

NAPHTHA

Naphtha is a generic term applied to a refined or partly refined petroleum product (Fig. 1) that distills below 240°C (465°F) under standardized distillation conditions.

Naphtha is valuable for solvents because of its good dissolving power. The wide range of naphthas available, from the ordinary paraffinic straight-run to the highly aromatic types, and the varying degree of volatility possible offer products suitable for many uses.

Naphtha is divided into two main types, aliphatic and aromatic. Aliphatic naphtha is composed of paraffinic hydrocarbons and cycloparaffins (naphthenes), and may be obtained directly from crude petroleum by distillation. Aromatic naphtha contains aromatics, usually alkyl-substituted benzene, and is very rarely, if at all, obtained from petroleum as straight-run materials; often reforming is necessary (Fig. 2).

In general, naphtha may be manufactured by any one of several methods, including:

1. Fractionation of straight-run, cracked, and reforming distillates, or even fractionation of crude petroleum
2. Solvent extraction
3. Hydrogenation of cracked distillates
4. Polymerization of unsaturated compounds (olefins)
5. Alkylation processes

In fact, the naphtha may be a combination of product streams from more than one of these processes.

The most common method of naphtha preparation is distillation. Depending on the design of the distillation unit, either one or two naphtha streams may be produced: (1) a single naphtha with an end point of about 205°C (400°F) and similar to straight-run gasoline, or (2) this same fraction divided into a light naphtha and a heavy naphtha. The end point of the light naphtha is varied to suit the subsequent subdivision of the naphthas into narrower boiling fractions and may be of the order of 120° C (250° F).

Process	Primary product	Secondary process	Secondary product
Atmospheric distillation	Naphtha		Light naphtha Heavy naphtha
Vacuum Distillation	gas oil	Catalytic cracking	Naphtha
	gas oil	Hydrocracking	Naphtha
	gas oil	Catalytic cracking	Naphtha
	residuium	Hydrocracking	Naphtha
		Coking	Naphtha
		Hydrocracking	Naphtha

FIGURE 1 Naphtha production in a petroleum refinery.

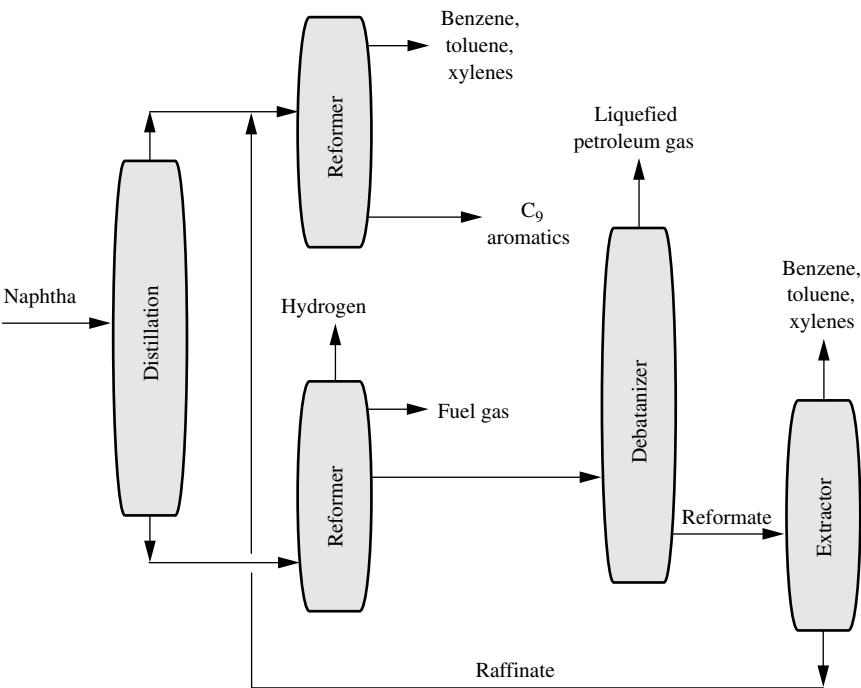


FIGURE 2 Naphtha reforming to aromatic products.

Before the naphtha is redistilled into a number of fractions with boiling ranges suitable for aliphatic solvents, the naphthas are usually treated to remove sulfur compounds, as well as aromatic hydrocarbons, which are present in sufficient quantity to cause an odor. Aliphatic solvents that are specially treated to remove aromatic hydrocarbons are known as *deodorized solvents*. *Odorless solvent* is the name given to heavy alkylate used as an aliphatic solvent, which is a by-product in the manufacture of aviation alkylate.

Naphtha that is either naturally sweet (no odor) or has been treated until sweet is subdivided into several fractions in efficient fractional distillation towers, frequently called *column steam stills*. A typical arrangement consists of primary and secondary fractional distillation towers and a stripper. Heavy naphtha, for example, is heated by a steam heater and passed into the primary tower, which is usually operated under vacuum. The vacuum permits vaporization of the naphtha at the temperatures obtainable from the steam heater.

The primary tower separates the naphtha into three parts:

1. The unwanted heavy ends, which are removed as a bottom product and sent to cracking coil stock
2. A side stream product of narrow boiling range, which after passing through the stripper may be suitable for the aliphatic solvent Varsol®
3. An overhead product, which is pumped to the secondary tower

The overhead product from the primary tower is divided into an overhead and a bottom product in the secondary tower, which operates under a partial vacuum with steam injected into the bottom of the tower to assist in the fractionation. The overhead and bottom products are finished aliphatic solvents, or if the feed to the primary tower is light naphtha instead of heavy naphtha, other aliphatic solvents of different boiling ranges are produced.

Several methods, involving solvent extraction or destructive hydrogenation, can accomplish the removal of aromatic hydrocarbons from naphtha. By destructive hydrodegeneration methods, aromatic hydrocarbon rings are first ruptured and then saturated with hydrogen, which converts aromatic hydrocarbons into the odorless, straight-chain paraffinic hydrocarbons required in aliphatic solvents.

Extractive distillation, that is, fractional distillation in the presence of a solvent, is used to recover aromatic hydrocarbons from, say, reformat fractions in the following manner. By means of preliminary distillation in a 65-tray prefractionator, a fraction containing a single aromatic can be separated from the reformat, and this aromatic concentrate is then pumped to an extraction distillation tower near the top, and aromatic concentrate enters near the bottom. A reboiler in the extractive distillation tower induces the aromatic concentrate to ascend the tower, where it contacts the descending solvent.

The solvent removes the aromatic constituents and accumulates at the bottom of the tower; the nonaromatic portion of the concentrate leaves the top of the tower and may contain about 1 percent of the aromatics. The solvent and dissolved aromatics are conveyed from the bottom of the extractive

distillation tower to a solvent stripper, where fractional distillation separates the aromatics from the solvent as an overhead product. The solvent is circulated to the extractive distillation tower, whereas the aromatic stream is treated with sulfuric acid and clay to yield a finished product of high purity.

Silica gel is an adsorbent for aromatics and has found use in extracting aromatics from refinery streams. Silica gel is manufactured amorphous silica that is extremely porous and has the property of selectively removing and holding certain chemical compounds from mixtures. For example, silica gel selectively removes aromatics from a petroleum fraction, and after the nonaromatic portion of the fraction is drained from the silica gel, the adsorbed aromatics are washed from the silica gel by a stripper (or desorbent). Depending on the kind of feedstock, xylene, kerosene, or pentane may be used as the desorbent.

The main uses of petroleum naphtha fall into the general areas of

1. Solvents (diluent) for paints, for example
2. Dry-cleaning solvents
3. Solvents for cutback asphalt
4. Solvents in the rubber industry
5. Solvents for industrial extraction processes

Turpentine, the older, more conventional solvent for paints, has now been almost completely replaced with the discovery that the cheaper and more abundant petroleum naphthas are equally satisfactory. The differences in application are slight; naphthas cause a slightly greater decrease in viscosity when added to some paints than does turpentine, and depending on the boiling range, they may show some differences in evaporation rates.

Naphthas are used in the rubber industry for dampening the play and tread stocks of automobile tires during manufacture to obtain better adhesion between the units of the tire. They are also consumed extensively in making rubber cements (adhesives) or are employed in the fabrication of rubberized cloth, hot-water bottles, bathing caps, gloves, overshoes, and toys. These cements are solutions of rubber and were formerly made with benzene, but petroleum naphtha is now preferred because of its less toxic character.

Naphthas are used for extraction on a fairly wide scale. They are applied in extracting residual oil from castor beans, soybeans, cottonseed, and wheat germ and in the recovery of *grease* from mixed garbage and refuse. The solvent employed in these cases is a hexane cut, boiling from about 65 to 120°C (150 to 250°F). When the oils recovered are of edible grade or

intended for refined purposes, stable solvents completely free of residual odor and taste are necessary, and straight-run streams from low-sulfur, paraffinic crude oils are generally satisfactory.

The recovery of wood resin by naphtha extraction of the resinous portions of dead trees of the resin-bearing varieties or stumps, for example, is also used in the wood industry. The chipped wood is steamed to distill out the resinous products recoverable in this way and then extracted with a naphtha solvent, usually a well-refined, low-sulfur, paraffinic product boiling from, say, 95 to 150°C (200 to 300°F).

Naphthas are also employed as solvents in the manufacture of printing inks, leather coatings, diluents for dyes, and degreasing of wool fibers, polishes, and waxes, as well as rust- and waterproofing compositions, mildew-proofing compositions, insecticides, and wood preservatives.

NAPHTHALENE

Naphthalene (melting point: 80.3°C, density: 1.175, flash point: 79°C) is very slightly soluble in water but is appreciably soluble in many organic solvents such as 1,2,3,4-tetrahydronaphthalene (tetralin), phenols, ethers, carbon disulfide, chloroform, benzene, coal-tar naphtha, carbon tetrachloride, acetone, and decahydronaphthalene (decalin).

Naphthalene is produced from coal tar. In the *coal tar process*, coal tar is processed through a tar-distillation step where approximately the first 20 wt % of distillate (*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 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.

Crude naphthalene product is obtained by fractional distillation of the tar acid-free chemical oil, and the distillation may be accomplished in either a batch process or a continuous process (Fig. 1). The tar acid-free chemical oil is charged to the system, where most of the low boiling components such as 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 approximately 130 to 200°C and is used as a general solvent and as a feedstock for hydrocarbon-resin manufacture because of its high content of compounds such as indene and coumarone.

The naphthalene-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, for example, naphthalene-filled vacuum jets and lines. A side stream that is rich in methylnaphthalenes may be taken near the bottom of the naphthalene column.

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

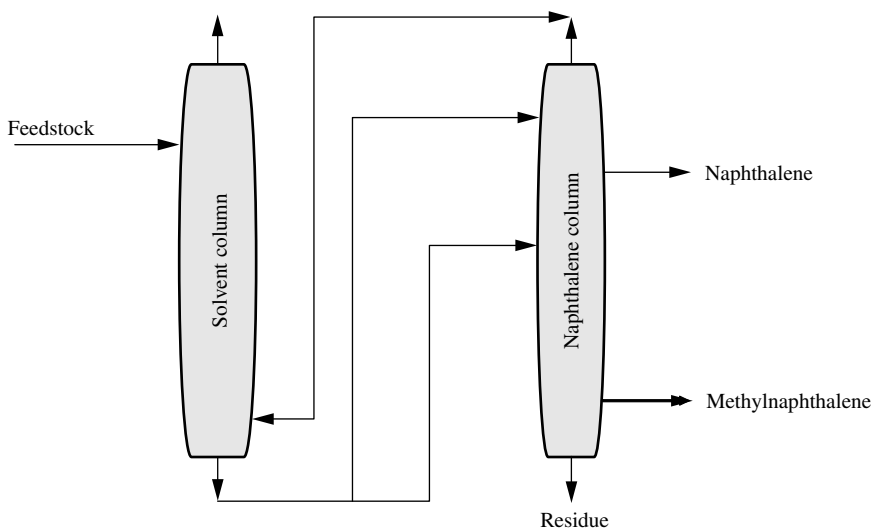


FIGURE 1 Production of naphthalene from naphthalene oil.

NATURAL GAS

Natural gas (predominantly methane, CH_4 , with ethane, propane, and butane) is a fuel gas, and it is also an important chemical raw material for various syntheses.

In addition to the industrially valuable hydrocarbons, natural gas contains undesirable water and hydrogen sulfide that must be removed before shipping to the consumer.

Four important methods are employed for the dehydration of gas: compression, treatment with drying substances, adsorption, and refrigeration. A plant for water removal by compression consists of a gas compressor, followed by a cooling system to remove the water vapor by condensation. The treatment of gas with drying substances has found widespread usage in this country. Glycols are used most widely for this purpose because of their high affinity for water, chemical stability, low foaming, and low solvent action for natural gas. For water dew points in the range of -90 to -100°C , molecular sieves are used in many plants. The beds are regenerated by countercurrent flow of hot gases (230 to 290°C).

Other drying agents are activated alumina and bauxite, silica gel, sulfuric acid, and concentrated solutions of calcium chloride or sodium thiocyanate. Plants of this type usually require a packed tower for countercurrent treatment of the gas with the reagent, together with a regenerator for the dehydrating agent.

Hydrogen sulfide and other sulfur compounds are objectionable in natural gas because they cause corrosion and also form air-polluting compounds during combustion. Carbon dioxide in the gas is objectionable because it lowers the heating value of the gas.

Monoethanolamine is the oldest and probably still the most widely used solvent (Fig. 1). For desulfurization of natural gas, a 10 to 30% aqueous solution of monoethanolamine is normally used and a variety of solvents are available that vary in solvent selectivity for absorption of hydrogen sulfide and carbon dioxide, and this property, as well as the composition of the impurities in the gas being treated, frequently determines the choice of solvent. Some of

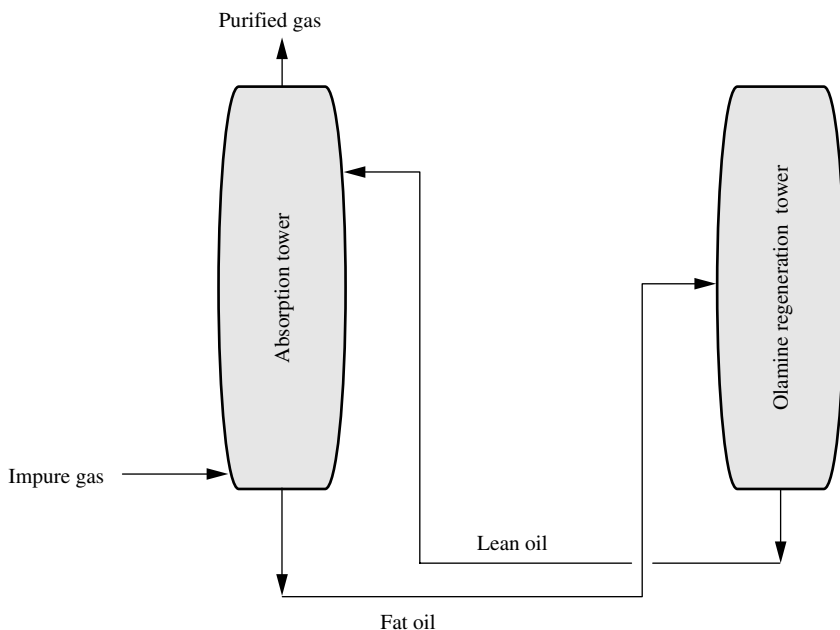


FIGURE 1 Gas purification using an amine.

the solvents also have a high affinity for higher hydrocarbons, and this is a disadvantage if the gas contains an appreciable quantity of these valuable compounds. If simultaneous dehydration and desulfurization is desired, the gas may be scrubbed with a solution of amine, water, and glycol. Solution compositions for this purpose are from 10 to 36% monoethanolamine, 45 to 85% diethylene glycol, and the remainder water.

One of the newest commercial methods of sweetening gas is the use of membranes. This separation works on the principle that there are different rates of permeation through a membrane for different gases.

Membrane materials used are polysulfone, polystyrene, Teflon, and various rubbers. This type of separation possesses many advantages over other types of gas separation, e.g., mild operating conditions, lower energy consumption, low capital cost, and economic operation at both low and high flow rates.

Natural gas with a high nitrogen content can be upgraded by a cryogenic process that dries feed gas at 4.9 MPa and cools it to 185 K. The natural gas is vaporized, and both this and the separated nitrogen gas leave the system via heat exchangers against incoming gas.

Natural gas can also be separated into its hydrocarbon constituents (Fig. 2), thereby producing feedstocks for petrochemical processes.

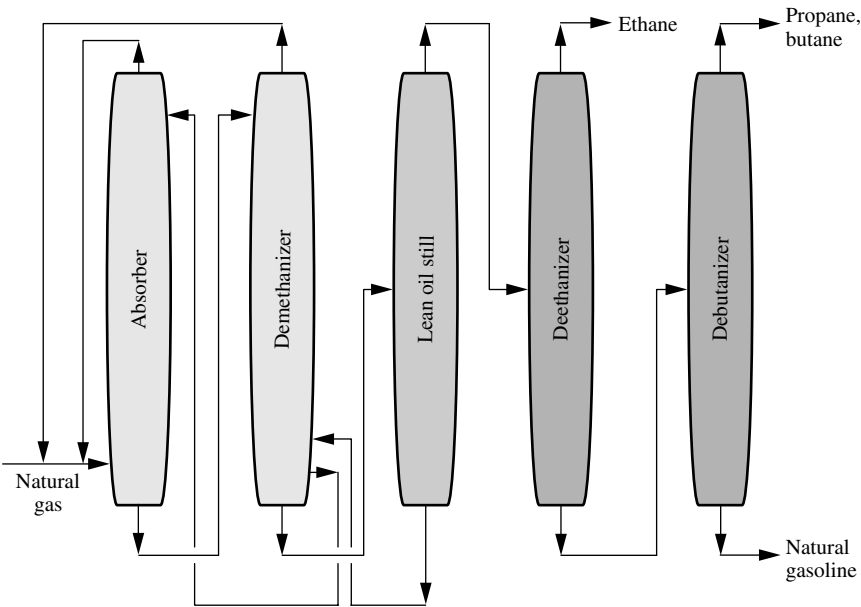


FIGURE 2 Separation of natural gas into hydrocarbon constituents.

NATURAL GAS (SUBSTITUTE)

Substitute natural gas is produced by a series of reactions in a variety of gasifiers that use coal as the feedstock (Fig. 1). The low- and medium-heat syngas (carbon monoxide and hydrogen) so produced are converted to a high-heat-content gas similar to natural gas:

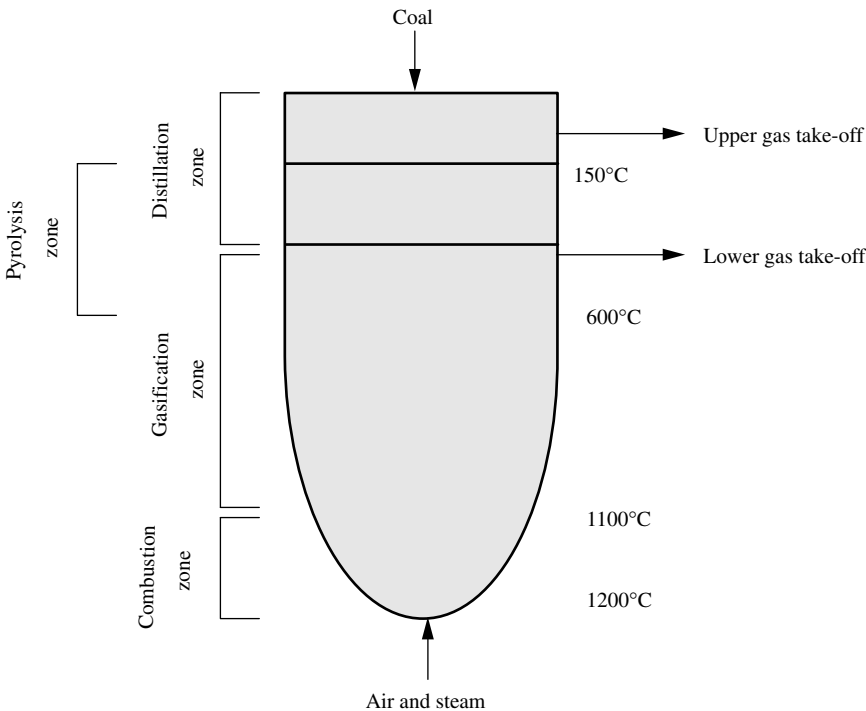
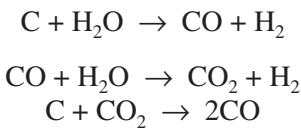
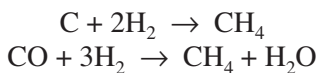


FIGURE 1 Production of natural gas substitute by coal gasification.

At sufficiently high pressures, the hydrogen produced by the first two reactions will hydrogenate some of the carbon to yield methane.



The gas thus produced was known originally as *synthetic natural gas*, but it can be argued that the correct name is *substitute natural gas*.

The sulfur and carbon dioxide are removed from the gas before it is methanated. The operating temperature can vary from 800 to about 1650°C with a pressure that will vary depending upon the gasifier and the desired product. The higher pressure and lower temperature result in the formation of a larger amount of methane.

Naphtha and other oils can be converted to substitute natural gas. The processes use mix naphtha with steam in a 1:2 ratio and gasify the mixture. The gas produced is methanated by the reaction of the carbon oxides with the hydrogen present. Purification requires the removal of any residual carbon dioxide.

See Naphtha.

NEON

See Rare Gases.

NICOTINE

Nicotine (melting point: -79°C , boiling point: 246.7°C , density: 1.0097) is a volatile alkaloid obtained by treating tobacco waste with aqueous alkali, followed by steam distillation. Most nicotine is converted to the less volatile sulfate and sold as a 40% solution.

In addition to being an active ingredient in tobacco smoke and having a pharmacological effect on humans, nicotine (in solution) is effective against aphids, thrips, and leaf hoppers and can be used as a fumigant.

NICOTINIC ACID AND NICOTINAMIDE

Nicotinic acid (melting point: 236°C, density: 1.473) and nicotinamide (melting point: 129°C, density: 1.400) are known as *niacin* and *niacinamide* in the food industry. Niacin is the most stable of all vitamins and is essential to humans and animals for growth and health. Niacin and niacinamide are nutritionally equivalent, and compete with one another.

For production of niacinamide in the past, methylethylpyridine was oxidized with nitric acid to yield niacin, and β -picoline was treated with air and ammonia to produce the nitrile that was then hydrolyzed to niacinamide. A more modern process can produce both niacin and niacinamide from a single feedstock, either β -picoline or 2-methyl-5-ethylpyridine by oxidative ammonolysis, a combination of oxidation and amination.

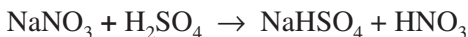
Either niacin or niacinamide can be selectively isolated from the hydrolysis by varying the hydrolysis time and nitrile concentration. A higher hydrolysis temperature favors production of niacin.

NITRIC ACID

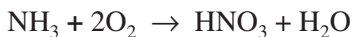
Nitric acid (HNO_3 ; freezing point: -41.6°C , boiling point: 86°C , density: 1.503 at 25°C) is a colorless, highly corrosive liquid and a very powerful oxidizing agent that in the highly pure state is not entirely stable and must be prepared from its azeotrope by distillation with concentrated sulfuric acid. Nitric acid gradually yellows because of decomposition to nitrogen dioxide. Solutions containing more than 80% nitric acid are called *fuming nitric acids*.

Reagent-grade nitric acid is a water solution containing about 68% by weight nitric acid. This strength corresponds to the constant-boiling mixture of the acid with water, which is 68.4% by weight nitric acid and boils at 121.9°C . Nitric acid is completely miscible with water and forms a monohydrate ($\text{HNO}_3 \cdot \text{H}_2\text{O}$, melting point: -38°C) and a dihydrate ($\text{HNO}_3 \cdot 2\text{H}_2\text{O}$, melting point: -18.5°C).

For many years nitric acid was made by the reaction of sulfuric acid and saltpeter, but this method is no longer used.



Nitric acid is now manufactured by combusting ammonia in air in the presence of a (platinum or other noble metal) catalyst, and the nitrogen oxides thus formed are oxidized further and absorbed in water to form nitric acid.



In this process (Fig. 1), the reactor contains a rhodium-platinum catalyst (2 to 10% rhodium) as wire gauzes in layers of 10 to 30 sheets at 750 to 920°C , 100 psi, and a contact time of 3×10^{-4} second. After cooling, the product gas enters the absorption tower with water and more air to oxidize the nitric oxide and hydrate it to nitric acid in water. Waste gases contain nitric oxide or nitrogen dioxide, and these are reduced with hydrogen or methane to ammonia or nitrogen gas. Traces of nitrogen oxides can be

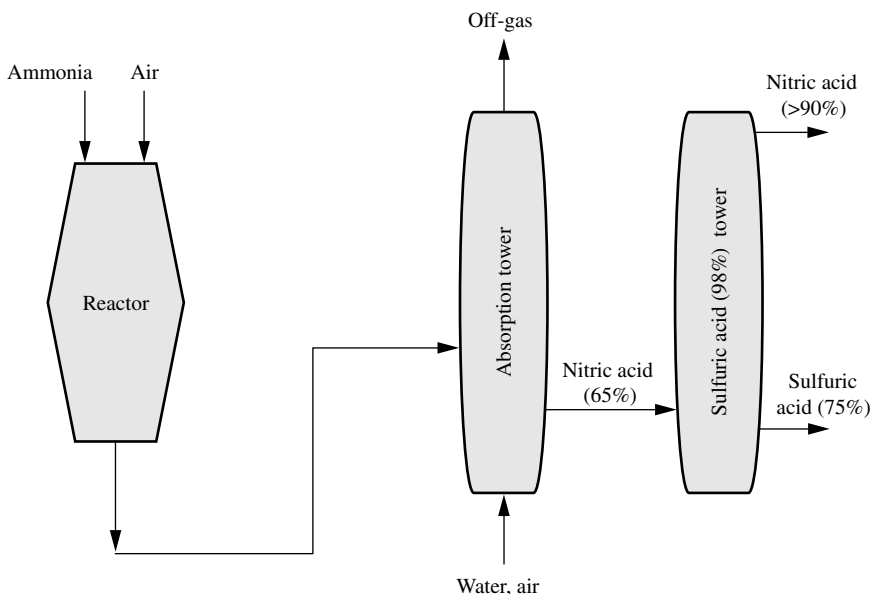


FIGURE 1 Manufacture of nitric acid.

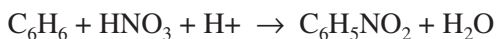
expelled. Concentration of the nitric acid in a silicon-iron or stoneware tower containing 98% sulfuric acid will give 90% nitric acid off the top and 70 to 75% sulfuric acid as the bottoms. This last step is necessary because simple distillation of nitric acid is not applicable; it forms an azeotrope with water at 68% acid. An alternative drying agent is magnesium nitrate, which can concentrate the acid to 100% nitric acid.

Manufactured acid contains some nitrous acid (HNO_2) when the concentration is between 20 and 45% nitric acid and dissolved nitrogen tetroxide (N_2O_4); when the concentration is over 55%. The oxidation potential of 20 to 45% acid stabilizes trivalent nitrogen (HNO_2), over 55% stabilizes tetravalent nitrogen (N_2O_4).

Nitric acid is predominantly used for fertilizer manufacture. It also finds use in the manufacture of adipic acid, nitroglycerin, nitrocellulose, ammonium picrate, trinitrotoluene, nitrobenzene, silver nitrate, and various isocyanates.

NITROBENZENE

Nitrobenzene (melting point: 5.9°C, boiling point: 210.9°C, density: 1.199, flash point: 88°C) is made by the direct nitration of benzene using a nitric acid–sulfuric acid mixture (Fig.1), usually in a cast-iron or steel kettle.



The majority of the nitrobenzene is used for the production of aniline with a minor amount being used for the production of acetaminophen.

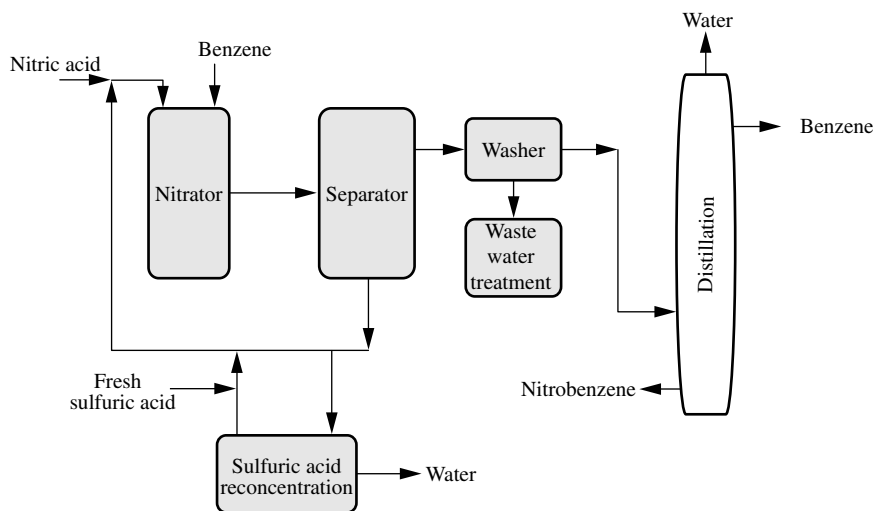
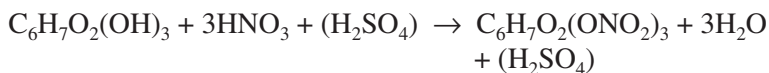


FIGURE 1 Manufacture of nitrobenzene.

NITROCELLULOSE

Nitrocellulose is a generic name for a product produced by the reaction of cellulosic materials with nitric acid and thereby containing the nitro group.

The commercial manufacture of cellulose nitrate involves treatment of cellulose with a mixture of nitric and sulfuric acids:



(simplified formula).

The finished nitrocellulose should not be allowed to become acid in use or in storage, since this catalyzes its further decomposition. A stabilizer is therefore added that reacts with any trace of nitrous, nitric, or sulfuric acid that may be released because of the decomposition of the nitrocellulose and thus stop further decomposition.

See Dynamite.

NITROGEN

Nitrogen is a gas (boiling point: -196°C) that occupies approximately 80% of the volume of the air. Thus, it is not surprising that the production of nitrogen from the air is the predominant method of manufacture.

In the process for the liquefaction of air (Fig. 1), air is filtered to remove particulates and then compressed to 77 psi. An oxidation chamber converts traces of hydrocarbons into carbon dioxide and water. The air is then passed through a water separator that removes some of the water. A heat exchanger cools the sample down to very low temperatures, causing solid water and carbon dioxide to be separated from the main components.

Most of the nitrogen-oxygen mixture, now at -168°C and 72 psi, enters the bottom of a fractionating column (approximately 100 feet high) where an expansion valve at this point causes further cooling. The more volatile nitrogen rises to the top of the column as a gas since nitrogen (boiling point -196°C , 77 K) has a lower boiling point than oxygen (boiling point -183°C , 90 K), and the column at 83 K is able to separate the two.

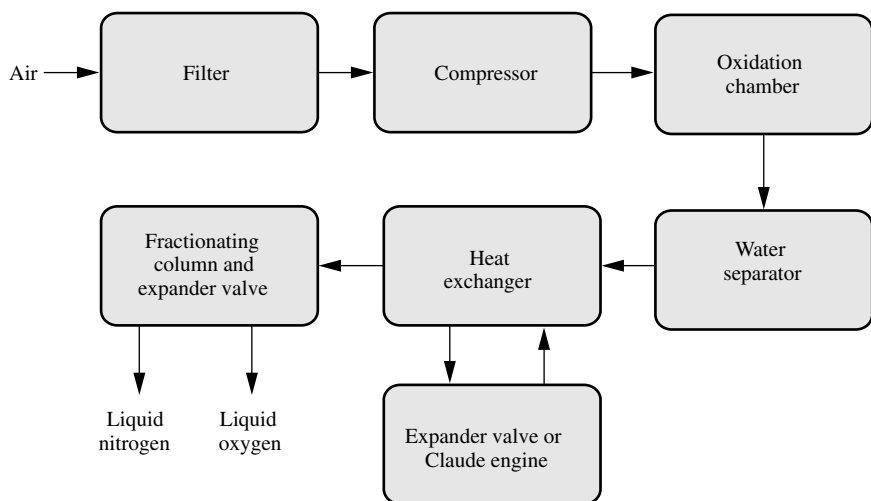


FIGURE 1 Manufacture of nitrogen by the liquefaction of air.

After being cooled in the heat exchanger, a small amount of nitrogen-oxygen mixture is fed to the main expander valve and the extremely cold gas is recycled into the heat exchanger to keep the system cold. Some argon remains in the oxygen fraction and this mixture can be sold as 90 to 95% purity oxygen. If purer oxygen is required, a more elaborate fractionating column with a greater number of plates gives an oxygen-argon separation. Oxygen can be obtained in 99.5% purity in this fashion. Not only argon, but also other rare gases, (neon, krypton, and xenon), can also be obtained in separations. Helium is *not* obtained from liquefaction of air. It occurs in much greater concentrations (2%) in natural gas wells and is isolated in the petroleum refinery.

Additional processes for the separation of pure nitrogen involve the use of cryogenics (Fig. 2), membranes (Fig. 3), or pressure-swing adsorption systems (Fig. 4). The use of any one of these processes either as a single adjunct or as a multiadjunct to the nitrogen process is known.

By far the largest use of nitrogen is in ammonia synthesis, and the fastest growing use of nitrogen is in enhanced oil recovery (EOR), where it maintains pressure in oil fields so that a vacuum is not formed underground when natural gas and oil are pumped out. It is competing with carbon dioxide in this application. Other uses include blanket atmospheres, food preservation, aerospace, cryogenics, metals processing, and electronic manufacturing.

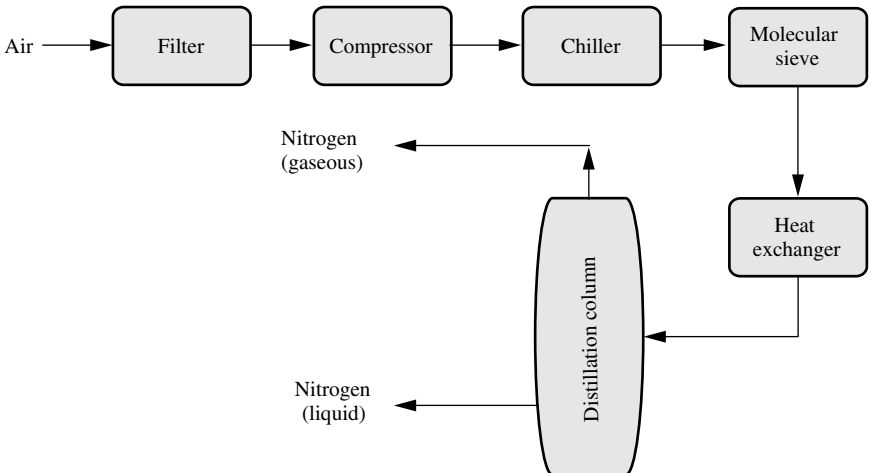


FIGURE 2 Nitrogen separation by cryogenics.

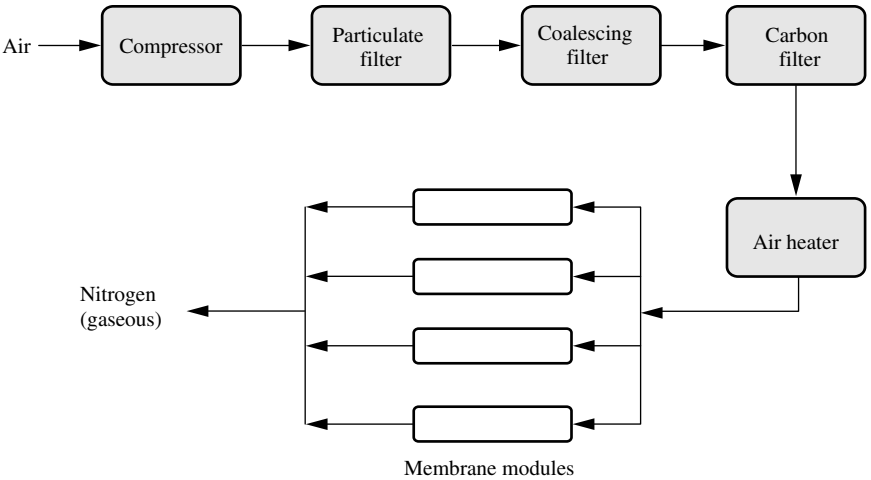


FIGURE 3 Nitrogen separation by the use of a membrane.

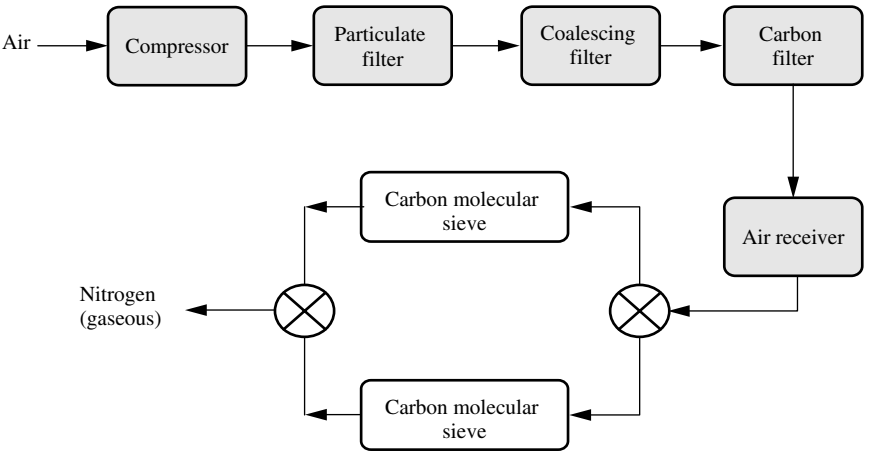


FIGURE 4 Nitrogen separation by pressure swing adsorption.

NITROGLYCERIN

Nitroglycerin ($\text{CH}_2\text{ONO}_2\text{OCHNO}_2\text{CH}_2\text{ONO}_2$, freezing point: 13°C) is a liquid similar in appearance to the original glycerol. However, the nitro compound is sensitive to percussion but is somewhat less sensitive in the solid phase. The solid tends to explode incompletely, so frozen nitroglycerin must always be thawed before using. To make nitroglycerin safer and easier to handle, it is usually manufactured into dynamite.

Nitroglycerin is manufactured by slowly (and cautiously!) adding glycerol ($\text{CH}_2\text{OHCHOHCH}_2\text{OH}$) of high purity (99.9%+) to a mixture having the approximate composition: sulfuric acid (H_2SO_4) 59.5%, nitric acid (HNO_3) 40%, and water (H_2O) 0.5%. Nitration is accomplished in agitated nitrators equipped with steel cooling coils carrying brine at 5°C to maintain the temperature below 10°C (Fig. 1).

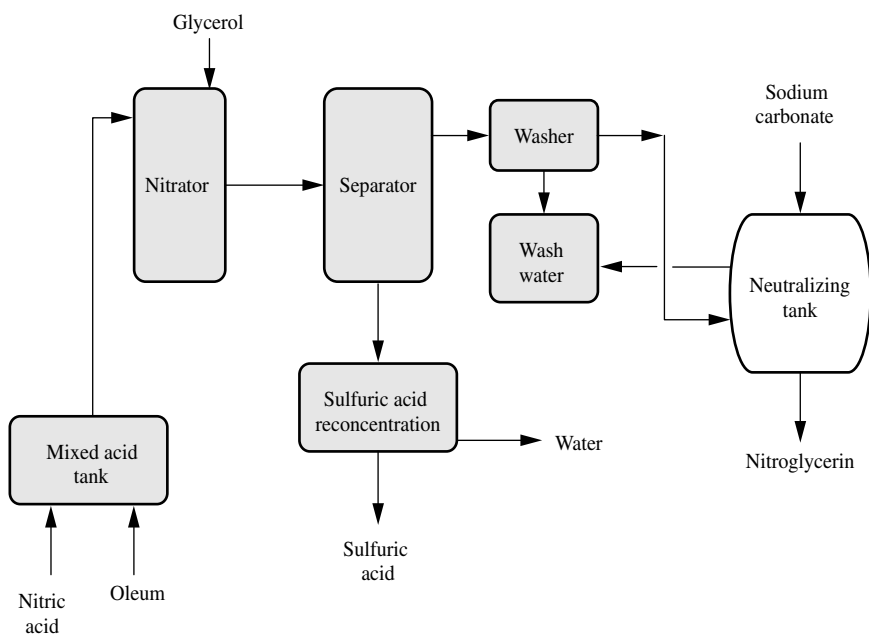


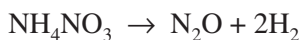
FIGURE 1 Manufacture of nitroglycerin.

After nitration, the mixture of nitroglycerin and spent acid is allowed to flow through a trough (a trough is easier to clean completely than a pipe) into separating and settling tanks some distance from the nitrator. The nitroglycerin is separated from the acid and sent to the wash tank, where it is washed twice with warm water and with a 2% sodium carbonate solution to ensure the complete removal of any remaining acid. Additional washes with warm water are continued until no trace of sodium carbonate (alkalinity) is evident.

See Dynamite.

NITROUS OXIDE

Nitrous oxide is manufactured by heating very pure ammonium nitrate to 200 to 260°C in aluminum retorts,



It is purified by treatment with caustic to remove nitric acid and with dichromate to remove nitric oxide.

See Ammonium Nitrate.

NONENE

Nonene (*n*-nonene; boiling point: 146°C, density: 0.730) was originally made by the trimerization of propylene ($\text{CH}_3\text{CH}=\text{CH}_2$) to give a branched nonene; this product now has limited use for detergents because of non-biodegradability.

Cracking and dehydrogenation of *n*-paraffins is now the preferred method, giving very linear chains.



With wax consisting of linear paraffins, an olefin product containing as much as 90% linear alpha olefins can be prepared.

Nonene is used in the manufacture of nonylphenol and ethoxylated nonylphenol nonionic surfactants. It is also used in the oxo process to make *iso*-decyl alcohol for esters as plasticizers.

See Oxo Reaction.

NOVOCAINE

Novocaine (procaine hydrochloride) is a local anesthetic that is considered to be less toxic than cocaine, and does not have the danger of habituation. It is used frequently in conjunction with a vasoconstrictor such as epinephrine to secure a prolonged anesthetic action.

Alkylating ethylenechlorohydrin with diethylamine, which is condensed with *p*-nitrobenzoyl chloride and reduced with tin and hydrochloric acid to obtain procaine, produces novocaine.

NYLON

See Caprolactam and Polyamides.