exhaustion to a chimney stack via a waste-heat coil. The coils through which the tar is pumped are, in some designs, set in the walls of the convection chamber only. In other designs, the main heating coil is partly set in the combustion chamber where it is heated by direct radiation.

In the Abderhalden plant, the crude tar leaves the waste-heat coil at ca 150°C under a back pressure and is expanded into the dehydrator. The temperature in this cylindrical baffled vessel is maintained by circulating hot, dehydrated tar through a coil at the base. The moisture and light oils flash off and pass directly to the side-stream fractionating column. The dehydrated tar from the base of the dehydrator is pumped at 400–500 kPa (ca 4–5 amt) through the main heating coil in the radiant section of the furnace. The hot tar at 350–360°C is injected into the pitch flash chamber together with superheated steam. Steam and oil vapors join the dehydrator overhead distillate at the base of the fractionation column, from which an overhead stream of water and light oils, side-stream oil fractions, and a heavy oil residue are taken. The overhead stream is separated in a decantor and the oil layer partly returned to the bubble-cap fractionating column for reflux. A similar design differs only in the extent of heat exchange (8).

Several descriptions have been published of the continuous tar stills used in the CIS (9–11). These appear to be of the single-pass, atmospheric-pressure type, but are noteworthy in three respects: the stills do not employ heat exchange and they incorporate a column having a bubble-cap fractionating section and a baffled enrichment section instead of the simple baffled-pitch flash chamber used in other designs. Both this column and the fractionation column, from which light oil and water overhead distillates, carbolic and naphthalene oil side streams, and a wash oil-base product are taken, are equipped with reboilers.

The original Koppers design, still in use at some older plants in Europe (12), is a single-pass, atmospheric-pressure design, but differs from other designs by employing separate bubble-tray columns for each oil fraction. After straining, alkali doping, and dehydration, the tar is pumped through the radiantly heated main furnace coil under pressure and, at 360°C, injected into the baffled-pitch column where the pitch is separated from the oil vapors. Steam is added to the pitch column to assist vaporization. These vapors then pass through four columns operated at atmospheric pressure and progressively lower temperature to yield the various oil fractions as base products. The temperature at the top of each column is automatically controlled by recycling part of the bottoms from each column as reflux to the preceding column. The overhead distillate from the final column consists of the benzole fraction and steam. It is condensed, the two layers are separated in a decantor, and part of the benzole fraction product is recirculated as reflux.

The simplest unit employing vacuum fractionation is that designed by Canadian Badger for Dominion Tar and Chemical Company (now Rütgers VFT Inc.) at Hamilton, Ontario (13). In this plant, the tar is dehydrated in the usual manner by heat exchange and injection into a dehydrator. The dry tar is then heated under pressure in an oil-fired helical-tube heater and injected directly into the vacuum fractionating column from which a benzole fraction, overhead fraction, various oil fractions as side streams, and a pitch base product are taken. Some alterations were made to the plant in 1991, which allows some pitch properties to be controlled because pitch is the only product; the distillate oils are used as fuel.

A unique design is employed in the Clairton refinery of the Aristech Chemical Corporation (formerly United States Steel Corporation), where a sequence of fractionation stages is operated at increasing temperature (14). Each stage consists of a helical-coil heater, a vacuum flash drum, and a vacuum fractionating column. Dehydration and the removal of light oil are carried out at atmospheric pressure. The topped tar is pumped to the first stage which yields a phenolic oil overhead. The bottoms pass to the second stage which yields a close cut naphthalene oil as the overhead product. The third stage separates residual oils from the pitch, and in the fourth the residual oils are separated into fractions required for various grades of creosote.

The modern Teerverwertung-Koppers design, based on the experience at the Rütgerswerke refinery at Meiderich (which was closed in 1994), was a single-pass atmospheric- and reduced-pressure unit (Fig. 1) (15). The crude tar was pumped through five heat exchangers to the dehydrator. The benzole fraction and steam from the top of this unit were cooled, condensed, and separated, and some of the oil recycled as reflux. The dehydrated tar was pumped through a heating coil in the tube furnace and, at 300–310°C, injected into the atmospheric-pressure fractionation stage, which consisted of two fractionating columns and a splitting column. The products taken from this first stage include residual light oils and water, which were taken overhead from the first column and passed back to the dehydrator. Naphthalene oil was taken as overhead distillate from the second column, whereas wash oil and methylnaphthalene oil were taken as the base product from the second column. The base tar from the base of the first column was picked up by a pump and passed through a separate coil in the furnace and, at 300°C, injected into the pitch flash chamber which, like the final fractionating column, was maintained under a vacuum of 13.3 kPa (100 mm Hg). The residual oil vapors, separated from the pitch residue, were split into a heavy wash oil and anthracene oils 1 and 2 in the vacuum column.

The former Rütgerswerke (now VFT, AG) plant at Castrop-Rauxel produces closely fractionated concentrates of a number of polynuclear hydrocarbons that are further separated and purified to provide the main source of these chemicals for western Europe (16).

The crude coke-oven tar is dehydrated by heat exchange with the dehydrator overhead distillate and passage through a low pressure steam heater. The dehydrated tar is heat-exchanged with the carbolic-oil stream and the pitch and enters the midpoint of the carbolic-oil column at 250°C. This column operates at atmospheric pressure and contains 40 bubble-cap trays; the reflux ratio is 16:1. Carbolic oil is taken overhead and naphthalene oil is taken as a side stream. The latter is upgraded in a 20-tray splitting column to give a fraction containing 84–88% naphthalene, equivalent to 95% of the naphthalene in the crude tar. The bottoms from the carbolic-oil column passes next to a vacuum fractionating stage consisting of a 40-tray column and a 20-tray splitting column to yield a methylnaphthalene concentrate, a light wash oil, and a fraction rich in fluorene and acenaphthene. The residual base tar is heated to 280°C and pumped to the anthracene column which is maintained at 9.3 kPa (70 mm Hg). Anthracene oil and heavy oil are separated from pitch and the overheads are further fractionated in a separate vacuum column into an anthracene–phenanthrene concentrate, a fraction containing 95% carbazole, and a heavy oil from which pyrene, fluoranthene, and chrysene can be isolated. In addition, separate base products from the splitting columns are reboiled by heat from the bottoms products of the main columns.

The most widely used design of continuous coal-tar is probably the Wilton design supplied by Bitwater Industrial Process Plant of Heywood (formerly Chemical and Thermal Engineering, Ltd.) in United Kingdom. Plants were installed in several refineries in the United Kingdom, Australia, New Zealand, India, Spain, Argentina, and Korea. The popularity of this design, which operates on the recycle principle, is the result of good thermal efficiency and flexibility in handling any type of tar over a wide range of throughputs (Fig. 2). The plant contains a helical-coil furnace, a dehydration column, two valve-tray fractionating columns, and a pitch column divided into an upper stripping section and a lower mixing section. The crude tar is pumped through coarse filters and, after the addition of alkali solution, passed via a heat exchanger to the waste-heat coil in the

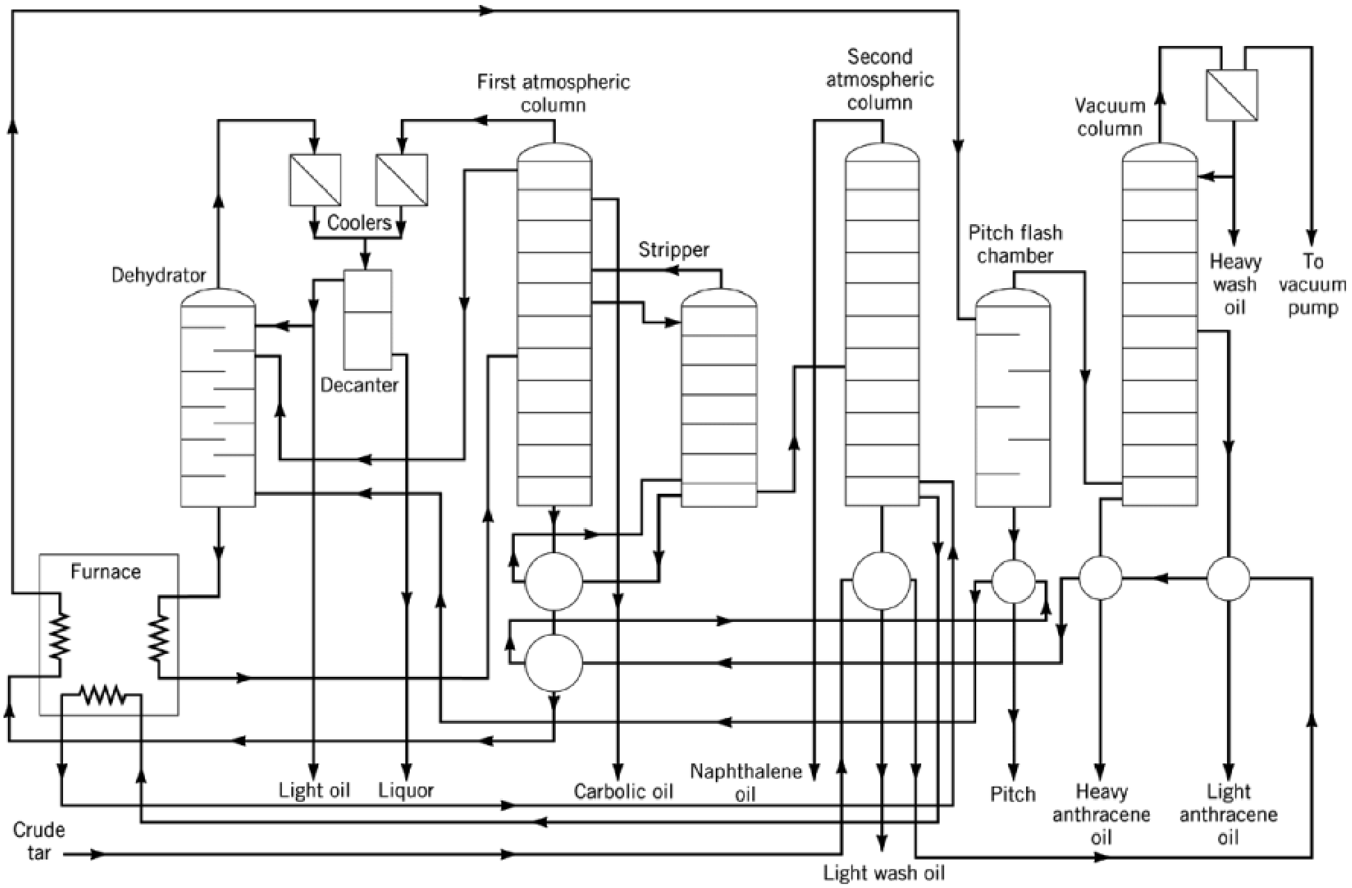

Fig. 1. Teerverwertung-Koppers tar distillation plant.

convection part of the furnace. The heated tar, under a moderate back pressure, enters the baffled dehydration column where the entrained liquor and light oils vaporize, leaving the dehydrated tar which is pumped to the bottom or mixing section of the pitch column. Here, it is mixed with a greater volume of hot pitch overflowing from the stripping section. This pitch-dehydrated tar mixture is pumped through the radiantly heated main furnace coil, which is backpressured to prevent vaporization.

At 350–360°C, the mixture leaves the furnace and enters the upper part of the pitch column where the distillate oil vapors flash off, leaving the pitch residue. Vaporization is assisted by injecting superheated steam at the base of the stripping section. A level of some pitch is maintained at this point, where the main pitch product is drawn off. The remainder of the pitch overflows into the mixing section from which it is recycled together with the dehydrated tar. The total vapors from the pitch column, including those produced in the mixing section by the contact of hot pitch with the dehydrated tar, pass to the base of the bottoms fractionating column. Here, wash oil and anthracene oil are taken as side streams and a heavy oil is taken as base product. Uncondensed vapors from this column, together with the vapors from the dehydrator, are fed to the base of the tops column from which an overhead benzole fraction–water fraction, carbolic oil, and naphthalene-oil side-streams are taken, together with a base product which is returned to the bottoms column as reflux. The benzole fraction–water fraction is condensed and separated in a decantor: part of the light oil serves as reflux

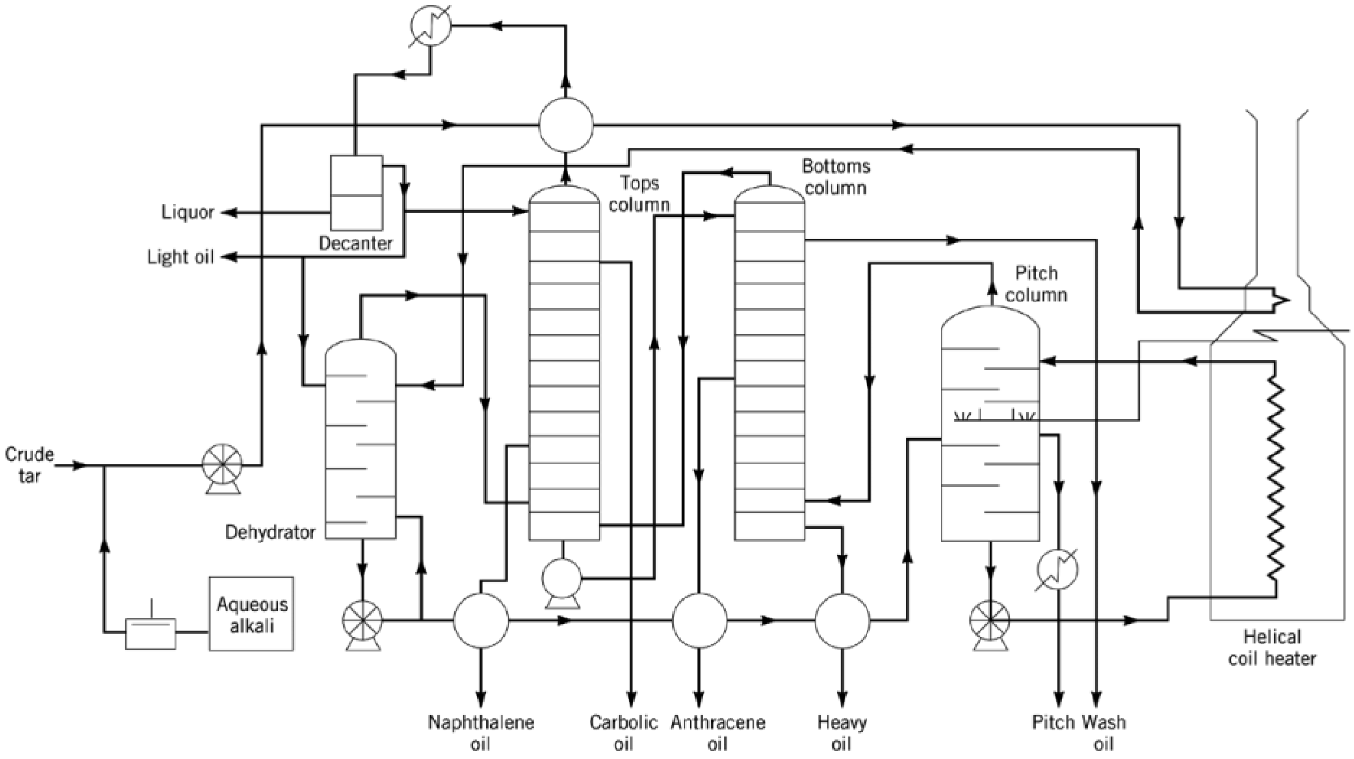

Fig. 2. The Wilton tar distillation plant.Courtesy of Chemical and Thermal Engineering, Ltd.

to the tops column. In South Africa the Wilton plant was decommissioned in the 1980s and replaced by a Koppers-design continuous distillation unit.

There are two serious problems associated with continuous tar distillation. Coal tar contains two types of components highly corrosive to ferrous metals. The ammonium salts, mainly ammonium chloride, associated with the entrained liquor remain in the tar after dehydration, tend to dissociate with the production of hydrochloric acid and cause rapid deterioration of any part of the plant in which these vapors and steam are present above 240°C. Condensers on the dehydration column and fractionation columns are also attacked. This form of corrosion is controlled by the addition of alkali (10% sodium carbonate solution or 40% caustic soda) to the crude tar in an amount equivalent to the fixed ammonia content.

The higher boiling phenols, present in considerable amounts in CVR and low temperature tars, are corrosive to mild steel, especially above 300°C. Cast iron, chrome steel, and stainless steel are more resistant. Furnace tubes, the insides of fractionating columns, and the rotors of pumps handling hot pitch and base tar are generally constructed of these metals. Nevertheless, to ensure satisfactory furnace tube life, particularly in plants processing CVR or low temperature tars, the tube temperature should be kept to a minimum.

A more important reason for operating furnaces at the lowest possible temperature is the fact that coal tar is thermally unstable. If heated above a certain temperature, coal tar decomposes, forming coke that rapidly blocks the furnace tubes. The critical temperature for coke formation is lower for vertical retort and low temperature tars than for coke-oven tars. To guard against overheating, different designs offer various options. In the Teerverwertung-Koppers design, in which vacuum is employed in the second stage, the tar need never be heated above 300–310°C, which is well below the critical temperature. If vaporization is allowed to proceed to any considerable extent in the furnace tubes combined with a high heat flux, tube wall temperatures

Table 1. Primary Coke Oven Tar Distillation

Product	CAS Registry Number	Distillation range, °C	Dry tar, %
distillates coal tar benzole fraction	[84650-02-2]	80–160	0.5–1.0
light oils or carbolic oil	[84650-03-3]	150–210	3–4
naphthalene oil	[84650-04-4]	200–250	10–12
wash oil or methyl-naphthalene oil	[90640-84-9]	240–280	6–8
anthracene oil 1	[90640-80-5]	300–400	20–25
anthracene oil 2	[90640-86-1]	300–400	20–25
pitch coal-tar[a]	[65996-93-2]		53–58

[a] High temperature.

Table 2. Primary CVR Tar Distillation

Product	Distillation range, °C	Dry tar, %
light oil	90–170	2–4
carbolic oil	180–240	12
light creosote oil	230–300	14
heavy creosote oil	275–360	11.5
residual oil	300–395	12.1
medium-soft pitch residue		44–46

might rise above the decomposition threshold at the zone where the tube contents change from foam to mist. Most plants operate the furnace tubes under a back pressure, which may be as high as 1 MPa (ca 10 atm) to suppress vaporization. The recycle of pitch in the Wilton design also minimizes vaporization and, by increasing the velocity through the tubes, improves the heat-transfer rate.

The main objectives in the primary distillation of crude tar are to obtain a pitch or refined tar residue of the desired softening point, to concentrate in certain fractions components that are subsequently to be recovered, and to yield distillate oils that are suitable for blending. A tar-distilling plant is designed to yield fractions that meet the specifications set by the purchaser, which depend on the product sales pattern. This pattern differs for different companies, and the result is that each plant is, to some extent, tailor-made and unique in its details and performance. Although at some refineries as many as seven distillate oil fractions are taken, in most plants the number of primary fractions is smaller. The situation is complicated by the fact that different names are given to identical fractions and, conversely, the same names are given by different distillers to fractions of different boiling ranges.

A typical primary distillation product pattern at a coke-oven tar-processing plant is given in Table 1. At some coke-oven distilleries, only one fraction, designated naphthalene oil, is taken between 180 and 240°C. Two fractions, light creosote or middle oil (230–300°C) and heavy creosote or heavy oil (above 300°C), are taken between the naphthalene oil and pitch.

When using a continuous vertical retort, phenols, cresols, and xylenols are collected in one fraction. A typical range of primary distillation fractions is given in Table 2.

The only valuable components in low temperature tar are the phenols and an oil fraction distilled over the range of 180–310°C, which is collected for tar-acid recovery is taken. A typical primary distillation is given in Table 3.

Table 3. Primary Low Temperature Tar Distillation

Product	Distillation range, °C	Dry tar, %
light oil[a]	up to 180	3.5
middle oil	180–310	29
wax oil[b]	300–400	37.5
medium-soft pitch residue		26

[a] Also called fresh oil.

[b] Solidifies at 20°C because of high paraffin wax content.

2.1.2. Secondary Processing of Tar Distillate Oils

2.1.2.1. Benzole (light oil) fraction, Refining of Benzene and Naphtha. The only processing that light oils might receive at the refinery is a fractional distillation into crude benzene (formerly called benzol or benzole) distilling up to 150°C, a naphtha fraction distilling from 150 to 190°C, and a creosote residue (see Btx processing; Benzene). Crude benzene from coke-oven tar is normally refined together with crude benzene separated from coke-oven gas. The naphtha is washed with alkali and acid to remove tar acids and bases, then treated with a small amount of sulfuric acid to remove sulfur compounds and olefins, and finally redistilled to give refined solvent naphtha. Alternatively, a special fraction rich in indene can be collected from which indene–coumarone resins are produced.

In the refining of the combined crude benzene, a defronting steam-stripping operation removes the lower boiling components. The defronted benzene may be fractionated in batch or continuous stills to yield a mixture of crude benzene, toluene, and mixed xylenes, and a naphtha residue. Each fraction is purified to meet grade specifications. Alternatively, the crude benzene, after defronting, may be refined and the refined product fractionated. In the refining of crude benzene or its distillate fractions, nonaromatic hydrocarbons and thiophene derivatives are removed. Formerly the oil was usually mixed with 2–4%-concentration sulfuric acid for a short time, washed, and separated from the spent acid. This treatment is followed by a dilute alkali and a water wash, and the product is refractionated. In the 1990s, however, a number of refineries in the United States, South Africa, and Europe employ hydrorefining, in which the vaporized hydrocarbon feedstock and hydrogen are passed over a cobalt molybdate-on-alumina catalyst at 400°C and 3550 kPa (500 psig). The olefins are converted to paraffins or cycloparaffins, and thiophene compounds to hydrogen sulfide. After washing with alkali to remove H_2S, small amounts of nonaromatic hydrocarbons are removed by the Udex process, the Shell Sulfolane process, or the *N*-methylpyrrolidone extraction process of Metallgessellschaft AG (see Extraction, liquid–liquid extraction).

Gasworks crude benzene and the lower boiling liquid products from low temperature carbonization, so-called fresh oil or low temperature spirit, are too low in aromatic hydrocarbon content to be refined economically to synthesis-grade benzene and toluene. Formerly, these fractions were used as a gasoline additive; in the 1990s, the lower boiling liquid products are used as fuel at the refinery.

2.1.2.2. Coumarone–Indene Resins. These should be called polyindene resins (17) (see Hydrocarbon resins). They are derived from a close-cut fraction of a coke-oven naphtha free of tar acids and bases. This feedstock, distilling between 178 and 190°C and containing a minimum of 30% indene, is warmed to 35°C and polymerized by adding 0.7–0.8% of the phenol or acetic acid complex of boron trifluoride as catalyst. With the phenol complex, tar acids need not be completely removed and the yield is better. The reaction is exothermic and the temperature is kept below 120°C. When the reaction is complete, the catalyst is decomposed by using a hot concentrated solution of sodium carbonate. Unreacted naphtha is removed, first with live steam and then by vacuum distillation to leave an amber-colored resin. It is poured into trays, allowed to cool, and broken up for sale.

2.1.2.3. Pyridine Bases. Formerly, pyridine bases were recovered from coal-tar light oils (18), but in more recent years synthetic pyridine and methylpyridine have mostly replaced the coal-tar products.

First, the tar acids were removed from the naphtha fractions of light oils and, in the case of CVR tars, carbolic oil. The oils were then mixed with 25–35% sulfuric acid. After separation of the sulfates, the aqueous solution was diluted with water and the resinous material skimmed off. The diluted sulfate solution was boiled to expel any neutral oils, dried by the addition of solid caustic soda or azeotropically with benzene, and fractionated to yield pyridine, 2-methylpyridine (α-picoline), and a fraction referred to as 90/140 bases, which consisted mainly of 3- and 4-methylpyridines and 2,6-dimethylpyridine (2,6-lutidine). Higher boiling fractions were termed 90/160 and 90/180 bases because 90% of the product distilled at 160 and 180°C, respectively.

2.1.2.4. Carbolic Oils and Low Temperature Tar Middle Oil, Tar Acids. The fractions of some coke-oven tars, distilling in the range of 180–240°C, and the middle oil fraction (180–310°C) from low temperature tars are treated for the recovery of tar acids (19).

The oils are mixed with a slight excess of 10% aqueous caustic soda in stirred vessels, continuous extraction columns, or, at some refineries, by circulating the contents of the mixing vessel by a gear pump. The extraction is carried out at ambient temperature or just above the crystallizing point of the oil. The extraction is best carried out in two stages, using 90% of the alkali to contact the fresh oil and the remainder to complete the removal of the phenols. The crude phenolate or cresolate solution is separated, and contains some neutral and basic material which must be removed by extracting with phenol-free light oil or crude benzole and/or treating with live steam.

The purified sodium phenolate solution is then decomposed by passing it down ring-packed or coke-filled towers at 80–85°C countercurrent to a gas containing 25–30% CO_2, generated in lime-coke kilns, or a flue gas containing 10–15% CO_2. This operation is called springing. Because the rate of CO_2 absorption depends on the CO_2 partial pressure, the richer gas reduces the number and size of the springing towers required. An upper layer of crude wet tar acids and a lower layer of sodium carbonate solution is obtained. The crude wet tar acids contain ca 20–25% of sodium carbonate solution. To reduce their moisture content to ca 10%, the crude wet tar acids are passed down an after-carbonation tower countercurrent to a stream of the CO_2-containing gas. Separation of the layers, into which the effluent from the various carbonation tower divides, yields crude tar acids containing ca 10% liquor and a solution of sodium carbonate and bicarbonate.

Caustic soda is removed from the carbonate–bicarbonate solution by treating with a slight excess of hard-burned quicklime (or slaked lime) at 85–90°C in a stirred reactor. The regenerated caustic soda is separated from the calcium carbonate precipitate (lime mud) by centrifuging or rotary vacuum filtration. The lime mud retains 30–35% liquid and, to avoid loss of caustic soda, must be well-washed on the filter or centrifuge. Finally, the recovered caustic solution is adjusted to the 10% level for recycle by the addition of 40% makeup caustic soda.

Disposal of the washed lime mud poses a problem. Drying and calcining to regenerate lime and CO_2 require an uneconomical expenditure of energy and, as of the mid-1990s, lime mud is dumped. The production of lime mud can be avoided by using sulfuric acid for springing and the partial electrolysis of the sodium sulfate to give a mixture of caustic soda and sodium sulfate as the recycled extracting medium. This alternative to caustic soda extraction and lime recausticization, although successful in laboratory and pilotscale tests, has not been applied in commercial practice as of 1996.

In the next stage in the recovery and refining of tar acids, water and pitch are removed from the crude tar acids in a continuous-vacuum still heated by superheated steam or circulating hot oil. The aqueous phenol overhead distillate is recycled, the stream of once-run tar acids is refined, and the phenolic pitch bottoms are burned.

The once-run tar acids are fractionated in three continuous-vacuum stills heated by superheated steam or circulating hot oil. These stills contain 40–50 bubble trays and operate at reflux ratios between 15 and 20:1. The overhead product from the first column is 90–95% phenol; from the second, 90% *o*-cresol; and from the third, a 40:60 *m*-cresol–*p*-cresol mixture. Further fractionation gives the pure products.

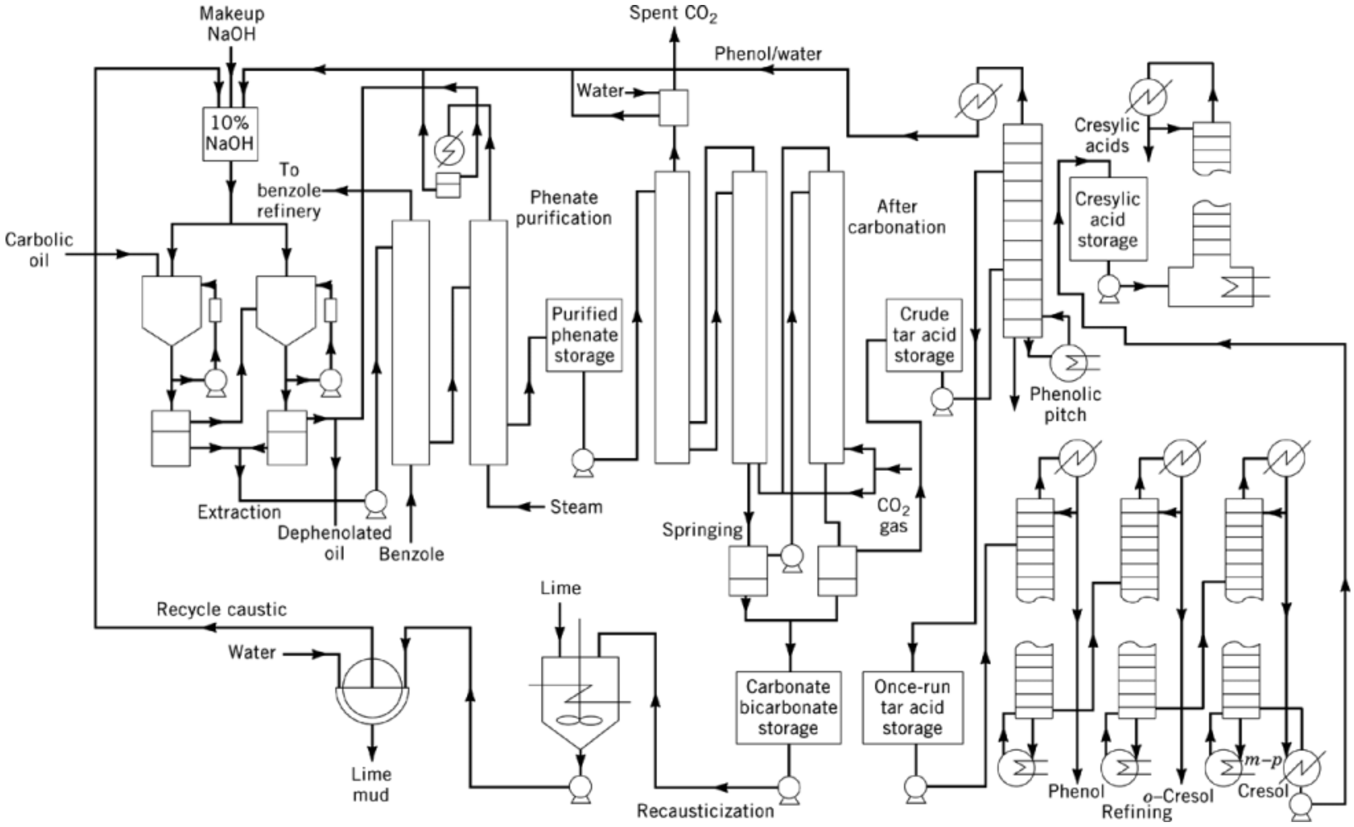

Fig. 3. Tar-acid extraction and refining.

At other refineries, only two continuous stills in series are used, but these are of 80–100 plate efficiency and yield pure grades of phenol and *o*-cresol and a base mixture of cresols, xylenols, and higher boiling tar acids. The latter are fractionated batchwise to various saleable grades of cresylic acids.

Fractionation columns in tar-acid refineries are generally operated under vacuum and heated by high pressure steam or circulating hot oil. Calandria in the reboilers, condensers, rundown lines, and receiving tanks are constructed of stainless steel, or, in the case of the condensers, of tin or nickel. Cast-iron column shells are satisfactory, but stainless-steel bubble or valve trays are preferred. A flow sheet of a typical tar acid extraction and refining plant is shown in Figure 3.

In the case of low temperature tar, the aqueous liquor that accompanies the crude tar contains between 1 and 1.5% by weight of soluble tar acids, eg, phenol, cresols, and dihydroxybenzenes. Both for the sake of economics and effluent purification, it is necessary to recover these, usually by the Lurgi Phenosolvan process based on the selective extraction of the tar acids with butyl or isobutyl acetate. The recovered phenols are separated by fractional distillation into monohydroxybenzenes, mainly phenol and cresols, and dihydroxybenzenes, mainly *o*-dihydroxybenzene (catechol), methyl *o*-dihydroxybenzene, (methyl catechol), and *m*-dihydroxybenzene (resorcinol). The monohydric phenol fraction is added to the crude tar acids extracted from the tar for further refining, whereas the dihydric phenol fraction is incorporated in wood-preservation creosote or sold to adhesive manufacturers.

2.1.2.5. Naphthalene Oils. Naphthalene is the principal component of coke-oven tars and the only component that can be concentrated to a reasonably high content on primary distillation. Naphthalene oils from coke-oven tars distilled in a modern pipe still generally contain 60–65% of naphthalene. They are further upgraded by a number of methods.

In the older method, still used in some CIS and East European tar refineries, the naphthalene oil is cooled to ambient temperatures in pans, the residual oil is separated from the crystals, and the crude drained naphthalene is macerated and centrifuged. The so-called whizzed naphthalene crystallizes at ca 72–76°C. This product is subjected to 35 MPa (350 atm) at 60–70°C for several minutes in a mechanical press. The lower melting layers of the crystals are expressed as liquid, giving a product crystallizing at 78–78.5°C (95.5–96.5% pure). This grade, satisfactory for oxidation to phthalic anhydride, is referred to as hot-pressed or phthalic-grade naphthalene.

The more modern processes adopted in the United Kingdom and some European plants (20) are also based on crystallization of the primary naphthalene oil, which is diluted with lower crystallizing material to give a feedstock crystallizing point at 55°C. This material is cooled in closed, stirred tanks to 30–35°C and the resultant slurry of naphthalene crystals and mother liquor is centrifuged, washed, and spun-dried. These operations are automatically timed and controlled. At other European and U.S. refineries, coke-oven naphthalene oil is upgraded by fractionation and further purification.

In a novel but no longer used naphthalene-purification method, oil containing ca 70% of naphthalene was charged to tall cylindrical tanks equipped with internal heating or cooling coils and cooled to 35°C. Mother liquor was allowed to drain from the base of the tank and, when drainage was complete, the tank was filled with methanol until the solvent levels was above the surface of the crystallized naphthalene. After standing for one hour, the methanol was drained. This procedure was repeated. Finally, the purified naphthalene was melted by passing steam through the internal coils and the liquid product discharged to storage. This product was pure enough for the manufacture of 2-naphthol.

Several refineries in Europe employ the Pro-Abd refiner to upgrade whizzed naphthalene to phthalic-grade quality or to convert the latter into the purer chemical grade. The device consists of a rectangular tank fitted with a nest of coils through which either steam or water circulates. The tank is filled with the feedstock, which is crystallized by circulating cold water in the coils. When the contents of the tank have solidified, a tap at the base is opened and hot water is circulated until the temperature is just below the desired crystallizing point of the product. This condition is maintained until no more oil drains from the base. The bottom tap is then closed and the contents of the tank are melted by steam circulation and drained.

In the Sulzer-MWB process the naphthalene fractions produced by the crystallization process are stored in tanks and fed alternately into the crystallizer. The crystallizer contains around 1100 cooling tubes of 25-mm diameter, through which the naphthalene fraction passes downward in turbulent flow and partly crystallizes out on the tube walls. The residual melt is recycled and pumped into a storage tank at the end of the crystallization process. The crystals that have been deposited on the tube walls are then partly melted for further purification. Following the removal of the drained liquid, the purified naphthalene is melted. Four to six crystallization stages are required to obtain refined naphthalene with a crystallization point of 80°C, depending on the quality of the feedstock. The yield is typically between 88 and 94%, depending on the concentration of the feedstock fraction.

In the late 1980s, Brodie crystallizers were installed in the United Kingdom and in France for upgrading phthalic-grade naphthalene to 99% purity or better. This apparatus, developed by Union Carbide Corporation, Australia, for separating *o*- and *p*-dichlorobenzene, was adapted for naphthalene refining. The one installed in the United Kingdom, however, has been closed (21) (see Naphthalene).

2.1.2.6. Wash Oils and Methylnaphthalene Oils. No tar chemicals are extracted commercially from tar oils distilling in the range of 250–300°C. Although the wash-oil fraction of coke-oven tars, distilling mainly in the range of 250–280°C, is employed at coking installations to scrub benzene from coal gas, most oils in this boiling point range are used in creosote blends.

Table 4. Correlations for Predicting the Physical Properties of Tars and Tar Products

Property	Applicable to	Correlation expression	Comments and references
density, d at 20°C, g/cm^3	coke-oven dry tars and tar oils	$d_{20} = 1.877 \times 10^{-3}\, M^{a} + 0.808$	22
		$d_{20} = 7.337 \times 10^{-4}\, t_b + 0.890$	23
variation of sp gr with temperature, t, g/cm^3	dry tars	(sp gr)/t = 0.001778 - 0.00098 sp gr at 15.6°C	nomograph available; 24
variation of density with temperature, t, g/cm^3	dry tars, tar oils, and pitches	$d_{t1} = d_{t2} - b(t_1 - t_2)^{c}$	25
	dry coke-oven tars and tar oils	$\beta = \frac{d_0 - d_t}{d_0 t}$	β has negative value; 25
		$\beta = (-10.5433 + 0.0122/t_{\mathrm{b}}) \times 10^{-4}$,	
		$\beta = (-12.6114 + 0.0346\, M^{a}) \times 10^{-4}$	
viscosity, η, mPa·s (=cP)	tar oils	$\log \eta_{20} = 0.0078\, t_b - 1.123^{d}$	nomograph available; 26
specific heat capacity, C, kJ/(kg·K)^{e}	tar oils	$C_t = ((0.7360 + 0.8951 d_{20} + 0.00360 t)/d_{20}) + (0.00904 - 0.0000221 t_b) T_a{}^{f}$	27
	pitches	$C_{\mathrm{t}} = 3.665/d_{20} - 1.729 + 0.00389 t$	28
thermal conductivity, K, W/(m·K)	tar oils	$K = (1.34 - 0.00084 t \pm 0.084) \times 10^{-5}$	
	pitches	$K = (1.423 \pm 0.084) \times 10^{-5}$	no significant variation over range 25–105°C; 29
surface tension, S, mN/m (=dyn/cm)	dry tars, tar oils, and pitches	$S = 93.8 d_{20} - 0.0496 t_b, - 47.5$, $S_t = 18.4 d_t^4$, $S_t = \frac{S_{20} d_t}{d_{20}^4}$	nomograph available; (30, 31)
latent heat of vaporization, L, kJ/kg^{b}	tar oils	$L = d_{20}(486.1 - 0.599 t_b)^{g}$	32

[a] Average molecular weight.

[b] Average boiling point defined as the mean of the temperatures in °C at which 10%, 20%,. . .90% by volume distills in a standard flask distillation.

[c] $b = 0.00068 \pm 0.00005$ for dry tars and $(162.7 - 86.2 d_{20} \pm 8) \times 10^{-5}$ for tar oils and pitches.

[d] At other temperatures, log η varies linearly with the absolute temperature. At t_{b}, the viscosity of any tar oil is approximately $0.25 \mathrm{mPa \cdot s} (= \mathrm{cP})$.

[e] To convert J to cal, divide by 4.184.

[f] T_{a}, % tar acids, is defined as the percentage by volume extracted by 10% aqueous caustic soda.

[g] At the average boiling point.

2.1.2.7. Anthracene Oils. In Europe but not in the United States, crude anthracene is isolated from coke-oven anthracene oils. In some cases where the anthracene oil gives only a small residue at 360°C, the oil is diluted using half its volume of drained naphthalene oil or a light wash oil and this blend is cooled to 35°C. The resulting solid–liquid slurry is filtered or centrifuged to give a crude anthracene containing 40–45% anthracene. With other samples of oil, it is necessary to recrystallize the first cake obtained by cooling the undiluted anthracene oil to 30–35°C and separating the crystals by filtration or centrifugation. This first crop of crystals generally contains 12–15% of anthracene and is recrystallized. The anthracene concentrate, termed 40-s anthracene, is sold as such.

2.2. Physical Properties

The physical properties of crude tars vary over a wide range. Investigation has been mainly concerned with establishing correlations between the more readily determined chemical and physical properties of the distillate oils and residual pitch, and other properties. Based on the correlations, other properties can be predicted with an accuracy sufficient for such purposes as plant design (Table 4).

Table 5. Viscosities of Fixed Points for Coal-Tar Pitch

Fixed point	Viscosity, Pa·s(= 10^3cP)	Difference between fixed point and EVT, °C	References
equiviscous temperature, EVT, °C	25		34
R-and-B softening point[a], °C	800	−19	37
K-and-S softening point, °C	5500	−27	38
penetration of 200[b]	2×10^4	−30	36
penetration of 10[b]	10^7	−51	39[c]
ductility point, °C[d]	10^7	−51	40
Fraas brittle point, °C	4×10^7	−65	41
transition to glassy state	10^{12}	−90	

[a] Ring-and-ball method (ASTM D36-26). In the United States, two other softening point methods are employed: cube-in-air (35) and cube-in-water (36). Cube-in-air softening point = R-and-B softening point +4°C. Cube-in-water softening point = R-and-B softening point +10°C.

[b] Penetration of 20 or 1 mm using a 100-g weight for 5 s at 25°C.

[c] Ref. 39 gives the relationship between viscosity and penetration (mm × 10): $\eta(\text{Pa·s}) = (1.58 \times 10^9)/\text{penetration}^{2.16}$.

[d] When a pitch is tested for ductility, the sample either suffers brittle fracture without elongation or elongates to the maximum distance without breaking. When tested at increased temperatures at a particular point, ie, the ductility point, the behaviour changes from the first type to the second.

2.2.1. Viscosity of Coal-Tar Pitch and Change with Temperature

Because pitch is mainly used as a hot-applied binder or adhesive, the viscosity and its change with temperature are important in industrial practice. Some useful correlations, by which the viscosity of pitch at any temperature can be predicted, have been developed. The data on which such correlations are based may be from one of the fixed equiviscous points that characterize a pitch (Table 5).

The viscosity of a straight-run or fluxed-back pitch can be calculated from the R-and-B (ring-and-ball) softening point:

$$\log \eta_t = -4.175 + \frac{711.8}{86.1 - t_S + t} \qquad (1)$$

where η_t is the viscosity at temperature t °C in Pa·s × 10^{-1}(= P) and t_S is the R-and-B softening point in °C (42). Mettler softening point is widely used in the 1990s as the equivalent to R and B + 3°C (ASTM D3104). Equation 1 covers a temperature range of 180°C and viscosity of 10^8. It cannot be used to predict the viscosity accurately because the softening point itself is only an approximate measure of the viscosity and also because there are small differences in the temperature susceptibility of different types of pitch. However, equation 1 provides a useful means of calculating viscosities at any temperature above the softening point, exhibiting an accuracy sufficient for most design purposes.

The general equation for the temperature function of coal-tar pitch takes the following form (43):

$$\log \log (\nu + 0.8) = K + K_1 \log t \qquad (2)$$

where ν is the kinetic viscosity (mm^2/s (=cSt)), t is the temperature in K and K and K_1 are constants. K_1 depends on the toluene-insoluble (TI) content (TI in wt %).

$$K_1 = 5.8 - 0.03\text{TI}$$

This relationship applies to a wide range of straight-run and heat-treated pitches but not to fluxed pitches. If the K-and-S (Krämer and Sarnow) softening point is taken as a fixed point, equation 2 can be written as

$$\log\log(\nu + 0.8) = 0.08 + 0.04 \log \mathrm{TI} + (5.8 - 0.03\mathrm{TI})\ \ (\log(t_S + 273) - \log t)$$

where t_S is the K-and-S softening point in °C.

Another equation has the form

$$\log \eta = AT^{-5} + B \qquad (3)$$

where η is the dynamic viscosity in $\mathrm{mPa{\cdot}s}(=\mathrm{cP})$, t is the temperature in K, and A and B are constants derived from data relating to a range of pitches and refined tars varying in softening point from 54 to 104°C. The value of A in equation 3 is closely related to the softening point and can be expressed as

$$A = (0.358t_S + 3.74) \times 10^{12} \qquad (4)$$

where t_S is the R-and-B softening point using glycerol as the heating medium or, using water as the heating medium, as follows:

$$A = (0.358t_S + 4.82) \times 10^{12} \qquad (5)$$

B in equation 3 is related to the TI content:

$$B = 0.0206\mathrm{TI} - 0.378 \qquad (6)$$

Using equation 3, the viscosity of any pitch can be calculated from two measurements in the range of 10^4–10^6 $\mathrm{mPa{\cdot}s}(=\mathrm{cP})$, exhibiting a precision similar to what may be expected of direct measurement. By employing equations 3, 4 or 5, and 6, the viscosity of pitch at any temperature can be calculated, with an accuracy adequate for most engineering purposes, from the R-and-B softening point and the TI content.

2.3. Chemical Composition

The tars recovered from commercial carbonization plants are not the primary products of the thermal decomposition of coal. The initial products undergo a complex series of secondary reactions. Although pilot-plant tests carried out by the U.S. Bureau of Mines show that at any given carbonizing temperature the yield of tar is related approximately linearly to the content of volatile matter of the coal, no clear trends could be distinguished between the nature of the coal and the physical properties or chemical composition of the tar produced under the same carbonizing conditions (44). More recent studies have given a clearer picture. The application of statistical structural analysis based on ir spectrometry and proton nmr (45), a combination of uv and ir spectrometry with gas chromatography (gc) of coal pyrolysis products (45, 46), and correlation of refractive index, molecular weights, and densities, have made important contributions (47, 48). Evidence suggests that, when coal is heated in the absence of air, relatively small molecules are released that are absorbed in the micropore structure of the coal, including straight-chain and branched-chain alkanes and alkenes having terminal double bonds and aromatic hydrocarbons such as benzene, toluene, naphthalene, methyl- and dimethylnaphthalenes, acenaphthene, and fluorene. The principal decomposition occurs at 450–500°C with the volatilization of 15–20% of the coal. This reaction appears to be depolymerization, probably by breaking the methylene, polymethylene, or conjugated olefin bridges between the aromatic ring clusters to yield free radicals. These radicals are believed to have molecular weights of 300–800 and to consist of systems containing

Table 6. Properties of Coal Tars

	Coke-oven tars				Fromer CVR tars		Low tempera-ture tars	Lurgi tars
	U.K		Germany	U.S.	U.K.		U.K.	U.K.
Property	Average	Range	Average	Average	Average	Range	Average	Average
yield, L/t	33.6	16.8–43.2	26.8		70.9	62.7–75.0	95.5	12.7
density at 20°C, g/cm^3	1.169	1.138–1.180	1.175	1.180	1.074	1.066–1.083	1.029	1.070
water, wt %	4.9	3.2–6.5	2.5	2.2	4.0	2.1–6.3	2.2	2.8
carbon, wt %	90.3	86.8–93.5	91.4	91.3	86.0	85.3–87.2	84.0	84.2
hydrogen, wt %	5.5	5.1–6.0	5.25	5.1	7.5	7.2–7.8	8.3	7.7
nitrogen, wt %	0.95	0.73–1.07	0.86	0.67	1.21	0.84–1.65	1.08	1.09
sulfur, wt %	0.84	0.68–0.96	0.75	1.2	0.90	0.67–1.16	0.74	1.39
ash, wt %	0.24	0.03–0.67	0.15	0.03	0.09	0.03–0.24	0.10	0.02
TI[a], wt %	6.7	2.7–7.5	5.5	9.1	3.1	0.9–5.1	1.2	0.7

[a] Toluene-insoluble components.

4–10 fused aromatic or cycloaromatic rings having paraffinic side chains or hydroxy substituents. Some of these free radicals condense to high molecular weight resins which remain in the coke; others are stabilized by hydrogen transfer. The stabilized free radicals undergo secondary cracking reactions as they come in contact with the hot coke.

The nature of the secondary reactions is uncertain. Some believe that the primary tar components are broken down to small free radicals that recombine as they travel toward the retort exit; others suggest that some components remain relatively intact except for the removal of peripheral substituent groups and that the higher molecular weight components of coal tar are, in effect, slightly altered fragments of the original coal structure.

Although these speculations are of academic interest only, it is clear that even tars produced at the lowest commercial carbonization temperatures are very different from primary tars. In fact, low temperature tar, continuous vertical-retort (CVR) tar, and coke-oven tar form a series in which the yield of tar decreases, the aromaticity of the tar increases, the content of paraffins and phenols decreases, and the ratio of substituted aromatic and heterocyclic compounds to their unsubstituted parent molecules decreases. These differences are reflected in the densities and carbon/hydrogen ratios of the tars recorded in Table 6. Higher aromaticity correlates with higher density and C/H ratio. The reactions accounting for these changes, ie, cracking and cyclization of paraffins, dehydration of phenols, and dealkylation of aromatic and heterocyclic ring compounds, are those that would be expected, on thermodynamic grounds, to occur at the temperatures prevailing in carbonization retorts.

The application of modern methods of analyses such as gc, low ionization voltage mass spectrometry, high pressure liquid chromatography (hplc), and nmr has greatly increased knowledge of coal-tar composition without materially altering the qualitative picture.

Coke-oven tar is an extremely complex mixture, the main components of which are aromatic hydrocarbons ranging from the monocyclics benzene and alkylbenzenes to polycyclic compounds containing as many as twenty or more rings. Heterocyclic compounds containing oxygen, nitrogen, and sulfur, but usually only one heteroatom per ring system are present. Small amounts of paraffinic, olefinic, and partly saturated aromatic compounds also occur. The aromatic and heterocyclic structures occur in both unsubstituted and substituted forms. The main substitutes are methyl, ethyl, or hydroxyl. Although longer aliphatic side chains are encountered in small amounts in the lower boiling fractions, they tend, like hydroxyl groups, to disappear in the higher boiling fractions. Molecules containing up to four rings are generally fully condensed, but in the more complex molecules, the degree of condensation is less complete and branched ring–chain structures, in which most of the rings are fused to no more than three other rings, predominate.

The normally distillable part at atmospheric pressure of coke-oven tar boiling up to about 400°C and amounting to up to 50% of the whole, contains principally aromatic hydrocarbons. In particular, benzene, toluene, and the xylene isomers, tri- and tetra- methylbenzenes, indene, hydrindene (indane), and coumarone occur in the first fraction normally taken, which represents about 3.5% of the tar and boils up to about 200°C. This fraction also contains polar compounds including the tar acids, phenol and cresols, and the tar bases, pyridine, picolines (methylpyridines), and lutidines (dimethyl pyridines). The most abundant component of this type of tar is naphthalene, which is taken in the second fraction and represents about 10% of the tar. It is contaminated with small but significant amounts of thionaphthene, indene, etc. The next fraction contains the two methylnaphthalene isomers equivalent to 2% of the tar. Then follow biphenyl, acenaphthene, and fluorene, all in the range 0.7 to 1% of the tar in each case and then diphenylene oxide at about 1.5%. The components anthracene and phenanthrene are usually present at about 1 and 6%, respectively. The series continues with the components boiling up to 400°, which about represents the limit of the usual commercial distillation range, ie, pyrene and fluoranthene.

The by the 1990s far less abundant continuous vertical-retort tars differ from coke-oven tars. Whereas the latter contain relatively small amounts of nonaromatic hydrocarbons, CVR tars contain a relatively high proportion of normal straight-chain or slightly branched-chain paraffins, the content of which decreases from ca 20% in the lower boiling fractions to 5–10% in the higher distillate oils. They contain 20–30% of hydroxy-substituted hydrocarbons, of which some 15% (based on tar) can be extracted from the oils distilling up to 350°C. These phenols are mainly xylenols; methylethyl- and diethylphenols; dihydric phenols, eg, catechol, resorcinol, and their methyl derivatives; hydroxy hydrindenes and their methyl and dimethyl derivatives; naphthols and hydroxy-substituted acenaphthenes; anthracenes and phenanthrenes. Furthermore, the aromatic hydrocarbons and heterocyclic structures in CVR tar are predominantly substituted by one or more methyl groups, and the content of unsubstituted ring structures, which are the main components of coke-oven tars, is comparatively small.

Low temperature tars contain 30–35 wt % nonaromatic hydrocarbons, ca 30% of caustic-extractable phenols in the distillate oils, and 40–50% of aromatic hydrocarbons. The latter usually contain one or more alkyl substituent groups. On atmospheric distillation, coke-oven tars yield 55–60% pitch, whereas CVR tars give 40–50% pitch. The pitch yield from low temperature tars is in the 26–30% range.

The number of individual components in coal tar can only be guessed. As many as 461 compounds have been identified (49). As an example, the minor components in a neutral fraction of coke-oven naphtha and naphthalene oil were investigated by a combination of high efficiency fractionation, zone refining, and ir spectroscopy. Although the oil analyzed constituted only 13.5% by weight of the tar, 49 components were identified, including all possible C_6–C_9 aromatic hydrocarbons, thiophene and indan and four methylindans, benzofuran (coumarone) and four methylbenzfurans, benzonitrile and three isomeric tolunitriles, and styrene, α-methylstyrene, *trans*-β-methylstyrene, and indene. Table 6 gives the average properties of various types of tar and Table 7 lists the amounts of components that have either current or potential industrial possibilities.

Of the total tar bases in U.K. coke-oven and CVR tars, pyridine makes up about 2%, 2-methyl pyridine 1.5%, 3- and 4-methylpyridines about 2%, and ethylpyridine and dimethylpyridines 6%. Primary bases, anilines and methylanilines, account for about 2% of the bases in coke-oven and CVR tars and 3.5% of the bases in low temperature tars. The main basic components in coke-oven tars are quinoline (16–20% of the total), isoquinoline (4–5%), and methylquinolines. These dicyclic bases are less prominent in CVR and low temperature tars, in which only a minority of the basic constituents have been identified.

Table 7. Constituents of Coal Tar

	Coke-oven tars				Former CVR tars		Low temperature tars	Lurgi tars
	U.K.		Germany	U.S.	U.K.		U.K.	U.K.
Component, wt % dry tar	Average	Range	Average	Average	Average	Range	Average	Average
benzene	0.25	0.12–0.42	0.4	0.12	0.22	0.14–0.26	0.01	0.02
toluene	0.22	0.09–0.35	0.3	0.25	0.22	0.17–0.29	0.12	0.05
o-xylene	0.04	0.02–0.07		0.04	0.06	0.05–0.08	0.05	0.05
m-xylene	0.11	0.08–0.18	0.2	0.07	0.13	0.11–0.18	0.10	0.07
p-xylene	0.04	0.02–0.07		0.03	0.05	0.04–0.07	0.04	0.03
ethylbenzene	0.02	0.01–0.05		0.02	0.03	0.02–0.04	0.02	0.04
styrene	0.04	0.02–0.04		0.02	0.04	0.02–0.06	0.01	0.01
phenol	0.57	0.14–1.15	0.5	0.61	0.99	0.49–1.36	1.44	0.97
o-cresol	0.32	0.10–0.34	0.2	0.25	1.33	0.77–1.53	1.48	1.14
m-cresol	0.45	0.16–1.0	0.4	0.45	1.01	0.58–1.33	0.98	1.83
p-cresol	0.27	0.07–0.70	0.2	0.27	0.86	0.50–1.03	0.87	1.51
xylenols	0.48	0.13–1.30		0.36	3.08	2.70–3.58	6.36	5.55
high boiling tar acids	0.91	0.31–2.09		0.83	8.09	6.57–11.1	12.89	11.95
naphtha	1.18	0.52–2.66		0.97	3.21	2.86–3.84	3.63	3.02
naphthalene	8.94	7.29–11.31	10.0	8.80	3.18	2.15–3.84	0.65	2.01
α-methylnaphthalene	0.72	0.60–0.86	0.5	0.65	0.54	0.46–0.64	0.23	0.63
β-methylnaphthalene	1.32	1.15–1.63	1.5	1.23	0.68	0.62–0.74	0.19	1.05
biphenyl	0.73	0.34–1.04			0.42	0.30–0.49	0.4	0.9
acenaphthalene	0.96	0.42–1.28	0.3	1.05	0.66	0.50–0.80	0.19	0.57
fluorene	0.88	0.46–1.80	2.0	0.64	0.51	0.33–1.23	0.13	0.62
diphenylene oxide	1.50	1.40–2.00	1.4		0.68	0.62–0.74	0.19	0.57
anthracene	1.00	0.52–1.38	1.8	0.75	0.26	0.18–0.30	0.06	0.32
phenanthrene	6.30	2.30–9.80	5.7	2.66	1.75	0.40–2.90	1.60	0.28
carbazole	1.33	0.58–1.73	1.5	0.60	0.89	0.14–1.43	1.29	0.22
tar bases	1.77	1.25–2.60	0.73	2.08	2.09	1.81–2.47	2.09	2.50
medium-soft pitch	59.8	49.5–63.9	54.4	63.5	43.7	41.0–49.3	26.0	33.1

Although gas chromatography and high pressure liquid chromatography have greatly assisted in the elucidation of the structure of tar distillate oils, the former has restricted applicability to pitch. It has, however, been applied to solvent extracts and vacuum distillates of pitch (50). More precise information about the principal components of the lower molecular weight fractions of coke-oven pitch have been obtained by the application of high pressure liquid chromatography, thin-layer chromatography (51), and low voltage mass spectrometric examinations of pitches and pitch solvent fractions at the U.S. Bureau of Mines (52). The results of these studies indicate that pitch contains the following high molecular weight constituents: aromatic hydrocarbons having four rings, eg, chrysene, fluoranthene, pyrene, triphenylene, naphthacene, and benzanthracene. Five-membered ring systems are represented by picene, benzopyrenes (BaP and BeP), benzofluoranthenes, and perylene. The next-highest fraction contains as the main components six-membered ring systems, such as dibenzopyrenes, dibenzofluoranthenes, and benzoperylenes. Seven-ring systems, eg, coronene, have also been identified. These basic hydrocarbon structures are accompanied by methyl and polymethyl derivatives and, in the case of the pitches from CVR and low temperature tars, by mono- and polyhydroxy derivatives. As in the case of the distillate oil range, heterocyclic compounds are also present.

Above this relatively low molecular weight range, which constitutes ca 40–50% of a medium soft coke-oven pitch, the information concerning the chemical structure of pitch is only qualitative and derived mainly from statistical structural analysis and mass spectra. The same sequence of polynuclear aromatic and heterocyclic compounds appears to continue, reaching molecules having 20–30 rings. As molecular weight increases, more heterocyclic atoms appear in the molecule, whereas the number and length of alkyl chains decreases and the hydrocarbon structures are not fully condensed. In the lower temperature pitches, some ring structures appear to be partly hydrogenated.

2.4. Shipment, Storage, and Handling

2.4.1. Crude Tar and Tar Products

Where the tar distillery is sited close to the carbonizing plant, the crude tar is transferred directly from the tar–liquor separating vessels on the by-product recovery unit to the storage tanks. Otherwise, it is shipped in rail or road tankers or by barge. Crude tar is stored in mild-steel tanks maintained at 40–50°C by steam coils.

Liquid tar products, eg, light oils, cresols, cresylic acids, creosote oil, and road tars, are generally transported in bulk in insulated mild-steel road or rail tankers. They are loaded at a temperature sufficiently high to ensure delivery at the desired viscosity. Small quantities are generally delivered in drums that may have to be steam-heated to ensure complete liquidity before discharge.

2.4.2. Pitch

Pitch used to be stored in solid form at the tar distillery in open bays, from which it was removed by small explosive charges. Loading of the lump pitch by mechanical shovel created a dust hazard both at the tar installation and at the customer's, where the lumps had to be ground before use. In the 1990s, pitch is stored in tanks heated by superheated steam or circulating hot-oil coils and transported in liquid form in insulated rail, road tankers, or ships. When transport as a hot liquid is not feasible, not acceptable by the customer, or for small amounts, the pitch is converted into a dust-free particulate form, ie, short rods termed pencils, pastilles, or flakes.

Several plants employ cooled-belt flakers. These consist of flexible steel belts, ca 1-m wide and up to 50-m long, that have short rubber skirting at the edges. Molten pitch flows from a thermostatically controlled tank over a weir to give a flat thin sheet on the belt, which is cooled from below by water sprays. At the end of the belt, the solid pitch is broken up by rotating tines. The pitch flakes are drained and transported to a covered storage silo by belt conveyor, during which time the surface moisture evaporates.

Direct water cooling is also employed in the pitch-pencilling plant at VFT, AG (formerly Rütgerswerke). Pitch at ca 50°C above its softening point is pumped through nozzles at a rate and pressure to give a series of almost horizontal jets. These jets project a short distance into horizontal tubes through which a cocurrent streamline flow of cooling water is maintained. The tubes extend for some 25 m and are bent into a semicircle at their exit end. The stream of pitch solidifies into solid rods about 10–20-mm thick, which break up into short lengths as they are forced round the bends. The pitch pencils are delivered into a cooling pond situated underneath the pipe assembly. A conveyor belt picks up the pitch from the pond and transports the pencils to a chute from which they fall to another conveyor belt which transports them to the storage silo. Surface drying is accomplished by warm-air jets.

Another type of pitch-pencilling plant, designed by Biwater Industrial Processes (formerly Chemical and Thermal Engineering, Ltd.), employs a vertical cooling tank. Liquid pitch at ca 150°C, held in a thermostatically controlled tank, is circulated round a ring main by a centrifugal pump. A horizontal section of the main contains an extrusion manifold consisting of a number (usually 6–10) of 9–12-mm-dia nozzles set 2000-mm apart. The circular streams of molten pitch from the nozzles fall by gravity into a deep rectangular tank containing water at 40–50°C where the pitch hardens into solid rods.

Table 8. Crude Tar Production[a]

	Volume, t × 10^3		
Country	1984	1989	1994
Belgium	195	258	~160
Brazil			318
Czech Republic	393	392	330
Canada	193	205	174
China			2800
Germany	890	739	390
France	354	250	206
Italy	267	232	182
Japan	2550	2200	1855
Netherlands	100	134	140
Poland			535[b]
CIS			2189[c]
Spain	141	129	125
South Africa			188
South Korea	246	361	445
United Kingdom	238	378	245
United States	1662	1794	1026
Total			11,348

[a] Ref. 53.

[b] 40 imports.

[c] Production value is from 1993, consisting of Russia, 1175; Ukraine, 918; and Kagakhstan, 96.

2.5. Economic Aspects

2.5.1. Crude Tar

Current world output of crude tar is estimated at between 11 and 12×10^6 t/yr. Table 8 gives such details as are available. The amount distilled is about 10×10^6 t/yr. Production of low temperature tar included in the U.K. total for 1994 was 35,000 t; at its zenith 203,000 t were produced in 1975. World production of all coal tar in 1975 was estimated at 17.3×10^6 t. The quantity of tar distilled at five yearly intervals since 1984 is shown in Table 9. Some comparative figures for the prices of coal-tar bulk products for 1982 and 1994 are given in Table 10.

2.6. Specifications

Tar bulk products are covered by both national specifications and those formulated by the user. For instance, creosote for timber preservation is covered by the American Wood Preserving Association Standards (AWPA) and ASTM D350.

In the United States creosote specification AWPA P1/89 is intended for the treatment of timber for land and fresh-water use, and the heavier grade AWPA P13/89 for the preservation of marine piling and timber. In the United Kingdom a British Standard Specification, BS.144/90, Part 1, specifies three grades of creosote: two for pressure impregnation and one for brushing application. The standards of the West European Institute for Wood Preservation (WEI) are often used in Europe.

These specifications include specific gravity, maximum water content, maximum values for toluene- or benzene-insoluble material, and maximum amounts distilling at 230°C, 270°C, 315°C, and 355°C. In the case of the AWPA specifications, there are minimum limits to the specific gravities of each of the distillate fractions;

Table 9. Distillation of Coal Tar[a]

	Volume, t × 10^3		
Country	1984	1989	1994
Belgium	189	183	~160
Brazil			223
Czech Republic	331	331	240
China			1250
Denmark	85	140	170
Germany	990	874	460
France	398	340	212
Italy	166	162	118
Japan	1840	2150	1758
Netherlands	100	105	115
Poland	228	277	290
CIS		3300[b]	
Spain	140	170	210
South Africa			189
South Korea	248	320	403
United Kingdom	178	308	245
United States	2205[c]	2422[c]	1026

[a] Ref. 53.

[b] Production value is from 1990.

[c] Capacity.

Table 10. Tar Bulk Prices

	1982		1994	
Product	\$/t	\$/L	\$/t	\$/L
United States				
wood-preservation creosote				
U.S. bulk		0.31		
U.S. drums		0.33		0.21–0.24
electrode pitch	281–295			
aluminium	305–325		320–322	
graphitized steel	325–340		330–332	
impregnated pitch for refractories	340			
pitch for fiber pipes and coal briquettes	235			
roofing pitch	290		340–345	
United Kingdom				
electrode pitch	297		242	
carbon black feedstock and coal-tar fuels	171		104–106	
Western Europe				
indene-coumarone resins	810			
wood-preservation creosote	252–261	0.25–0.26	258–273	0.26–0.27

in the case of the WEI specifications, limits for the contents of benzo[a]pyrene and water-soluble phenols (tar acids).

Other national specifications for wood preservation creosote are CAM 972 (Argentina), AS T505/1965 and AS 1143/1978 (Australia), NBN 439 (Belgium), DS Rec. M314/TP (Denmark), IS 218-1961 (India), DGN R21-1952 (Netherlands), SASS 17-1943 (South Africa), and GOST 2770-59 (CIS). These are generally similar to the U.S. and U.K. specifications.

Tar-based road binders are the subject of ASTM Specification D3515-77 (United States), BSS 76/1974 (United Kingdom), AS 63-1947 (Australia), DIN 51-551 (1961) (Germany), IS 215-1961 (India), JIS K2472 (Japan), and GOST 4641-49 (CIS). These cover a range of road tars of different viscosity ranges and generally include maximum values for moisture content, phenols, toluene-insoluble material, and, in some cases, naphthalene content. They also give the permissible ranges for specific gravity, for the amount of oils distilling between 200 and 270°C and between 270 and 300°C, and for the softening point of the residue above 300°C. No tar-based road binders are used in Germany, the Netherlands, or Denmark in the 1990s.

A few national specifications cover electrode-binder pitch, eg, GOST 10200-62 (CIS), but in general, this product is supplied to specifications set by the aluminium- or steel-manufacturing companies. The requirements for the binder for Söderberg electrodes differ from those for prebaked electrodes and include a minimum specific gravity or density, a narrow softening point range (95–100°C (R and B) for Söderberg electrodes and 105-115°C for prebaked electrode binder), a minimum C/H ratio, a minimum coking value, maximums for the permissible ash content, moisture content, and amount of volatile matter at 360°C, a range for quinoline-insoluble matter (8–13% for Söderberg electrode binder and 5–10% for prebaked electrode binder), and a minimum of ca 20% for the amount of toluene-insoluble/quinoline-soluble (β-resin) content. However, in addition to the published specification requirements, aluminum-smelting companies demand that the pitch binder should pass certain preacceptance tests involving flow measurement at various temperatures of the pitch-petroleum coke electrode paste and measurements of strength, porosity, electrical resistance, and reactivity of test electrodes made by slowly carbonizing the electrode paste under compression to 900°C (see Carbon and artificial graphite).

Coal-tar pitch for other uses is similarly subject to a few national specifications but mainly sold to users' specifications. Pitch intended for roofing, dampproofing, and waterproofing is the subject of ASTM specification D450 and Federal specification R-P-381; hot-applied tar-based coatings (pipeline enamels) are the subject of BSS 4164/1987, amended in 1988, and, in the United States, of American Water Works Association (AWWA) specification C203.

2.7. Analytical Methods

2.7.1. Tar

Before the development of gas chromatography (gc) and high pressure liquid chromatography (hplc), the quantitative analyses of tar distillate oils involved tedious high efficiency fractionation and refractionation, followed by identification or estimation of individual components by ir or uv spectroscopy. In the 1990s, the main components of the distillate fractions of coal tars are determined by gc and hplc (54). The analytical procedures included in the specifications for tar bulk products are given in the relevant Standardization of Tar Products Tests Committee (STPTC) (33), ISO (55), and ASTM (35) standards.

2.7.2. Pitch

For the solvent analysis of pitch, a number of methods have been proposed. The solvents may be used sequentially or a fresh sample may be used with each solvent. Either the least or the most powerful solvent may be used first. The ratio of solvent to pitch or pitch fraction and the temperature and time of extraction vary.

In the Broche-Nedelmann procedure, the pitch is separated into material insoluble in benzene (α-component), material soluble in benzene but insoluble in petroleum ether (β-component), and material soluble in petroleum ether (γ-component). A modification of this procedure is now most widely used in the United States and the United Kingdom. Separate samples of the predried pitch are extracted using petroleum ether having 100–120°C boiling range (5 g of pitch is extracted using 100-mL portions of solvent until the extract is colorless), toluene (1 g of pitch is extracted using 100 mL of toluene under reflux for 20 min and the residue is washed using hot toluene until the washings are colorless), and quinoline (1 g of pitch is extracted using 25 mL of quinoline at 70–80°C for 20 min and the residue is washed with hot quinoline). The residues are dried and weighed and the analysis calculated to give the m/m percentages of the following four fractions: (*1*)

Petroleum ether-soluble (crystalloids or γ-fraction), generally containing 4–50% of medium soft coke-oven pitch and having a molecular weight range of 175–300; (*2*) toluene-soluble–petroleum ether-insoluble (β-resins), generally containing 20–30% of a medium soft coke-oven pitch and having a molecular weight range of 300–700; (*3*) quinoline-soluble–toluene-insoluble (C-2 fraction or resins), generally containing 8–15% of a medium soft coke-oven pitch and having a molecular weight range of 1000–2000; and (*4*) quinoline-insoluble (C-1 fraction), the amount of which in coke-oven pitches varies from 5 to 15% but rarely exceeds 5% in CVR pitches or 1% in low temperature pitches. Quinoline-insoluble appears to be similar to carbon black. In an earlier U.K. procedure, the crystalloid fraction was recovered by evaporation of the petroleum ether extract, and, after drying and weighing, reextracted using boiling benzene until the solution was colorless. The β-resin fraction was recovered by evaporating the benzene extract. Finally, the benzene-insoluble residue was treated with boiling pyridine to give the pyridine-insoluble material. The pyridine extract was evaporated to obtain the C-2 fraction. The extractions can be carried out in a Soxhlet extraction apparatus.

The Mallison solvent analysis method is still used in Europe (56) in the 1990s. A sample of the dry pitch is extracted using a mixture of anthracene oil and pyridine to leave a residue of pyridine-insoluble material, the so-called H-resins. This fraction is roughly equivalent to the C-1 fraction obtained by the methods described earlier. A second sample of pitch is extracted on the water bath using benzene and the fraction-insoluble in this solvent is isolated, dried, and weighed. This residue is termed the H + M − resins (high and medium molecular weight resins). By subtraction, the M-resins (roughly equivalent to the C-2 fraction) are obtained. A third pitch sample is extracted using hot methanol to give an insoluble fraction regarded as the H + M + N-resins (high, medium, and low molecular weight resins). Again, by subtraction, the N-resins are obtained. The methanol extract is diluted using ammonium chloride solution which precipitates a fraction termed the m-oils, whereas the fraction soluble in the diluted methanol is termed the n-oils.

Pitch used as an anode binder for the aluminium industry may be analyzed and tested by the following International Organization for Standardization: ISO 6257, ISO 5939, ISO 5940, ISO 6376, ISO 6791, ISO 6998, ISO 6999, and ISO 8006 (55).

2.8. Health and Safety Factors

The volatile components of coal tar, ie, mononuclear aromatic hydrocarbons, phenols, and pyridine bases, are toxic when ingested, inhaled, or absorbed through the skin and the usual precautions must be taken when crude benzene or tar light oils are handled. Most polynuclear aromatic compounds are primary skin and eye irritants but are tolerated internally. Naphthalene was at one time prescribed as an internal antiseptic and antihelminthic in daily doses of 0.1–0.5 g. The probable lethal dose is between 5 and 15 g. Anthracene passes through the gastrointestinal tract mainly unchanged, as do most higher polynuclear hydrocarbons. The lowest lethal oral dose for coal-tar creosote is given as 140-mg/kg body weight in the 1974 Toxic Substances Control Act (TSCA) list.

In the European Union, coal-derived complex chemical substances, ie, those contained in the European Inventory of Existing Commercial Chemical Substances, have been classified for carcinogenicity in the twenty-first adaptation to technical progress of the European Commission (EC) Dangerous Substances Directive 1994 67/548/EEC (57). The EC Regulation 793/93 requires data sets to be submitted by producers or importers to the European Commission for these and other substances by nominated dates. The toxicological data and estimation of exposure will form the basis of risk analysis and determination of the appropriate restriction and control of substances in the work place (58). Restriction of the sales of dangerous substances and preparations to the general public is enforced under Directive 76/769 EC (59).

2.8.1. Carcinogenic Hazard of Tar and Tar Products

The main health hazard usually associated with coal tar and its products is carcinogenicity. Although this hazard undoubtedly exists, the risk is by no means as serious as some reports suggest and is constantly being reduced by improving working conditions. There is no evidence that the use of tar products in road surfacing, preservation of telegraph and transmission poles, pitch fiber or coal-tar enamels for water pipes constitutes any danger to the general public.

Cancer was first recognized as an occupational hazard in 1775 when the prevalence of scrotal cancer among London chimney sweeps was noticed. The chemical origin of this form of cancer was not universally accepted until 1922 when it was demonstrated that tumors could be induced on mouse skin using an etheral soot extract (60). Skin cancer was also noted to be an occupational hazard of workers exposed to pitch dust in the coal-briquetting industry (61) and to workers exposed to crude tar (62). In 1915, tumors were produced in rabbits' ears by prolonged application of crude coal tar (63). Some 38 cases per year have been reported of cutaneous epithelioma in the tar distilling industry over a 25-year period up to 1945 (64).

However, it was shown that only the higher boiling fractions were carcinogenic and that the spectra of these fractions resembled those of benz[a]anthracene (65). This work culminated in the isolation of a highly carcinogenic compound, benzo[a]pyrene (BaP) from coal-tar pitch (66). Cancerous skin lesions of workers exposed to pitch dust undoubtedly support the belief that these lesions are caused by polynuclear aromatic hydrocarbons, although it had not been possible to demonstrate their carcinogenic action in animals more closely related to humans, such as monkeys.

Although high temperature BaP-containing coal-tar creosote causes skin cancer in mice (67), evidence of skin cancer among workers in the timber-creosoting industry is limited. Moreover, modern creosotes contain <50 ppm of BaP. However, protective clothing should be worn to avoid skin irritation. Although epitheliomas can result from prolonged exposure to creosote (68), there is no evidence that the large volume of creosote used for wood preservation constitutes a hazard to the workers or the public. Similar large amounts of coal-tar pitch and tar oils were employed for the construction and maintenance of roads but are now being replaced by bitumen because of the latter's greater availability and cheaper price. Again, no evidence links any health hazard to either the road-working personnel or the general public.

The main risk is long-term, continual exposure of the skin to finely divided solid pitch (dust). In a relatively small, but statistically significant proportion of persons exposed in this manner, premalignant pitch warts appear, usually around the scrotum, hands, and face, particularly around the nostrils. These lesions, if untreated, develop into malignant epitheliomas. Such skin cancers are readily curable if diagnosed early. Premalignant warts usually heal spontaneously after excision, but malignant epitheliomas must be treated by radiation. A total surface treatment of 50 Gy (5000 rad) is generally enough to destroy the malignant cells. The condition clears up about one month after treatment, leaving some alteration in skin pigmentation. There are no reports of recurrence (69). Skin cancer caused by coal-tar pitch may take many years to manifest itself. Epidemiological studies at creosoting plants have proved inconclusive.

A more serious hazard might be thought to exist in the pitch-roofing and road-tar industries where some personnel are continually exposed to the inhalation of pitch fumes, which contain BaP and other carcinogens (70). However, epidemiological studies of such workers have not revealed any increased risk of cancer of the lungs, esophagus, or internal organs (71, 72).

The risk of skin cancer by contact with pitch dust has in more recent years been reduced by the transport and handling of pitch as a liquid or as dust-free flakes or pencils. Nevertheless, in handling coal-tar products, certain precautions should be taken. These have become obligatory in tar distilleries and plants using pitch or creosote.

Where the lower boiling products are handled, effective ventilation must be ensured. Protective clothing, including eye protection and PVC gloves, must be worn, suitable respirators must be available, and regular medical checkups must be carried out on all personnel, including those who are at risk of exposure to benzene in significant concentrations. A high standard of personal hygiene must be maintained. Barrier creams, properly formulated against aromatic hydrocarbons, should be provided and used.

2.9. Uses

Coumarone-indene resins have outlets in paints, as tackifiers in rubber compounding, and as adhesives in the manufacturing of flooring tiles (see Hydrocarbon resins).

2.9.1. Cresylic Acids

The higher boiling cresylic acids are mixtures of cresols or xylenols with higher boiling phenols (see Phenol; Alkylphenols). Their main uses are in phenol-formaldehyde resins, solvents for wire-coating enamels, as metal-degreasing agents, froth-flotation agents, and synthetic tanning agents. Statistics do not distinguish between the various grades or between cresylic acids derived from coal tar or petroleum or made synthetically (see Phenolic resins).

2.9.2. Naphthalene

Until the 1960s, the principal outlet for naphthalene was the production of phthalic anhydride; however, more recently, *o*-xylene has replaced naphthalene as the preferred feedstock (see Phthalic acids). Nevertheless, of the 201,000 t produced in 1994 in Japan, 73.2% was used for phthalic anhydride production. The rest was consumed in dye stuffs manufacture and a wide variety of other uses. Naphthalene is also used to produce phthalic anhydride in the United Kingdom, Belgium, and the Czech Republic, and can be used by Koppers in the United States in time of *o*-xylene shortages. In Europe, the traditional uses for naphthalene have been for the manufacture of β-naphthol and for dye stuff intermediates (see Dyes and dye intermediates).

In more recent times, naphthalene has been used in condensation products from naphthalene sulfonic acids, utilizing formaldehyde as additives to improve the flow properties of concrete; these are referred to as superplasticizers. Another newer application is the production of diisopropylnaphthalenes. The mutual depression of the melting points in the mixture gives a liquid which is used as a solvent for dyes in the production of carbonless copy paper.

2.9.3. Creosote

In coal-tar refining, the recovery of tar chemicals leaves residual oils, including heavy naphtha, dephenolated carbolic oil, naphthalene drained oil, wash oil, strained anthracene oil, and heavy oil. These are blended to give creosotes conforming to particular specifications.

Creosote oils are by far the most widely used timber preservatives (see Wood). This use dates back to 1850. For the treatment of railway ties and marine pilings, the Bethell or full-cell process is preferred. The timber to be treated is charged to a pressure cylinder, which is evacuated to extract the air from the wood cells. The cylinder is then filled with hot creosote and the pressure increased to 0.8–1 MPa (ca 8–10 atm) to force the oil into the cells. When uptake of the oil has ceased, residual creosote is drained from the cylinder and the treated timber is briefly subjected to a vacuum before discharge.

For the treatment of telegraph and transmission poles, fence posts, and farm buildings, where a clean outer surface is desired, the empty-cell process is generally used. The Rueping process employs an impregnation cycle in which the timber is first subjected to a moderate air pressure to compress the air in the cells before the cylinder is charged with hot creosote. The pressure in the cylinder is increased to force the oil into the wood cells. When no more oil is absorbed, the pressure is released, allowing the air inside the timber to expand and force the creosote out; a protective film remains on the cell wall. After discharging surplus creosote, the treated timber is evacuated for a short time to complete the removal of oil before the timber is removed from the cylinder. The Lowry process is similar but omits the initial pressurization.

Timber-preservation creosotes are mainly blends of wash oil, strained anthracene oil, and heavy oil having minor amounts of oils boiling in the 200–250°C range. Coal-tar creosote is also a feedstock for carbon black manufacture (see Carbon, CARBON BLACK). Almost any blend of tar oils is suitable for this purpose, but the heavier oils are preferred. Other smaller markets for creosote were for fluxing coal tar, pitch, and bitumen in the manufacture of road binders and for the production of horticultural winter wash oils and disinfectant emulsions.

2.9.4. Pitch

The principal outlet for coal-tar pitch is as the binder for the electrodes used in aluminum smelting. These are of two types. Older plants employ Söderberg furnaces, which incorporate paste electrodes consisting of a mixture of about 70% graded petroleum coke or pitch coke and 30% of a medium-hard coke-oven pitch. This paste is added periodically to the top of the monolithic electrode as it is consumed. The more modern smelters employ prebaked electrodes requiring less binder, about 18%.

The specification requirements for electrode binder pitch, eg, high C/H ratio, high coking value, and high β-resin content, effectively ruled out pitches from gasworks or low temperature tars. The crude tar is distilled to a medium-soft pitch residue and then hardened by heating for several hours at 385–400°C. This treatment increases the toluene-insoluble content and produces only a slight increase in the quinoline-insoluble (QI) material, the latter by the formation of mesophase.

Coke-oven tar distilleries are usually equipped for the heat treatment of pitch, either batch or continuous, but apparently not in either the United States or Australia. In some cases, pot stills, arranged in cascade, are still used. The more sophisticated plants employ one or more carbon steel or cast-iron vessels heated electrically and equipped with temperature controls for both the bulk liquid and the vessel walls. Contact time is usually 6–10 h. However, modern pitches are vacuum-distilled, producing no secondary quinoline insolubles, to improve the rheological properties.

The demand for electrode binder pitch has grown as aluminium output has expanded and the requirement for aluminium smelting is now between 1.5 and 2×10^6 t/yr. In Japan pitch is used for mixing with coal for carbonization in coke ovens to make metallurgical coke.

Coal-tar pitch of electrode binder quality but on a smaller scale is used as the binder for graphitized electrodes used in electric-arc steel-making convertors. Pitch of low quinoline-insoluble content is used for impregnation of such electrodes before graphitization. More recent uses are in the manufacture of carbon fibers and premium coke (73). These uses, which are not restricted to coal-tar pitch, depend on the formation of mesophase, an optically visible liquid crystal phase appearing as anisotropic spherulites, observable under the microscope using polarized light and size ranged upward from submicron to several microns in diameter. These are formed when coal-tar pitch, among others, is thermally treated at temperatures of between 300 and 500°C for protracted periods, usually several hours. Mesophase of this origin is insoluble in quinoline (74).

Mesophase formation in coal-tar pitch is encouraged by a reduction of the natural quinoline-insoluble matter content, which resembles carbon black but is not optically anisotropic and is characterized by an atomic carbon hydrogen ratio of 4:1. In contrast, the atomic carbon hydrogen ratio of mesophase is about 2:1.

The property of mesophase that makes it suitable for carbon fiber and premium coke manufacture is that it forms ordered structures under stress which persist following carbonization. However, most carbon fiber production in the 1990s is based on polyacrylonitrile (PAN).

In Europe, the production of coal briquettes by pressing a mixture of powdered bituminous coal using 8–10% medium-soft pitch (80°C R-and-B softening point), heated to 90°C in a pug mill, into blocks or ovoids was formerly a big outlet for pitch. Smokeless precarbonized briquettes using indigenous pitch and coal were made in the United Kingdom as a product called Phurnacite, produced from steam coal fines briquetted again using medium-soft coke-oven pitch and subjected to carbonization in a continuous vertical retort. This is now made in a different way using molasses as the binder in place of pitch.

In North America, coal-tar pitch is used as an adhesive in membrane roofs (see Adhesives; Roofing materials). However, its uses for the same purpose in the Netherlands have been abandoned since the 1980s. The concrete or timber decking of flat-topped buildings is first covered with a layer of soft coke-oven pitch. While the pitch is still fluid, this base is covered with tar-impregnated paper on which a second layer of molten pitch is poured. This sandwich construction is repeated until the required number of pitch-paper layers (from 3 to 5) has been installed. The top paper membrane is coated with molten pitch and covered with slag chippings or gravel.

2.9.5. Pitch Coke

The manufacture of pitch coke provides a large tonnage outlet for coke-oven pitch in Japan, the CIS and, until more recently, Germany (75, 76). Pitch coke is used either alone or mixed with petroleum coke as the carbon component of electrodes, carbon brushes, and shaped carbon and graphite articles.

In the CIS pitch coke is made by carbonizing a hard coke-oven pitch in modified coke ovens. The hard pitch has an R-and-B softening point of 140–150°C and is made by air-blowing a mixture of medium-soft pitch and recycled coking oils. This feedstock is charged in the molten state over a period of 5 h and coked for 17–18 h at 1250–1300°C. The coke yield is 70%. Oils, which are recycled, amount to 20% by weight of the pitch fed. The gas yield (80% hydrogen) is 10%.

A more modern process used in Japan and a unit in Germany employs the Lummus delayed-coking process (77). The feedstock is a soft coke-oven pitch from adjacent coke ovens. This flows into the bottom section of the so-called combination tower where it mixes with the vapors from the active coking drum after these have passed through the empty drum for preheating. The lighter components of the feedstock and the vapors are fractionated into fuel gas and light distillates in the upper part of the combination tower. The liquid from the base is heated to its incipient coking temperature and discharged into the preheated drum. The exothermic coking reaction proceeds for about 20 h. At the end of this period, the contents of the drum are steamed and cooled and the green coke discharged by high pressure water lances. The empty drum is steamed, then pressure-tested; subsequently it is ready to be preheated in preparation for the next charge. The green coke is produced in ca 61% yield and has an apparent density of 960–1088 kg/m^3 and a volatile matter content of 7.5–9.5%. It is calcined in a separate kiln to reduce the volatile matter to the 0.5% level required for electrode carbon. Figure 4 illustrates the Lummus delayed-coking plant installed at the refinery of the Nittetsu Chemical Industries at Tobata, Japan, which makes needle coke.

Other uses for coal-tar pitch include production as a binder for foundry cores, as a sealant for dry batteries, and in the manufacture of clay pigeons. Pelleted pitch used as the binder in foundry cores is a hard pitch supplied as spherical granules which are formed by a spray-cooling process. Clay pigeons consist of disks molded from a mixture of hard pitch and a mineral filler such as clay or limestone dust.

2.10. Fluxed Pitches and Refined Tars

2.10.1. Road Tars

In the United States, which has a large supply of bitumen, tar is little used in road construction or maintenance, but in Europe road binders still constitute an important, though declining, market for tar bulk products, mainly in France, Belgium, and Luxemburg. This is little used now in the United Kingdom and discontinued in Denmark, Netherlands, Germany or Spain. Road tars consist essentially of medium-soft pitch fluxed back using higher boiling tar oils. They are produced in a range of viscosities to suit the particular application and the climatic conditions under which they are to be used. They are employed as binders in road bases and base courses and in tar macadam. For road maintenance, they are used as inexpensive surface dressing to restore the riding qualities of a road surface. The road surface is first swept free of dust, the potholes are filled, and a layer of hot tar sprayed on the surface. While the tar is still fluid, the surface is covered with an evenly applied layer of stone or slag chippings which are rolled into the new surface.

As a road binder, tar has advantages and disadvantages. Because the temperature interval between the R-and-B softening point and the brittle point is only 46°C (see Table 5), tar tends to flow in hot weather and suffer brittle fracture in cold weather. Its internal cohesive strength is low. On the other hand, it adheres well to stone and the bond is impervious to water or petroleum-based oils. The disadvantage of the high temperature

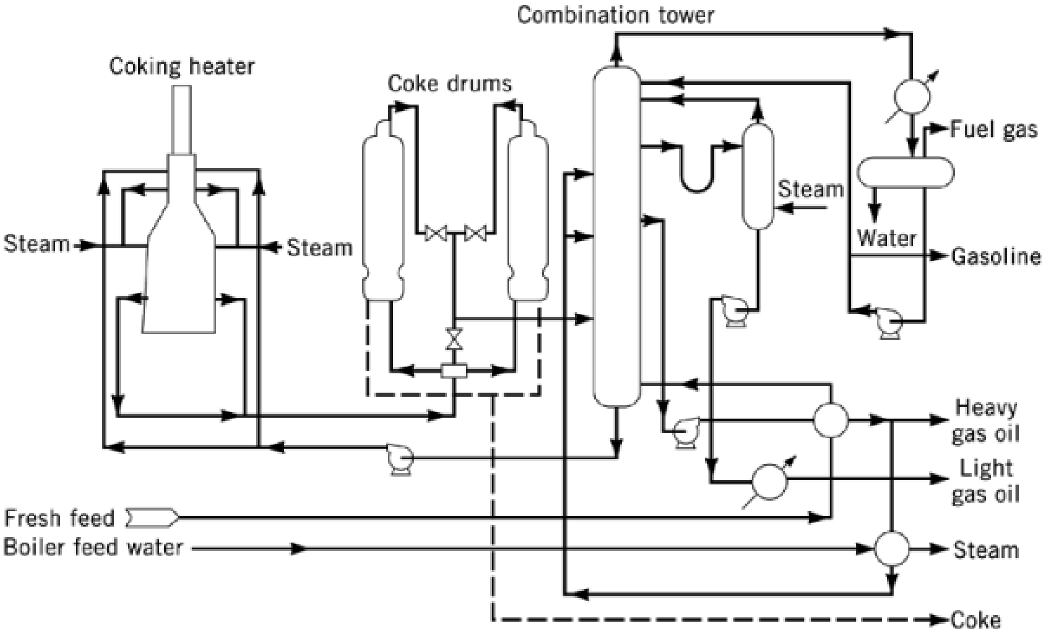

Fig. 4. Lummus delayed-pitch coking process.Courtesy of Lummus Co., Ltd.

coefficient of viscosity of road tars can be overcome without sacrificing the favorable properties by blending it with petroleum bitumen. Tar–bitumen blends are now preferred surface dressing binders. By adding 1–2% of PVC or certain types of synthetic rubber to road tar, a useful degree of elasticity is imparted. For surface dressing of heavily trafficked roads, polymer-modified road tars are popular, particularly in France.

The most widely used binder for the hot-rolled asphalt or asphaltic concrete-wearing courses of heavily trafficked roads is a penetration-grade petroleum bitumen. Such surfacings tend to polish under traffic and lose their resistance to skidding. Addition of 20–25% of coal-tar pitch improves and maintains the skid resistance. Asphalt road surfacings containing pitch–bitumen binder are used to some extent in France, Belgium, and Luxemburg.

The market for tar-based road binders has declined considerably for a variety of reasons. Less crude tar is available and the profits from the sales of electrode pitch and wood-preservation creosote or creosote as carbon-black feedstock are higher than those from road tar. In most industrial countries, road construction in more recent years has been concentrated on high speed motorways. Concrete, petroleum bitumen, or lake asphalt are used in the construction of these motorways. In the United Kingdom, for example, the use of tar products in road making and maintenance had fallen from 330,000 t in 1960 to 100,000 t in 1975 and is less than 100 t in 1994, mainly based on low temperature pitch which is not suitable for electrode or briquetting binders, but which is perfectly satisfactory as the basis for road binders.

2.10.2. Surface Coatings

Tar-based surface coatings range from the so-called black varnishes, which consist of a soft pitch fluxed back to brushing or spraying consistency using coal-tar naphtha, to pipe-coating enamels and pitch-polymer coatings. The black varnishes, occasionally mixed with small amounts of chlorinated rubber or powdered coal to improve film elasticity, are still used to some extent for the protection of industrial steel work and timber buildings and as antifouling marine paints.

The pipe-coating enamels are used for the corrosion protection of buried gas, water, or oil pipes. They are made from a ground coal dispersed in a coke-oven pitch fluxed back using strained anthracene oil as the basis and have a softening point of 105–125°C. Suitable mineral filler, eg, slate dust, is added to these enamels. To ensure good adhesion, the pipe is first primed with chlorinated rubber and chlorinated paraffin wax or chlorinated diphenyl dissolved in a mixture of toluene and trichloroethylene, and the coated pipe is wrapped with glass fiber impregnated with coal tar while the enamel coating is still hot and plastic. They are produced in the United States, Colombia, Australia, Denmark, and the United Kingdom.

The demand for pipe-coating enamels tends to fluctuate, depending on the success of oil and gas exploration. In the United Kingdom plastic-coated pipes are used on shore. Most production is exported for use in the Middle and Far Eastern regions.

Refined tars are used as extenders for epoxy and polyurethane resins to give surface coatings, which have developed into a sizeable and growing market (78). These formulations harden into tough abrasion-resistant, waterproof films. They are now widely used for coating underground storage tanks, structural steel items, water storage tanks, marine pilings, and bridge decks. The refined tar supplied for this purpose must meet stringent specifications requiring high aromaticity, low phenolic and base contents, and low quinoline-insoluble components. Such properties are secured by fluxing a pitch, made by distillation of a centrifuged coke-oven tar to a relatively low softening point residue, with coke-oven-strained anthracene or heavy oils that have been treated for the removal of phenols and bases. In the Netherlands this use will be forbidden probably at the end of the 1990s, on the grounds of pollution of their waterways.

The increasing use of carbon-bonded and carbon-impregnated refractories is providing another growing market for refined tars. These vary from a soft pitch to a refined tar of as low as 30°C equiviscous temperature (EVT) (see Refractories). Liquid fuels were formerly important outlets for coal-tar, pitch–oil blends, and topped tar which could not be disposed of more profitably (79). However, as a result of reduced tar supplies this usage has been phased out.

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