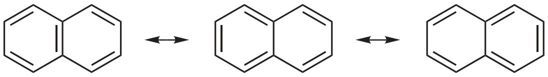
NAPHTHALENE

1. Introduction

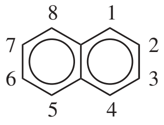
This article deals mainly with naphthalene [91-20-3]. The hydrogenated naphthalenes, the alkylnaphthalenes (particularly methyl- and isopropylnaphthalenes), and acenaphthene also are discussed (see also NAPHTHALENE DERIVATIVES).

2. Properties

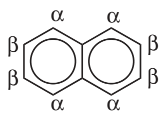
The accepted configuration of naphthalene, ie, two fused benzene rings sharing two common carbon atoms in the ortho position, was established in 1869 and was based on its oxidation product, phthalic acid (1). Based on its fused-ring configuration, naphthalene is the first member in a class of aromatic compounds with condensed nuclei. Naphthalene is a resonance hybrid:



In chemical reactions, naphthalene usually acts as though the bonds were fixed in the positions as shown in the first structure above at the left. For most purposes, the conventional formula (**1**) is adequate; the numbers represent the carbon atoms with attached hydrogen atoms.



(**1**)



(**2**)

The two carbons that bear no numbers are common to both rings and carry no hydrogen atoms. From the symmetrical configuration of the naphthalene molecule, it should be possible for only two isomers to exist when one hydrogen atom is replaced by another atom or group. Therefore, positions 1, 4, 5, and 8 are identical and often are designated as "α" positions; likewise, positions 2, 3, 6, and 7 are identical and are designated as "β" positions, as shown in (**2**).

Some selected chemical and physical properties of naphthalene are given in Table 1. Selected values from the vapor pressure–temperature relationship for naphthalene are listed in Table 2, as are selected viscosity–temperature relationships for liquid naphthalene. Naphthalene forms azeotropes with several compounds; some of these mixtures are listed in Table 3.

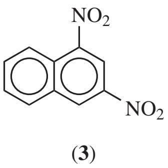
Naphthalene is very slightly soluble in water but is appreciably soluble in many organic solvents, eg, 1,2,3,4-tetrahydronaphthalene, phenols, ethers, carbon disulfide, chloroform, benzene, coal-tar naphtha, carbon tetrachloride, acetone, and decahydronaphthalene. Selected solubility data are presented in Table 4.

The infrared (ir), ultraviolet (uv), mass, nuclear magnetic resonance (nmr), and ^{13}C nmr spectral data for naphthalene and other related hydrocarbons have been reported (7–11). Additional information regarding the properties of naphthalene has been published (3,6,12,13).

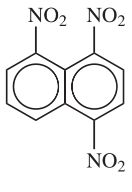
3. Reactions

3.1. Substitution. Substitution products retain the same nuclear configuration as naphthalene. They are formed by the substitution of one or more hydrogen atoms with other functional groups. Substituted naphthalenes of commercial importance have been obtained by sulfonation, sulfonation and alkali fusion, alkylation, nitration and reduction, and chlorination.

The hydrogen atoms in the 1 position of naphthalene can be substituted somewhat more easily than hydrogen atoms in benzene, and they tend to do so under mild conditions. For example, 1-chloronaphthalene [90-13-1] can be formed by direct substitution with little or no catalyst, and 1-nitronaphthalene [86-57-7] can be prepared using dilute nitric acid. Sulfonation of naphthalene also occurs readily in the 1 position but can be influenced by temperature. When a second group substitutes, its position also is influenced by the nature and position of the first group. In the case of the substitution of the second identical group during nitration or sulfonation, it predominately attaches to the unsubstituted ring. For identical groups, there are seven possible disubstituted isomers. If the two substituting groups are different, 14 disubstitution isomers are possible. The number of possibilities is still larger when the substituents are different and three or more hydrogen atoms are replaced. The number of possible isomeric substitution products from naphthalene has been calculated and reported (14). In naming substituted naphthalenes, positions are designated numerically according to the lowest position number for the first substituent, eg (**3**), 1,3-dinitronaphthalene [606-37-1]. The sum of the position numbers should be the lowest possible, eg (**4**), 1,4,5-trinitronaphthalene (not 1,4,8-trinitronaphthalene).



(**3**)



(**4**)

3.2. Sulfonation. Sulfonation of naphthalene with sulfuric acid produces mono-, di-, tri-, and tetranaphthalenesulfonic acids (see NAPHTHALENE DERIVATIVES). All of the naphthalenesulfonic acids form salts with most bases. Naphthalenesulfonic acids are important starting materials in the manufacture of organic dyes (15) (see AZO DYES). They also are intermediates used in reactions, eg, caustic fusion to yield naphthols, nitration to yieldnitronaphthalenesulfonic acids, etc.

3.3. Nitration. Naphthalene is easily nitrated with mixed acids, eg, nitric and sulfuric, at moderate temperatures to give mostly 1-nitronaphthalene and small quantities, 3–5%, of 2-nitronaphthalene. 2-Nitronaphthalene [581-89-5] is not made in substantial amounts by direct nitration and must be produced by indirect methods, eg, the Bucherer reaction starting with 2-naphthalenol (2-naphthol [135-19-3]). However, the 2-naphthylamine [91-59-8] made using this route is a carcinogen; thus the Bucherer method is seldom used in the United States.

3.4. Halogenation.

Under mild catalytic conditions, halogen substitution occurs, and all of the hydrogen atoms of the naphthalene molecule can be replaced. The only commercially significant halogenated naphthalene products are the mixed chlorinated naphthalenes. Naphthalene is chlorinated readily by introducing gaseous chlorine into molten naphthalene at ambient pressure and temperatures of 100–220°C in the presence of small amounts of a catalyst, eg, ferric chloride. The chlorination of molten naphthalene gives a mixture of mono-, di-, and polychloronaphthalenes; the degree of chlorination is controlled by monitoring the specific gravity or melting point of the crude reaction product.

The commercial products are mixtures ranging from liquids, eg, mono- and mixed mono- and dichloronaphthalenes, to various wax-like solids, which contain di-, tri-, and polychloronaphthalenes, with high melting points, ie, 90–185°C. Chloronaphthalenes are flame resistant and have high dielectric constants. Their high degree of chemical stability is indicated by their resistance to most acids and alkalies as well as to dehydrochlorination. They also are resistant to attack by fungi and insects. The U.S. demand for chloronaphthalenes has declined steadily. Koppers Co., Inc., the sole U.S. producer, ceased manufacturing their chloronaphthalene products (Halowax) in 1977.

The toxicity of chloronaphthalenes requires that special attention and caution be used during their manufacture and use; acne is the most common result of excessive skin exposure to them and the most frequently affected areas are the face and neck (16). Liver damage has occurred in workers who have been exposed repeatedly to vapors, particularly to those of penta- andhexachloronaphthalene [1335-87-1] (17,18). Uses for the chlorinated naphthalenes include solvents, gauge and instrument fluids, capacitor impregnants, components in electric insulating compounds, and electroplating stop-off compounds.

3.5. Alkylation.

Naphthalene can be easily alkylated using various alkylating agents, eg, alkyl halides, olefins, or alcohols, in the presence of a suitable catalyst (19,20). In vapor-phase alkylations, phosphoric acid on kieselguhr and silica–alumina catalysts are useful. In liquid-phase reactions, acid catalysts, eg, sulfuric acid, hydrofluoric acid, and phosphoric acid, are used widely when olefins are the alkylating agent. Aluminum chloride and other metal halides, eg, iron and zinc chlorides, are also active alkylating catalysts; however, their use often involves reactions that yield undesirable resinous by-products. Sulfuric acid is the preferred catalyst for alkylations with alcohols, since the active aluminum chloride forms a complex with alcohols and must be used in prohibitively large quantities.

Isopropylnaphthalenes produced by alkylation of naphthalene with propylene have propylene commercial importance as chemical intermediates, eg, 2-isopropylnaphthalene [2027-17-0], and as multipurpose solvents, eg, mixed isopropylnaphthalenes. Alkylation of naphthalene with alkyl halides (except methyl halides), acid chlorides, and acid anhydrides proceeds in the presence of anhydrous aluminum chloride by Friedel–Crafts reactions (qv). The products are alkylnaphthalenes or alkyl naphthyl ketones, respectively (see ALKYLATION).

3.6. Chloromethylation. The reactive intermediate, 1-chloromethylnaphthalene [86-52-2], has been produced by the reaction of naphthalene in glacial acetic acid and phosphoric acid with formaldehyde and hydrochloric acid. Heating of these ingredients at 80–85°C at 101.3 kPa (1 atm) with stirring for ~6 h is required. The potential hazard of such chloromethylation reactions, which results from the possible production of small amounts of the powerful carcinogen methyl chloromethyl ether [107-30-2], has been reported (21).

3.7. Addition. The most important addition products of naphthalene are the hydrogenated compounds. Of less commercial significance are those made by the addition of chlorine.

Hydrogenation. Hydrogen is added to the naphthalene nucleus by reagents that do not affect benzene. Two, four, six, eight, or ten hydrogen atoms may add. Of these, only the tetra- and decahydronaphthalenes are commercially significant. In addition to the commercially important 1,2,3,4-tetrahydronaphthalene, the 1,4,5,8-isomer has been reported. A review of the other hydronaphthalenes is available (22). Some chemical and physical properties of 1,2,3,4-tetrahydronaphthalene and the decahydronaphthalenes are given in Table 5.

1,2,3,4-Tetrahydronaphthalene [119-64-2] (tetralin) is a water-white liquid that is insoluble in water, slightly soluble in methanol alcohol, and completely soluble in other monohydric alcohols, ethyl ether, and most other organic solvents. It is a powerful solvent for oils, resins, waxes, rubber, asphalt, and aromatic hydrocarbons, eg, naphthalene and anthracene. Its high flash point and low vapor pressure make it useful in the manufacture of paints, lacquers, and varnishes; for cleaning printing ink from rollers and type; in the manufacture of shoe creams and floor waxes; as a solvent in the textile industry; and for the removal of naphthalene deposits in gas-distribution systems (25). The commercial product typically has a tetrahydronaphthalene content of $\geq$97 wt%, with some decahydronaphthalene and naphthalene as the principal impurities.

1,2,3,4-Tetrahydronaphthalene reacts similarly to an alkylbenzene because its structure contains only one aromatic nucleus. It can be sulfonated readily, nitrated, oxidized, and hydrogenated. Sulfonation occurs first in the 6 and, to some extent, in the 5 position. Nitration with mixed acid yields the 5- and 6-nitro compounds in the cold; 4,6- and 5,7-dinitro compounds are formed at 35–40°C (22). 1,2,3,4-Tetrahydronaphthalene is oxidized to a hydroperoxide by passing air or oxygen through the warm liquid (26,27).

Further hydrogenation under pressure in the presence of a nickel catalyst gives a mixture of *cis*- and *trans*-decahydronaphthalene [493-02-7] (Decalin). 1,2,3,4-Tetrahydronaphthalene dehydrogenates to naphthalene at 200–300°C in the presence of a catalyst; thermal dehydrogenation takes place at ~450°C and is accompanied by cracking to compounds, such as toluene and xylene.

Tetrahydronaphthalene is produced by the catalytic treatment of naphthalene with hydrogen. Various processes have been used, eg, vapor-phase reactions at 101.3 kPa (1 atm) as well as higher pressure liquid-phase hydrogenation where the conditions are dependent upon the particular catalyst used. Nickel or modified nickel catalysts generally are used commercially; however, they are sensitive to sulfur, and only naphthalene that has very low sulfur levels can be used. Thus many naphthalene producers purify their product to remove the thionaphthene, which is the principal sulfur compound present. Sodium treatment and catalytic hydrodesulfurization processes have been used for the removal of sulfur from naphthalene; the latter treatment is preferred because of the hazardous nature of sodium treatment.

1,2,3,4-Tetrahydronaphthalene is not a highly toxic compound. A threshold limit value of 25 ppm or 135 mg/m^3 has been suggested for tetralin. Tetralin vapor is an irritant to the eyes, nose, and throat, and dermatitis has been reported in painters working with it (28). The single-dose oral toxicity LD_{50} for rats is 2.9 g(kg (29).

Decahydronaphthalene [91-17-8] (decalin) is the product of complete hydrogenation of naphthalene. Like tetralin, it is a clear, colorless liquid with excellent solvent properties. It is produced commercially by the catalytic hydrogenation of naphthalene or 1,2,3,4-tetrahydronaphthalene and consists of a mixture of cis and trans isomers (22,30–32). The commercial product typically has a decahydronaphthalene content of ≥97 wt%, with the principal impurity being1,2,3,4-tetrahydronaphthalene. Decahydronaphthalene can be converted to naphthalene by heating with platinum, palladium, or nickel catalyst at 300°C (33).

Decahydronaphthalene is slightly to moderately toxic (29). The vapors are irritating to the eyes, nose, and throat. Excessive exposure to high concentrations causes numbness, nausea, headache, and vomiting. Dermatitis has been noted among painters handling decahydronaphthalene. No serious cases of industrial poisoning have been reported (34). A threshold limit value has not been established, although a value of 25 ppm has been suggested (28).

The uses of decahydronaphthalene are similar to those of 1,2,3,4-tetrahydronaphthalene. Mixtures of the two are used for certain applications where a synergistic solvency effect is noted.

Some selected chemical and physical properties of 1,2,3,4-tetrahydronaphthalene and the decahydronaphthalenes are listed in Table 5.

Chlorine Addition. Chlorine addition and some chlorine substitution occurs at normal or slightly elevated temperatures in the absence of catalysts. The chlorination of molten naphthalene under such conditions yields a mixture of naphthalene tetrachlorides, a monochloronaphthalene tetrachloride, and a dichloronaphthalene tetrachloride, as well as mono- and dichloronaphthalenes (35). Sunlight or uv radiation initiates the addition reaction of chlorine and naphthalene resulting in the production of the di- and tetrachlorides (36). These addition products are relatively unstable and, at ~40–50°C, they decompose to form the mono- and dichloronaphthalenes.

3.8. Oxidation.

Naphthalene may be oxidized directly to 1-naphthalenol (1-naphthol[90-15-3]) and 1,4-naphthoquinone, but yields are not good. Further oxidation beyond 1,4-naphthoquinone [130-15-4] results in the formation of *o*-phthalic acid [88-99-3], which can be dehydrated to form phthalic anhydride [85-44-9]. The vapor-phase reaction of naphthalene over a catalyst based on vanadium pentoxide is the commercial route used throughout the world. In the United States, the one phthalic anhydride plant currently operating on naphthalene feedstock utilizes a fixed catalyst bed. The fluid-bed process plants have all been shut down, and the preferred route used in the world is the fixed-bed process.

The naphthalene is vaporized, mixed with air, and fed to the top of the reactor. This process also allows for mixtures of *o*-xylene [95-47-6] to be mixed with the naphthalene and air, which permits the use of dual feedstocks. Both feedstocks are oxidized to phthalic anhydride. The typical range of reactor temperature is 340–380°C. The reactor temperatures are controlled by an external molten salt.

The quality of naphthalene required for phthalic anhydride manufacture is generally 95% minimum purity. The fixed plants do not require the high (>98%) purity naphthalene product and low (<50 ppm) sulfur. The typical commercial coal-tar naphthalene having a purity ~95% (freezing point, 77.5°C), a sulfur content of ~0.5%, and other miscellaneous impurities, is acceptable feedstock for the fixed-bed catalyst process based on naphthalene.

4. Manufacture

Two sources of naphthalene exist in the United States; coal tar and petroleum (qv). Coal tar was the traditional source until the late 1950s, when it was in short supply. In 1960, the first petroleum–naphthalene plant was brought on stream, and by the late 1960s, petroleum naphthalene accounted for >40% of total naphthalene production. The availability of large quantities of *o*-xylene at competitive prices during the 1970s affected the position of naphthalene as the prime raw material for phthalic anhydride. In 1971, 45% of U.S. phthalic anhydride capacity was based on naphthalene, as compared to only 29% in 1979 and 17% in 1990. Production for 1992 was <50% of the levels in the early 1980s. The last dehydroalkylation plant for petroleum naphthalene was shut down late in 1991.

Allied Chemicals was sold to Honeywell in 1999 who exited the naphthalene business in the fourth quarter 2000. There is only one remaining coal tar naphthalene producer in the United States; Koppers Industries, Inc. Coal tar has stabilized at $\sim 70 - 80\mu \times 10^3$ t/yr , and petroleum–naphthalene production is $\sim 20 - 25 \times 10^3$ t/yr. The reduction of production has opened the door for import naphthalene, mainly from Canada, where there is one producer; Recochem. The 2001 United States naphthalene capacities are given in Table 6.

4.1. Coal-Tar Process. Coal tar is condensed and separated from the coke-oven gases formed during the high temperature carbonization of bituminous coal in coke plants (see Coal; Coal conversion processes). Although some naphthalene is present in the oven gases after tar separation and is removed in subsequent water-cooling and scrubbing steps, the amounts are of minor importance. The largest quantities of naphthalene are obtained from the coal tar that is separated from the coke-oven gases. A typical dry coal tar obtained in the United States contains ~10 wt% naphthalene. The naphthalene content of the tar varies somewhat depending on the coal source, the coke-oven operating temperature, and the coking cycle times: the higher the coking temperature and rate, the higher the naphthalene content of the tar.

The coal tar first is processed through a tar-distillation step where about the first 20 wt% of distillate, ie, chemical oil, is removed. The chemical oil, which contains practically all the naphthalene present in the tar, is reserved for further processing, and the remainder of the tar is distilled further to remove additional creosote oil fractions until a coal-tar pitch of desirable consistency and properties is obtained.

The chemical oil contains ~50 wt% naphthalene, 5 wt% tar acids, 3 wt% tar bases, and numerous other aromatic compounds. The chemical oil is processed to remove the tar acids by contacting with dilute sodium hydroxide and, in a few cases, is next treated to remove tar bases by washing with sulfuric acid.

The principal U.S. producers obtain their crude naphthalene product by fractional distillation of the tar acid-free chemical oil. This distillation is accomplished in continuous fashion. One such method for the continuous recovery of naphthalene by distillation is shown in Figure 1. The tar acid-free chemical oil is charged to the system where most of the low boiling components, eg, benzene, xylene, and toluene, are removed in the light-solvent column. The chemical oil next is fed to the solvent column, which is operated under vacuum, where a product containing the prenaphthalene components is taken overhead. This product, which is called coal-tar naphtha or crude heavy solvent, typically has a boiling range of ~130–200°C and is used as a general solvent and as a feedstock for hydrocarbon-resin manufacture because of its high content of resinifiables, eg, indene and coumarone (see HYDROCARBON RESINS). Thenaphthalene-rich bottoms from the solvent column then are fed to the naphthalene column where a naphthalene product (95% naphthalene) is produced. The naphthalene column is operated at near atmospheric pressure to avoid difficulties that are inherent to vacuum distillation of this product, eg, naphthalene-filled vacuum jets and lines. A side stream which is rich in methylnaphthalenes may be taken near the bottom of the naphthalene column.

However, since the naphthalene produced from petroleum is of high purity and quality, the production of refined naphthalene by such chemical treatments essentially has ceased in the United States. Not only are such treatments expensive, but they also generate a significant amount of waste sludge, which creates additional costs for appropriate waste-disposal facilities.

A recent patent concerns a process for purifying naphthalene. The process compreses selective hydrotreatment of olefins while limiting naphthalene hydrogeneration. The catalyst is a matrix (one group (VIII) metal, at least one group (V) metal, and optionally phosphorus). The procedure is carried out at 150–325°C and 0.1–0.9 MPa. The effluent undergoes naphthalene separation by distillation or preferably crystallization. The recycling of the separated tetralin to the hydrotreatment step can substantially increase the naphthalene yield (38)

The main impurity in crude 78°C coal-tar naphthalene is sulfur that is present in the form of thionaphthene (2–3%). Methyl- and dimethylnaphthalenes also are present (1–2%) with lesser amounts of indene, methylindenes, tar acids, and tar bases.

5. Economic Aspects

Total nameplace capacity for all U.S. naphthalene producers in 2001 is 110×10^3 t, with 110×10^3 t produced from coal tar and 30×10^3 t from petroleum. Naphthalene production from 1968 to 2000 is listed in Table 7.

The decline in naphthalene production in 1973 primarily resulted from competition with *o*-xylene as the feedstock for phthalic anhydride. Periods of feedstock shortages and the loss of one principal producer also affected petroleum naphthalene output.

Naphthalene imports provided ~10–20% of the material consumed in the United States until ~1963, when that percentage dropped to and leveled off at less than 5%. Imports increased again in 1992 to 10–15%, owing to the closure of Texaco's plant.

The economics of naphthalene recovery from coal tar can vary significantly, depending on the particular processing operation used. A significant factor is the cost of the coal tar. As the price of fuel oil increases, the value of coal tar also increases. The price history of naphthalene from 1975 to 2000 is given in Table 8.

The higher price of the petroleum product results from its higher quality, ie, higher purity and, lower sulfur content. The price of crude coal-tar naphthalene is primarily associated with that of *o*-xylene, its chief competitor as phthalic anhydride feedstock.

The preferred route to higher purity naphthalene, either coal-tar or petroleum, is crystallization. This process has demonstrated significant energy cost savings and yield improvements. There are several commercial processes available: Sulzer-MWB, Brodie type, Betz, BEFS and Recochem (39). Nalonchem has just started producing a high purity naphthalene from a new hydrotreating process. The economics and yield may be comparable with the older established routes for high purity naphthalene.

6. Specifications and Test Methods

Naphthalene usually is sold commercially according to its freezing or solidification point, because there is a correlation between the freezing point and the naphthalene content of the product; the correlation depends on the type and relative amount of impurities that are present (40). Because the freezing point can be changed appreciably by the presence of water, values and specifications are listed on a dry, wet, or as-received basis, using an appropriate method agreed upon between buyer and seller, eg, ASTM D1493.

Gas–liquid chromatography is used extensively to determine the naphthalene content of mixtures. Naphthalene can be separated easily from thionaphthene, the methyl- and dimethylnaphthalenes, and other aromatics. Analysis of the various other impurities may require the use of high resolution capillary columns.

Other tests that are routinely performed on commercial grades of naphthalene include evaporation residues (ASTM D2232), APHA color (ASTM D1686), water (ASTM D95), and acid-wash color (ASTM D2279). Three methods used to measure sulfur content are the oxygen-bomb combustion method (ASTM D129), the lamp-combustion method (ASTM D1266), and the Raney nickel reduction technique (41). Some typical specifications of commercially available grades of coal-tar (42) andpetroleum naphthalene and the ASTM specifications for refined naphthalene are listed in Table 9.

7. Health and Safety Factors

7.1. Handling. Naphthalene is generally transported in molten form in tank trucks or tank cars that are equipped with steam coils. Depending on the transportation distance and the insulation on the car or truck, the naphthalene may solidify and require reheating before unloading. Without inert-gas blanketing and at the temperature normally used for the storage of molten naphthalene, ie, 90°C, the vapors above the liquid are within the flammability limits. Thus, storage tanks containing molten naphthalene have a combustible mixture in the vapor space and care must be taken to eliminate all sources of ignition around such systems. Naphthalene dust also can form explosive mixtures with air, which necessitates care in the design and operation of solid handling systems. Perhaps the greatest hazard to the worker is the potential for operating or maintenance personnel to be accidentally splashed with hot molten naphthalene while taking samples or disassembling process lines (ASTM D3438). Molten naphthalene tank vents must be adequately heated and insulated to prevent the accumulation of sublimed and solidified naphthalene. A collapsed tank can result easily from pumping from a tank with a plugged vent.

7.2. Toxicology. The acute oral and dermal toxicity of naphthalene is low with LD_{50} values for rats from 1780–2500 mg/kg orally (43) and <2000 mg/kg dermally. The inhalation of naphthalene vapors may cause headache, irretanced eyes nausea, confusion, and profuse perspiration, and if exposure is severe, vomiting, optic neuritis, real shutdown and hematuria may occur (28). Chronic exposure studies conducted by the NTP in mice for 2 years showed that naphthalene caused irritation to the nasal passages, but no other overt toxicity was noted. Rabbits that received 1–2 g/d of naphthalene either orally or hypodermically developed changes in the lens of the eye after a few days, followed by definite opacity of the lens after several days (43). Rare cases of such corneal epithelium damage in humans have been reported (28). Naphthalene can be irritating to the skin, and hypersensitivity does occur.

In reports submitted to the U.S. Environmental Protection Agency (EPA), there was no mutagenicity in the Ames test, no mutagenicity in the mouse micronucleus test, and no mutagenicity in the rat hepatocyte–DNA repair test. It was confirmed in other trials that naphthalene is nonmutagenic in the Salmonella microsome mutagenicity (Ames) test (44,45). In tests submitted to the EPA, there were no developmental or teratogenic effects noted in rabbits treated while pregnant.

The octanol–water partition coefficient, which is used as an indicator of the tendency of an organic chemical to accumulate in living tissue, was low. This indicates that naphthalene is unlikely to accumulate in the body.

In additional EPA studies, subchronic inhalation was evaluated in the rat for 4 and 13 weeks, respectively, and no adverse effects other than nasal irritation were noted. In the above-mentioned NTP chronic toxicity study in mice, no chronic toxic effects other than those resulting from bronchial irritation were noted. There was no treatment-related increase in tumors in male mice, but female mice had a slight increase in bronchial tumors. Neither species had an increase in cancer. Naphthalene showed no biological activity in other chemical carcinogen tests, indicating little cancer risk (46). No incidents of chronic effects have been reported as a result of industrial exposure to naphthalene (28,43).

Because naphthalene vapors can cause eye irritation at concentrations of 15 ppm in air and because continued exposure may result in adverse effects to the eye, a threshold limit value of 10 ppm (50 mg/m^3) has been set by the ACGIH (47). This amount is ~30% of the air-saturation value at 27°C.

Workers who handle naphthalene should be provided with impervious clothing, boots, glove, and face sheilds. Cartridge type respirators should be supplied for vapor concentrations of ~10 ppm.

8. Uses

The U.S. naphthalene consumption by markets for 2000 is listed in Table 10. The production of phthalic anhydride by vapor-phase catalytic oxidation has been the main use for naphthalene. Although its use has declined in favor of *o*-xylene, naphthalene is expected to maintain its present share of this market, ie, ~12–14%. Both petroleum naphthalene and coal-tar naphthalene can be used for phthalic anhydride manufacture. U.S. phthalic anhydride capacity was 615×10^3 t in 2000 (37).

Naphthalene sulfonates represent the second largest outlet for naphthalene, ie, ~27% of supply in 2000, and growing by 1–2% annually. The products are used as wetting agents and dispersants in paints and coatings and in a variety of pesticides and cleaner formulations. Their application as surfactants is expected to continue as a growth item in uses such as concrete and gypsum board additives (see SURFACTANTS).

Another large use of naphthalene is as a raw material for the manufacture of 1-naphthyl-*N*-methylcarbamate [63-25-2] (carbaryl, Sevin). Crude or semirefined coal-tar or petroleum naphthalene can be used for carbaryl manufacture. Carbaryl is used extensively as a replacement for DDT and other products that have become environmentally unacceptable (see INSECT CONTROL TECHNOLOGY).

Miscellaneous uses include several organic compounds and intermediates, eg, 1-naphthalenol, 1-naphthylamine [134-32-7], 1,2,3,4-tetrahydronaphthalene,decahydronaphthalene, and chlorinated naphthalenes.

9. Alkylnaphthalenes

Methyl- and dimethylnaphthalenes are contained in coke-oven tar and in certain petroleum fractions in significant amounts. A typical high temperature coke-oven coal tar, eg., contains ~3 wt% of combined methyl- and dimethylnaphthalenes (6). In the United States, separation of individual isomers is seldom attempted; instead a methylnaphthalene-rich fraction is produced for commercial purposes. Such mixtures are used for solvents for pesticides, sulfur, and various aromatic compounds. They also can be used as low freezing, stable heat-transfer fluids. Mixtures that are rich in monomethylnaphthalene content have been used as dye carriers (qv) for color intensification in the dyeing of synthetic fibers, eg, polyester. They also are used as the feedstock to make naphthalene in dealkylation processes. Phthalic anhydride also can be made from methylnaphthalene mixtures by an oxidation process that is similar to that used for naphthalene.

A mixed monomethylnaphthalene-rich material can be produced by distillation and can be used as feedstock for further processing. By cooling this material to ~0°C, an appreciable amount of 2-methylnaphthalene crystallizes, leaving a mother liquor consisting of approximately equal quantities of 1- and 2-methylnaphthalene. Pure 2-methylnaphthalene [91-57-6] (bp = 341.1°C; mp = 34.58°C) is used primarily as a raw material for the production of vitamin K preparations. Oxidation produces 2-methyl-1,4-naphthoquinone [58-27-5] (menadione, vitamin K_3), which itself and in the form of water-soluble sodium hydrogen sulfite adducts shows similar antihemorrhagic effects similar to the natural vitamin K_1 (see BLOOD, COAGULANTS AND ANTICOAGULANTS). Other compounds of the vitamin K series can be prepared from menadione (48) (see VITAMINS).

1-Methylnaphthalene [90-12-0] (bp = 244.6°C; mp = −30.6°C) can be used as a general solvent because of its low melting point. It also is used as a test substance for the determination of the cetane number of diesel fuels (see GASOLINE AND OTHER MOTOR FUELS). By side-chain chlorination of 1-methylnaphthalene to 1-chloromethylnaphthalene and formation of naphthaleneacetonitrile, it is possible to produce 1-naphthylacetic acid, which is a growth regulator for plants, a germination suppressor for potatoes, and an intermediate for drug manufacture (48) (see GROWTH REGULATORS, PLANT).

Of the individual dimethylnaphthalenes, 2,6-dimethylnaphthalene [28804-88-8] has been of particular interest as a precursor to 2,6-naphthalenedicarboxylic acid [1141-38-4], a potentially valuable monomer for polyesters.

Isopropylnaphthalenes can be prepared readily by the catalytic alkylation of naphthalene with propylene. 2-Isopropylnaphthalene [2027-17-0] is an important intermediate used in the manufacture of 2-naphthol (see NAPHTHALENE DERIVATIVES). The alkylation of naphthalene with propylene, preferably in an inert solvent at 40–100°C with an aluminum chloride, hydrogen fluoride, or boron trifluoride–phosphoric acid catalyst, gives 90–95% wt% 2-isopropylnaphthalene; however, a considerable amount of polyalkylate also is produced. Preferably, the propylation of naphthalene is carried out in the vapor phase in a continuous manner, over a phosphoric acid on kieselguhr catalyst under pressure at ~220–250°C. The alkylate, which is low in di- and polyisopropylnaphthalenes, then is isomerized by recycling over the same catalyst at 240°C or by using aluminum chloride catalyst at 80°C. After distillation, a product containing >90 wt% 2-isopropylnaphthalene is obtained (49).

Mixtures containing various concentrations of mono-, di-, and polyisopropylnaphthalenes have been prepared by treating molten naphthalene with concentrated sulfuric acid and propylene at 150–200°C followed by distillation (41). Products comprised of such isomeric mixtures have extremely low pour points, ie, ca −50°C, are excellent multipurpose solvents, and have been evaluated as possible liquid-phase heat-transfer oils.

Of the higher alkylnaphthalenes, those of importance are the amyl-, diamyl-, polyamyl-, nonyl-, and dinonylnaphthalenes. These alkylnaphthalenes are used in sulfonated form as surfactants and detergent products.

9.1. Acenaphthene. Acenaphthene [83-32-9] is a hydrocarbon ($C_{12}H_{10}$) present in high temperature coal tar (6). Acenaphthene may be halogenated, sulfonated, and nitrated in a manner similar to naphthalene (43). Oxidation first yields acenaphthenequinone, followed by 1,8-naphthalenedicarboxylic acid anhydride [81-84-5], an important intermediate for dyes, pigments, fluorescent whiteners, and pesticides. Acenaphthylene [208-96-8] is formed upon catalytic dehydrogenation of acenaphthene (44). Acenaphthene can be isolated and recovered from a tar-distillation fraction by concentrating it by fractional distillation followed by crystallization, to give ∼40% recovery of 98–99% pure acenaphthene. This material can be further purified by recrystallization from a suitable solvent, eg, ethanol (45).

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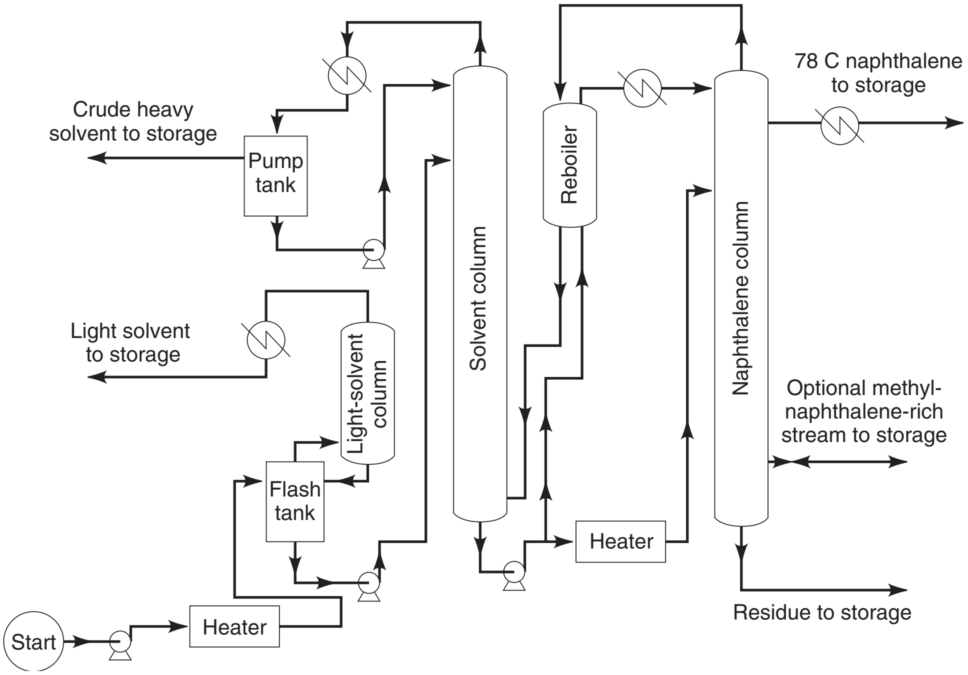

Fig. 1. Typical coal-tar naphthalene distillation, starting with naphthalene-rich chemical oil.

Table 1. **Properties of Naphthalene**

Property	Value	Reference
molecular wt	128.17	
mp, °C	80.290	2
normal bp at 101.3 kPa[a], °C	217.993	3
triple point (t_{tp}), °C	80.28	3
critical temperature (t_c), °C	475.2	3
critical pressure (p_c), kPa[a]	4051.0	3
flash point (closed cup), °C	79	4
ignition temperature, °C	526	4
flammable limits, vol %		
upper	5.9	5
lower	0.9	5
heat of vaporization, kJ/mol[b]	43.5	3
heat of fusion at triple point, kJ/mol[b]	18.979	3
heat of combustion, at 15.5°C and 101.3 kPa[a],kJ/mol[b]	5158.41	3
heat capacity, at 15.5°C and 101.3 kPa[a],J/(mol·K)[b]	159.28	3
heat of formation at 25°C, kJ/mol[b]		
solid	78.53	3
gas	150.58	3
density, g/mL		
at 25°C	1.175	3
at 90°C	0.97021	3

[a] To convert kPa to atm, divide by 101.3.

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

Table 2. **Selected Values of Vapor Pressure–Temperature and Viscosity–Temperature Relationships for Naphthalene**[a]

Vapor pressure data		Viscosity data	
Temperature, °C	Pressure, kPa[b]	Temperature, °C	Viscosity, mPa·s(=cP)
0	0.0008	80.3	0.96
10	0.003	90	0.846
20	0.007	100	0.754
40	0.043	110	0.678
87.6	1.33	120	0.616
119.1	5.33	150	0.482
166.3	26.66	180	0.394
191.3	53.33	220	0.320
214.3	93.33		
218.0	101.33		
230.5	133.32		
250.6	199.98		

[a] Ref. 6.

[b] To convert kPa to mm Hg, multiply by 7.5.

Table 3. **Azeotropes of Naphthalene**[a]

Compound	Bp[b] of azeotrope, °C	Naphthalene, wt%	Bp[b] of azeotrope, °C
water	100.0	16.0	98.8
dodecane	216.3	60.5	140.2
dipropylene glycol	231.8	87.6	142.9
ethylene glycol	197.4	49.0	183.9
benzyl alcohol	205.2	40.0	204.1
p-ethylphenol	218.8	55.0	215.0
p-chlorophenol	219.8	63.5	216.3
diethylene glycol	245.5	78.0	216.6
3,4-dimethylphenol	226.8	84.0	217.6
benzoic acid	249.2	95.0	217.7

[a] Ref. 3.

[b] At 101.3 kPa = 1 atm.

Table 4. **Naphthalene Solubility Data**[a]

Solvent	Solubility at 25°C, mol fraction
ethylbenzene	0.2926
benzene	0.2946
toluene	0.2920
cyclohexane	0.1487
carbon tetrachloride	0.2591
n-hexane	0.1168
water	0.18×10^{-5}

[a] Ref. 3.

Table 5. **Properties of Tetra- and Decahydronaphthalenes**[a]

Property	Tetralin	Decalin		
		cis	Mixed isomers	trans
mol wt	132.2048	138.2522		
mp, °C	−35.749[b]	−42.98		−30.38
normal bp at 101.3 kPa[c], °C	207.62	195.815		187.310
density at 25°C, g/mL	0.9659[b]	0.8929		0.8660
viscosity at 25°C, mPa·s(=cP)	2.012[b]	2.99		1.936
flash point, closed cup, °C	71[d]		57.8	
ignition temperature, °C	385[d]		250	
flammable limits, vol %				
upper	5.0[d,e]		4.9[d,f]	
lower	0.8[d,f]		0.7[d,f]	

[a] Tetralin and decalin, respectively; data from Ref. 23 unless otherwise noted.

[b] Ref. 24.

[c] To convert kPa to mmHg, multiply by 7.5.

[d] Ref. 4.

[e] At 150°C.

[f] At 100°C.

Table 6. **U.S. Naphthalene Capacities, 2001**[a]

Producer	Location	Coal tar/petroleum	Capacity, $x10^3$t
Creekside Industries	Baytown, Tex.	petroleum	16.33
Koppers Industries, Inc.	Follansbee, W. Va.	coal tar	65.32
		Total	*81.65*

[a] Ref. 37.

Table 7. **U.S. Naphthalene Production History**[a]

Year	Coal-tar naphthalene, 10^3 t	Petroleum naphthalene, 10^3 t	Total, 10^3 t
1980	142	59	201
1981	159	64	223
1982	104	57	161
1983	105	42	147
1984	85	38	123
1985	84	23	107
1986	86	24	110
1987	85	24	109
1988	84	24	108
1989	86	24	110
1990	82	23	105
1991	80	23	103
1992	78	14	92
1993	77	10	87
1994	90	11	101
1995	100	11	111
1996	100	11	111
1997	100	11	111
1998	100	12	112
1999	95	13	108
2000	90	13	103

[a] Ref. 37.

Table 8. **U.S. Naphthalene Pricing History**[a]

Year	Petroleum naphthalene, \$/kg (\$lb)	Coal tar naphthalene, \$/kg (\$/lb)
1980	5.50 (12.05)	6.60–11.30 (14.6–25)
1981	5.50 (12.05)	9.30–12.4 (20.5–27)
1982	5.50 (12.05)	9.30–12.25 (20.5–27)
1983	5.50 (12.05)	9.30–12.25 (20.5–27)
1984	5.50 (12.05)	9.30–12.25 (20.5–27)
1985	5.50 (12.05)	9.30–12.25 (20.5–27)
1986	5.50 (12.05)	9.30–12.25 (20.5–27)
1987	5.50 (12.05)	9.30–12.25 (20.5–27)
1988	5.50 (12.05)	9.30–12.25 (20.5–27)
1989	5.00 (11.00)	9.30–12.25 (20.5–27)
1990	8.20 (18.00)	9.30–12.25 (20.5–27)
1991	8.20 (18.00)	9.30–12.25 (20.5–27)
1992	9.00 (20.00)	10.00–13.60 (22–30)
1993	8.60 (19.00)	9.60–13.60 (21–30)
1994	8.20 (18.00)	9.30–13.60 (20–30)
1995	10.00 (22.00)	10.00–14.50 (22–32)
1996	8.20 (18.00)	9.30–13.60 (20–30)
1997	8.20 (18.00)	9.30–13.60 (20–30)
1998	7.25 (16.00)	9.30–13.60 (20–30)
1999	7.25 (16.00)	9.30–13.60 (20–30)
2000	8.20 (18.00)	9.30–13.60 (20–30)

[a] Ref. 37

Table 9. **Naphthalene Specifications**[a]

Analysis	Crude coal tar	Petroleum	High purity
solidification point, min, °C	78.0	79.3	80.0
assay, min, wt%	95.9	99.6	99.9
sulfur, max, wt%	0.8	0.1	<5 ppm
color, max, APHA	10	10	1
nonvolatiles, max, wt%	0.25	0.1	0.05
water, max, wt%	0.25	0.25	0.1

[a] Ref. 42.

Table 10. **U.S. Naphthalene Consumption, 2000**[a]

Use	Consumption, 10×10^3	% of Total
phthalic anhydride	70,000	62
surfactants	23,000	20
THN	10,000	9
moth repellants	7,500	7
miscellaneous	3,000	2
Total	*113,500*	

[a] Ref. 37.