22

Synthetic Nitrogen Products

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Nitrogen products are among the most important chemicals produced in the world today. The largest quantities are used as fertilizers, but nitrogen products also find very important uses in the manufacture of nylon and acrylic fibers, methacrylate and other plastics, foamed insulation and plastics, metal plating, gold mining, animal feed supplements, and herbicides.

NITROGEN

Characteristics

Nitrogen is colorless, odorless, and slightly lighter than air with a density of 0.967 (air = 1.0). Some people consider nitrogen to be one of the most dangerous gases. This is because a person in an atmosphere of nitrogen can lose consciousness without any warning symptoms in as little as 20 seconds. Death can follow in 3 to 4 minutes. One deep breath of 100 percent nitrogen can be fatal because nitrogen will displace carbon dioxide in the body completely. In the absence of a carbon dioxide signal to the brain, breathing stops.

No one should work in or enter atmospheres containing less than 19.5 percent oxygen, unless equipped with a self-contained breathing apparatus or a breathing air mask. This is also true of rescue personnel who can be overcome by the same oxygen-deficient atmosphere as the initial victim.[39]

The properties of nitrogen are listed in Table 22.1.

Although the ability of nitrogen to easily unite with other elements is quite limited, it does form some interesting compounds. When nitrogen combines with certain elements, it produces dyes that rival the rainbow in the brilliance of their colors. With other elements, nitrogen forms drugs such as morphine, quinine, and acetanilid that ease pain and combat diseases. With other compounds, nitrogen forms some of our most powerful explosives such as nitroglycerin and guncotton. Nitrogen can also be used to make some very deadly compounds such as ptomaines. Some nitrogen compounds provide pleasant-tasting flavors and sweet perfumes and others are so vile in taste and odor that they are beyond description. In nitric acid we find

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TABLE 22.1 Physical Properties of Nitrogen

Property	*Value*
Molecular weight	14.0067
Boiling point, °C (°F)	−195.8 (−320.5)
Freezing point, °C (°F)	−209.86 (−346.0)
Critical temperature, °C (°F)	−146.95 (−232.4)
Critical pressure, kPa (psi)	3,393 (492.3)
Critical volume, cc/g-mol	89.5
Specific heat	
20°C and 147 psia	
c_p (BTU/lb °F)	0.247
c_v (BTU/lb °F)	0.176
21°C (J/(kg-K)	1,046
$k = c_p/c_v$	1.41
Heat of formation of gas, ΔH, (kJ/mole)	0.3604
Heat of fusion at melting point	
J/g	25.6
Heat of vaporization at boiling point	
J/g	199
BTU/lb	85.5
Solubility in water, g N_2 per 100 g H_2O at 760 mm	
0°C	0.00239
20°C	0.00189
40°C	0.00139
60°C	0.00105
Specific gravity	
Relative to air	0.967
−195.8°C (liquid)	0.808
−252°C (solid)	1.026
Specific volume (70°F and 1 atm), ft^3/lb	13.80
Density, kg/m^3	
20°C	1.16
Liquid at boiling point	808.6
Solid at melting/freezing point	1028
Thermal conductivity, W/m-K	
Gas @ 21°C	0.026
Liquid @ −200°C	0.14456

nitrogen in a strong acid whereas in ammonium hydroxide we have it in a well-known base.[7]

Nitrogen Production Processes

Economical fixation of nitrogen from the atmosphere has been a never-ending quest. It has been a difficult task because elemental nitrogen is comparatively unreactive. It only combines with most elements under high pressure and/or high temperature. As a result industry meets its demand for high-purity nitrogen by obtaining most of it from liquid air. See Reference 1 and Chapter 27 (Industrial Gases).

Nitrogen production via PSA (pressure swing absorption) is based on the principle that nitrogen and oxygen have different absorption rates on carbon molecular sieves (CMS). Some of the nitrogen production processes that use this technology are described in References 1 and 3–6.

NITROGEN FIXATION

Nature uses nitrogen fixation to combine free nitrogen with other elements. Nodules on the roots of many plants contain bacteria that extract nitrogen from the air and convert it into soluble nitrates that fertilize the soil. Most nitrogen products are based on nitrogen oxides and ammonia, as described on the following pages.

Nitrogen Oxides

The five oxides of nitrogen are:[7] Nitrous Oxide (N_2O), Nitrogen Dioxide (NO_2), Nitric Oxide (NO), Nitrogen Pentoxide (N_2O_5), and Nitrogen Trioxide (N_2O_3). Nitrogen trioxide and nitrogen pentoxide are the anhydrides of nitrous acid and of nitric acid.

Nitrous oxide (laughing gas) is a colorless gas. Since the 1840s the major use of nitrous oxide has been as an anesthetic, especially by dentists. It is also used as a propellant in some aerosol cans, in atomic absorption spectrophotometry, in cryosurgery, and in racecar engines to provide extra power and acceleration.

Nitric oxide is a colorless gas that is insoluble in water. The most noticeable chemical characteristic of nitric oxide is the ease with which it combines with oxygen to form nitrogen dioxide. Its major use is in the industrial preparation of nitric acid.

In the late 1980s nitric oxide (NO) was discovered as a product of enzymatic synthesis in mammals. And in 1998 the Nobel Prize in Physiology was awarded to the scientist that discovered the role of NO as a biological messenger. Nitric oxide uses range from its role as a critical endogenous regulator of blood flow and thrombosis to a principal neurotransmitter mediating erectile function to a major pathophysiological mediator of inflammation and host defense. These major discoveries have stimulated research into a vast array of fields. The Nitric Oxide Society has been formed to coordinate meetings, and they also publish a research journal. More information is available at www.apnet.com/no.

Nitrogen dioxide is a red-brown gas that is very soluble in water. It has an unpleasant odor and is quite poisonous. When nitrogen dioxide is cooled, its brown color fades to a pale yellow.

$$\underset{\substack{\text{Nitrogen Dioxide}\\ \text{(Brown)}}}{2\,NO_2} \quad \leftrightarrows \quad \underset{\substack{\text{Nitrogen Tetroxide}\\ \text{(Yellow)}}}{N_2O_4}$$

The importance of nitrogen dioxide lies in the fact that it combines readily with water to form nitric acid.

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$$

This is the final step in the synthetic production of nitric acid. Nitrogen dioxide also acts as an oxidizing agent in the manufacture of sulfuric acid.

Nitrous oxide production technology can be licensed from the Sanghi Organization in Worli, India (www.sanghioverseas.com). Their technology is based on heating ammonium nitrate to 250°C and then purifying the resulting gas stream.

Research continues on the formation of nitrogen oxides. The high-temperature fixation of nitrogen as oxides remains an environmental problem rather than a commercially attractive process, as large quantities of nitrogen oxides are produced by fixation in high-temperature combustion processes such as power plants, automobile engines, and home furnaces. The U.S. EPA promulgated regulations in 2000 (NOx SIP Call) that require several states in the eastern United States to reduce their NOx emissions by a combined total of 35 to 40 percent by 2005 (see www.epa.gov/ttn/otag).

Ammonia

Ammonia was prepared by the alchemists by distilling leather scraps, hoof, horns, and other animal refuse. Because they found that the best ammonia was obtained by distilling deer antlers, the alchemists called ammonia "Spirits of Hartshorn."[7] Nature forms ammonia by decomposition of proteins. The odor of ammonia can often be detected around manure piles and other decaying organic matter.

A process for synthesizing ammonia from nitrogen and hydrogen, using high temperatures and pressures and an iron-containing catalyst, was invented by Fritz Haber at BASF in 1908.[1] In 1909, C. Bosch of BASF built a pilot plant using an osmium-based catalyst, and in 1913 a larger plant was built in Germany.[9–14] The chemistry for this process is:

$$N_2 + 3\,H_2 \leftrightarrows 2\,NH_3$$

In 1883 the Mond gas process produced ammonia by gasifying coal at a relatively low temperature by using a mixture of air and steam.[1] It was invented primarily to produce ammonia that was needed for the Solvay process that makes sodium carbonate.[29, 30]

Some other processes that have been used to make ammonia are:

- The Casale ammonia process in Switzerland in 1921.[1,12,19]
- The high-pressure Claude–Casale ammonia synthesis process in the 1920s.[1,12,20,21]
- The Fauser process in Italy in 1924.[12]
- The Mont Cenis process that was similar to the Haber–Bosch process except that it used coke-oven gas.[1] It was started up in The Netherlands in 1929.[31,32]
- The Braun process is a variation on the classic ammonia synthesis process in which the synthesis gas is purified cryogenically.[1] It has been widely used since the mid-1960s.[18]
- The AMV process for making ammonia was invented by ICI and announced in

1982.[1] It is described in References 15–17.

- The LCA (**L**eading **C**oncept **A**mmonia) is essentially a simplified form of the standard ammonia synthesis process that is more suitable for smaller plants. It is described in References 1, 26, 27, and 29.
- The BYAS (**By**pass **A**mmonia **S**ynthesis) process can be used for economical expansion of existing ammonia synthesis plants. It is described in Reference 1.
- The KAAP (**K**ellogg **A**dvanced **A**mmonia **p**rocess) process is the first high-pressure ammonia synthesis process that makes ammonia from nitrogen and hydrogen without the aid of an iron-containing catalyst.[1] It is described in References 22–25.

Ammonia and some of its salts and derivatives are used as fertilizers. Ammonia also is a very important building block for many other chemical commodities as shown in Fig. 22.1.

NITROGEN CONSUMPTION

The demand for nitrogen in a chemically fixed form (as opposed to elemental nitrogen gas) drives a huge international industry that encompasses the production of many nitrogen products. Nitrogen products had a total annual commercial value on the order of $50 billion in 1996. The cornerstone of this industry is ammonia. Virtually all ammonia is produced in anhydrous form via the Haber process. Anhydrous ammonia is the basic raw material in the manufacture of fertilizers, livestock feeds, commercial and military explosives, polymer intermediates, and miscella- neous chemicals.[35]

On a worldwide basis, nitrogen fertilizer consumption accounts for more than 85 percent of the total nitrogen industry. In the United States, with its significant industrial markets, fertilizer use accounts for only approximately 80 percent of total nitrogen consumption.[35] About 97 percent of nitrogen fertilizers are derived from synthetically produced ammonia. The rest are produced as byproduct ammonium sulphate from caprolactam processes, acrylonitrile processes, metal refining operations, and small quantities of natural nitrates, especially from Chile.[35] Ammonia is the starting material for six primary nitrogen fertilizer products: urea, ammonium nitrate, ammonium phosphates, ammonium sulfate, nitric acid, and nitrogen solutions.[36]

Up through the 1960s, the development of the nitrogen industry took place in the developed countries of Western Europe, North America, and Japan. However, in the 1970s and early 1980s, the construction of new plants shifted to the gas-rich countries of the Caribbean and Middle East. Additional plants were also built in some large consuming countries such as China, India, Indonesia, and Pakistan. At the same time, many plant closures occurred in Western Europe and Japan. Western European share fell from 20 percent in 1980/81 to 11 percent in 1997/98. In 1980/81 the developing countries accounted for 31 percent of nitrogen fertilizer production. By 1997/98 their share had increased to 55 percent[36] (see Fig. 22.2). The main regions that produced nitrogen fertilizers in 1997/98 are summarized in Table 22.2. Although at least 60 countries produce urea, over one third of the world's production is in just two countries: China and India.[36]

World ammonia capacity increased by nearly 14 percent from 1984 to 1996 and capacity for urea, the primary downstream nitrogen product, increased by 45 percent. The increases were due primarily to (1) a desire by some major importing countries to become more self-sufficient and (2) the construction of export-oriented capacity in the Middle East and in the former Soviet Union. Ammonium nitrate capacity declined by 2 percent from 1984 to 1996 and ammonium sulfate capacity declined by 8 percent.[35] Ammonium phosphate capacity increased by 9 percent during this time.

In the future developing nations are expected to continue to account for most of the increases in ammonia and urea capacity. Ammonia capacity is expected to increase by about 13.5 million tonnes and urea capacity

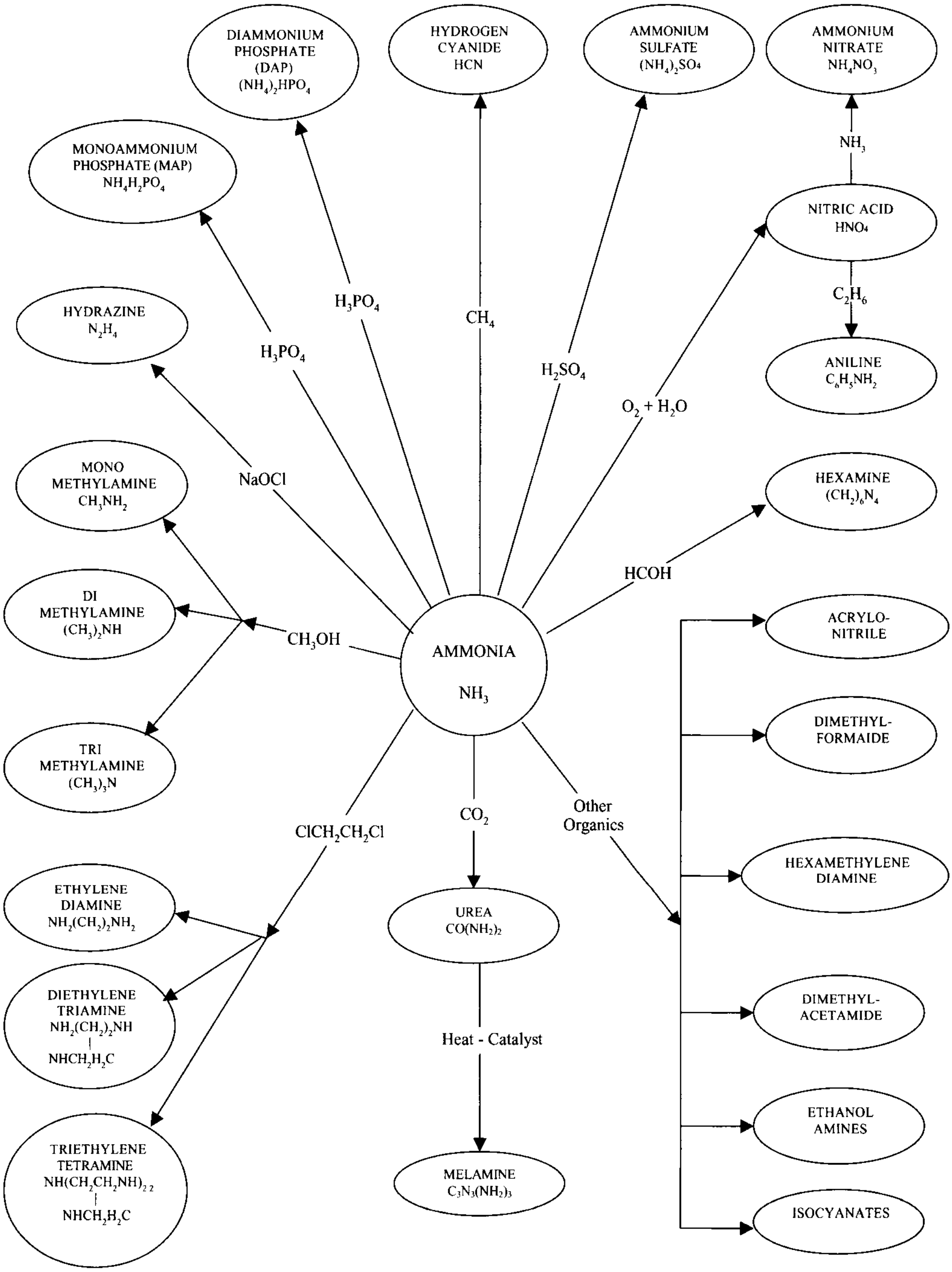

Fig. 22.1. Synthetic nitrogen products.

by about 15 million tonnes between 1999 and 2004. The availability of relatively low-cost feedstock (usually natural gas) will be a major determinant as to where this new capacity is installed.[35,148]

The apparent consumption of ammonia increased by about 15 percent between 1984 and 1996, and the apparent consumption of urea increased by about 54 percent. The developing countries are largely responsible for the increased consumption.

In 2002, urea accounted for almost 61 percent of worldwide consumption of the four major downstream nitrogen products. World

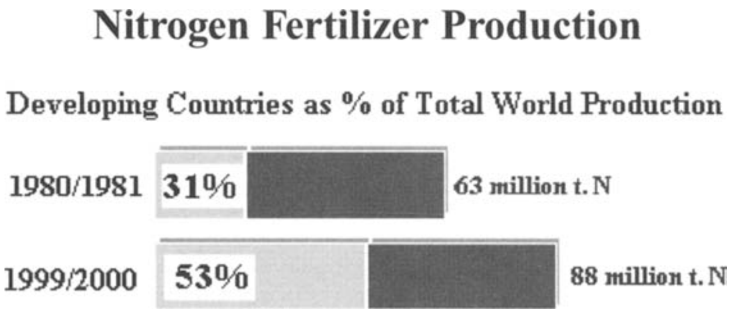

Fig. 22.2. Nitrogen fertilizer production 1980/81 and 1999/2000.[36] (Reproduced by permission of the International Fertilizer Industry Association, IFA.)

TABLE 22.2 Main Producing Regions for Nitrogen Fertilizers

Region	*% of World Production*
China	23
North America	18
South Asia	15
Western Europe	11
Former Soviet Union (FSU)	10
Other Countries	7
Central Europe	5
Middle East	5
Indonesia and Japan	4
Mexico and the Caribbean	2

urea consumption is forecast to increase at an average annual rate of 2.4 percent between 1999 and 2004. Only ammonium phosphate consumption, at 4.3 percent per year, is expected to grow more rapidly.[35,36]

Although world fertilizer consumption grew substantially between 1984 and 1996, it actually peaked at 79.6 million tonnes of nitrogen in 1989 and declined through 1994 because of a sharp drop in fertilizer consumption in Eastern Europe, the Former Soviet Union (FSU), and Western Europe. Total world nitrogen fertilizer consumption resumed its long-term upward growth trend in 1995, and substantial growth is expected.[35] Japan is one of the few countries where the use of slow-release fertilizers is developing on field crops, especially in crops grown in paddies.[36]

Estimates of world industrial nitrogen consumption by region show that the four largest markets in 1984 were North America, Socialist Asia, Western Europe, and the Former Soviet Union.[35] By 1996 South Asia had replaced the FSU as one of the four largest markets.

Trade is an important component of the world nitrogen industry, and trade in each of the nitrogen products analyzed (ammonia, urea, ammonium nitrate, ammonium sulfate, and ammonium phosphates) increased substantially between 1986 and 1998. The percentage of production that is traded internationally varies from 10 percent for ammonia up to 40 percent for ammonium phosphates.[35]

ENVIRONMENTAL ISSUES

Since 1980 the nitrogen industry has made major improvements in environmental controls to reduce atmospheric emissions and liquid effluents.

The primary pollution problem in nitric acid manufacture is the abatement of nitrogen oxides (NO_X) in tail gases. In the United States, gaseous emissions from newly constructed nitric acid plants must be limited to 1.5 kilograms of NO_X per tonne of nitric acid (100% basis) produced, with a maximum stack opacity of 10 percent. Modern acid towers, with extended sections, can reduce NO_X emissions to less than 200 parts per million.[35]

The most important environmental concern about the use of nitrogen fertilizers is the loss of nitrogen to groundwater. This is having a significant impact on the use of nitrogen fertilizers, particularly in Western Europe. There is a lesser but still significant concern about nitrate levels in groundwater in the United States. Other than this runoff aspect, which most seriously affects ammonium nitrate, no serious environmental concerns exist with the use of the major nitrogen products as fertilizer materials.[35]

Environmental issues play an important role in the ammonium sulfate industry. This is because a significant portion of the world's ammonium sulfate production is the direct result of the necessity to remove sulfur dioxide from stack gases at various metal smelting and refining operations in order to conform to government regulations on sulfur dioxide emissions. A large potential source of additional byproduct ammonium sulfate production is sulfur dioxide recovery from coal-fired electrical generating stations. It is estimated that a 500 megawatt plant that is burning 3.5 percent sulfur coal could generate 250 thousand tonnes of ammonium sulfate per year.[35] This is equivalent to ~7 percent of the total worldwide ammonium sulfate production in 2000.

AMMONIA PRODUCTION

Because no economical nitrogen fixation process that starts with nitrogen oxides has been discovered, ammonia has developed into the most important building block for synthetic nitrogen products. Anhydrous ammonia is produced in about 80 countries.[36]

In the USA only 80 percent of the ammonia is used to make fertilizers. Chemical intermediates (such as acrylonitrile and caprolactam) account for 19 percent of the ammonia use and the remaining 1 percent is used in pulp and paper, metals, and refrigeration applications.[37]

Worldwide, ammonia capacity grew from 119 million tonnes in 1980 to a peak of 141 million tonnes in 1989.[36] Ammonia demand grew at a rate of 3.2 percent per year from 1993 to 1998, but the growth rate is expected to slow to 0.5 percent per year from 1998 through 2002.[37] U.S. capacity declined in the 1970s, and it continued to decline during the 1990s by 5 to 10 percent to about 13 million tonnes per year. During the 1990s U.S. ammonia capacity was between 13 and 14 million tonnes per year with operating rates over 95 percent. The U.S. capacity is forecast to reach 15 million tonnes per year by 2002, and worldwide ammonia capacity is forecast to grow at over 2 percent per year and exceed 140 million tonnes per year by 2002.[35]

By 2002 30 percent of North American ammonia production was curtailed, and in 2004 four more plants were shut down. Although periodic downtimes of plants are not uncommon, the combination of import competition that depressed prices and very high feedstock costs in many industrialized countries has resulted in shutdowns of high-cost plants which resulted in a decline in world capacity.[38,57,299]

In 1998 most of the ammonia production capacity was located in the regions shown in Table 22.3.[36,57]

TABLE 22.3 Ammonia Capacity by Region (thousands of metric tons *N*)

	1987		*1998*	*1999*		*2005*	
Region	*Quantity*	*Share (%)*	*Share*	*Quantity*	*Share (%)*	*Capacity*	*Share (%)*
China	18,675	16.9	22	30,450	23.6	33,460	24.6
Former Soviet Union	21,725	19.7	17	19,340	15.0	18,455	13.6
North America	16,390	14.8	15	18,955	14.7	18,410	13.6
South Asia	8,935	8.1	12	15,750	12.2	16,705	12.3
Western Europe	15,635	14.1	9	11,870	9.2	11,255	8.3
Middle East	4,100	3.7	7	5,950	4.6	7,795	5.7
Central Europe	9,830	8.9	6	7,560	5.9	6,820	5.0
Indonesia and Japan	5,800	5.3	4	7,725	6.0	8,340	6.1
Mexico and the Caribbean (including Venezuela)	5,705	5.2	3	6,415	5.0	8,265	6.1
Other Countries	3,700	3.4	5	4,790	3.7	6,330	4.7
Totals	110,495			128,805		135,835	

About 90 percent of world ammonia production is processed or used in the countries where it is produced. The remaining 10 percent of production enters international trade. The major net exporters in 1997 were Russia and Ukraine (43% of world exports), Trinidad (22%), and the Middle East (13%). The major net importers were the United States (43% of world imports) and Western Europe (26%).[36]

In the mid-1990s the ammonia industry accounted for about 5 percent of worldwide natural gas consumption. For economic and environmental reasons, natural gas is the feedstock of choice. However, processes for ammonia production can use a wide range of energy sources. For example, 60 percent of China's nitrogen fertilizer production is currently based on coal. At present natural gas is the most economic feedstock for the production of ammonia as shown in Table 22.4.[53]

All commercial ammonia manufacturing processes are based on the synthesis of ammonia from nitrogen and hydrogen. Thus the many processes are differentiated by the method of producing the hydrogen and nitrogen for the synthesis. Preparation of nitrogen can be by separation from air in a standard "air" plant. Or air can be fed to the ammonia unit where the oxygen is used to burn a portion of the hydrocarbon feed, leaving the nitrogen for ammonia synthesis. The latter is the dominant type. Most of the hydrogen for ammonia manufacture is prepared from hydrocarbon feeds.

Some physical properties of ammonia and densities of aqueous solutions of ammonia are given in Tables 22.5 and 22.6, respectively.

TABLE 22.4 Feedstock Economics for Ammonia Production: Relative Consumptions and Economics for Different Feedstocks

	Natural Gas	*Heavy Oil*	*Coal*
Energy consumption	1.0	1.3	1.7
Investment cost	1.0	1.4	2.4
Production cost	1.0	1.2	1.7

Source: EFMA. Reproduced by permission of European Fertilizer Manufacturers Association.

TABLE 22.5 Physical Properties of Ammonia

Property	*Value*
Molecular Weight	17.03
Boiling Point, °C	−33.35 @ 760 mm Hg
Freezing Point, °C	−77.7
Color	Colorless
Critical Temperature, °C	133.0
Critical Pressure, kPa (psi)	1,425 (1657)
Specific Heat. J/ kg K)	
0°C	2097.2
100°C	2226.2
200°C	2105.6
Heat of Formation of gas, ΔH, kJ/ kg mol, (Btu,/lb-mol)	
0°K	−39,222 (−16,862)
298°K	−46,222 (−19,872)
Solubility in Water, wt.%	
0°C	42.8
20°C	33.1
25°C	31.8
40°C	23.4
60°C	14.1
Specific Gravity[a]	
−40°C	0.690
0°C	0.639
40°C	0.580
Vapor Pressure, mm Hg	7,500 @ 25°C
Vapor Density	0.6 (Air = 1.0) at 0°C
Flammable Limits in Air, % by Volume	
Lower Explosion Limit (LEL)	15
Upper Explosion Limit (UEL)	28
Autoignition Temperature	651°C (1204°F)

[a] Anhydrous ammonia.

HYDROGEN PRODUCTION

Ammonia production is the single largest consumer of hydrogen for use in chemical manufacture. Hydrogen production is typically

TABLE 22.6 Densities of Aqueous Ammonia at 15°C

Ammonia, wt.%	*Density, g/liter*
8	0.970
16	0.947
32	0.889
50	0.832
75	0.733
100	0.618

integrated into the overall plant design, so most ammonia producers regard themselves as consumers of natural gas (or another feedstock) rather than hydrogen. Worldwide, a few ammonia plants have been located near byproduct sources of hydrogen. In the United States, Coastal Refining & Marketing, Inc. brought a new ammonia plant onstream in late 1997 in Freeport, Texas using purchased pipeline hydrogen. Air Liquide America purifies 45 million standard cubic feet per day of byproduct hydrogen from Dow Chemical Company for pipeline delivery to Coastal's Freeport facility. In 2002 this was the only U.S. ammonia plant using purchased hydrogen.[40] Hydrogen requirements in the main world regions are shown in References 40 and 41and more details are given in Chapter 27 (Industrial Gases).

To help meet increased hydrogen requirements, a methodology has been developed for assessment of hydrogen sources that is based on an analogy with the problem of process heat recovery. A hydrogen surplus diagram allows the engineer to find the "hydrogen pinch" and to set targets for hydrogen recovery, hydrogen plant production, and import requirements. This method also gives insights into the effective use of hydrogen purification units. It has been shown that a purification unit should not be placed below the hydrogen pinch. Purifying gas above the pinch may have some benefits, but placing the purifier across the pinch is the best option.[43]

Hydrogen Pinch Technology has been applied commercially by several companies including AspenTech, BP-Amoco, Engineers India, Exxon, ICI, Linnhoff-March, M.W. Kellogg and UOP.[44,45]

Hydrogen is a nontoxic, colorless, odorless, and tasteless gas. It is the lightest and most abundant element (making up over 90% of the atoms in our universe), but it is present at only extremely low levels (0.1 ppm) as a pure element in the earth's atmosphere. More than 50 percent of the atoms in our environment are hydrogen.

Hydrogen is present in fossil fuels and water in sufficient amounts that it can be produced from these sources on a large scale by several different methods: (1) petrochemical processes, (2) coal-based chemical processes, and (3) electrochemical processes (electrolysis).

TABLE 22.7 World Hydrogen Production and Type of Manufacturing Process (in %)[46]

Process	*1974*	*1984*	*1988*
Cracking of crude oil	48	77	80
Cracking of natural gas	30		
Coal & coke gasification	16	18	16
Electrolysis	3	4	4
Miscellaneous processes	3	1	

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In Table 22.7, the percentage of hydrogen production is broken down by type of manufacturing process.[46]

In the petrochemical processes, both natural gas and crude oil fractions can be converted into synthesis gas using two basically different methods:[46]

- With the allothermal steam reforming method, catalytic cracking takes place in the presence of water vapor. The necessary heat is supplied from external sources.
- With the autothermal cracking process, heat for the thermal cracking is supplied by partial combustion of the feed. Water is used and carbon dioxide (CO_2) may be recycled to attain a desired CO/H_2 ratio.

The processes for the manufacture of synthesis gas were originally based on the gasification of coke from hard coal and low-temperature coke from brown coal by means of air and steam. After World War II, the easy-to-handle liquid and gaseous fossil fuels—oil and natural gas—were also employed as feedstocks. Their value lies in their high hydrogen content that produces higher molar ratios of hydrogen (H_2) to carbon monoxide (CO) in the synthesis gas (see Table 22.8). By using excess steam in the reforming of methane, the

TABLE 22.8 H_2/CO Molar Ratio in Synthesis Gas

Method of Manufacture	*H_2/CO Molar Ratio*
Oxygen-coke-steam	0.6
Air-coke-steam	0.9
Oxygen-coal-steam	1.0
Oxygen-fuel oil-steam	1.0
Propane-steam	1.33
Methane-oxygen	1.7
Oil-steam	2.1
Petroleum ether-steam	2.4
Methane-steam	3.0 to 5.0

H_2-to-CO molar ratio can be as high as 5.0 (see Table 22.8).

Selection of a process for hydrogen manufacture from hydrocarbons and coal therefore depends on: the raw material and its cost, the scale of operation, the purity of the synthesis gas to be produced, the pressure level of the natural gas feed, and the number and type of downstream processes that will consume the carbon monoxide and hydrogen.

Hydrogen is also manufactured industrially by direct electrolysis of H_2O, HF, and 22 to 25 percent hydrochloric acid (HCl). However, the hydrogen produced by electrolysis accounts for a small percentage of the total H_2 production (see Table 22.7). In contrast to the steam reforming of hydrocarbons, the hydrogen from electrolysis is very pure (>99 vol%) which eliminates the costly purification steps.

Manufacturing Processes

Hydrogen is manufactured by four principal processes (see Table 22.7 and Fig. 22.3); steam reforming of natural gas; partial combustion of natural gas or oil with pure oxygen; gasification of coal or coke with air (or oxygen) and steam; and recovery of byproduct hydrogen from petroleum refinery gases or other cracking operations. Small amounts of hydrogen also are manufactured by electrolysis. These processes are discussed in more detail in the following sections.

Reforming. Reforming is a general name for the reaction of a hydrocarbon, such as methane, with water and/or carbon dioxide, to produce a mixture of carbon monoxide and hydrogen. The different reforming processes can be divided into the following types.[53]

- Conventional steam reforming with a fired primary reformer and stoichiometric air secondary reforming (stoichiometric H/N ratio)
- Steam reforming with mild conditions in a fired primary reformer and excess air secondary reforming (under-stoichiometric H/N ratio)
- Heat exchange autothermal reforming, with a process gas heated steam reformer (heat exchange reformer) and a separate secondary reformer, or in a combined autothermal reformer, using excess or enriched air (under-stoichiometric or stoichiometric H/N ratio)

The typical steps in the reforming process and how they tie into ammonia production are shown in Fig. 22.4.

If water is used, the process is called steam reforming or steam cracking. The reforming reaction (22-1) is endothermic and requires a catalyst[1].

$$CH_4 + H_2O \rightleftarrows 3\,H_2 + CO \qquad (22\text{-}1)$$
$$\Delta H = +49 \text{ kcal/mol or } 205 \text{ kJ/mol}$$

Other reactions that proceed at the same time as the reforming reaction are:[46]

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad (22\text{-}2a)$$
$$\Delta H = -10 \text{ kcal/mol or } 42 \text{ kJ/mol}$$

(The Homogenous Water Gas Reaction or Water Gas Shift)

$$CH_4 \rightleftarrows 2\,H_2 + C \qquad (22\text{-}3)$$
$$\Delta H = +17.9 \text{ kcal/mol or } 75 \text{ kJ/mol}$$

$$2\,CO \rightleftarrows CO_2 + C$$
Boudouard Reaction (22-4)
$$\Delta H = -41.4 \text{ kcal/mol or } 173 \text{ kJ/mol}$$

The equilibrium composition of the synthesis gas depends on: the steam-to-gas ratio entering the reactor, the reaction temperature, the reaction pressure, and the quantity of inerts in the reaction mixture. To avoid carbon formation as indicated by reactions 22-3 and 22-4, the steam-to-gas ratio must be kept high

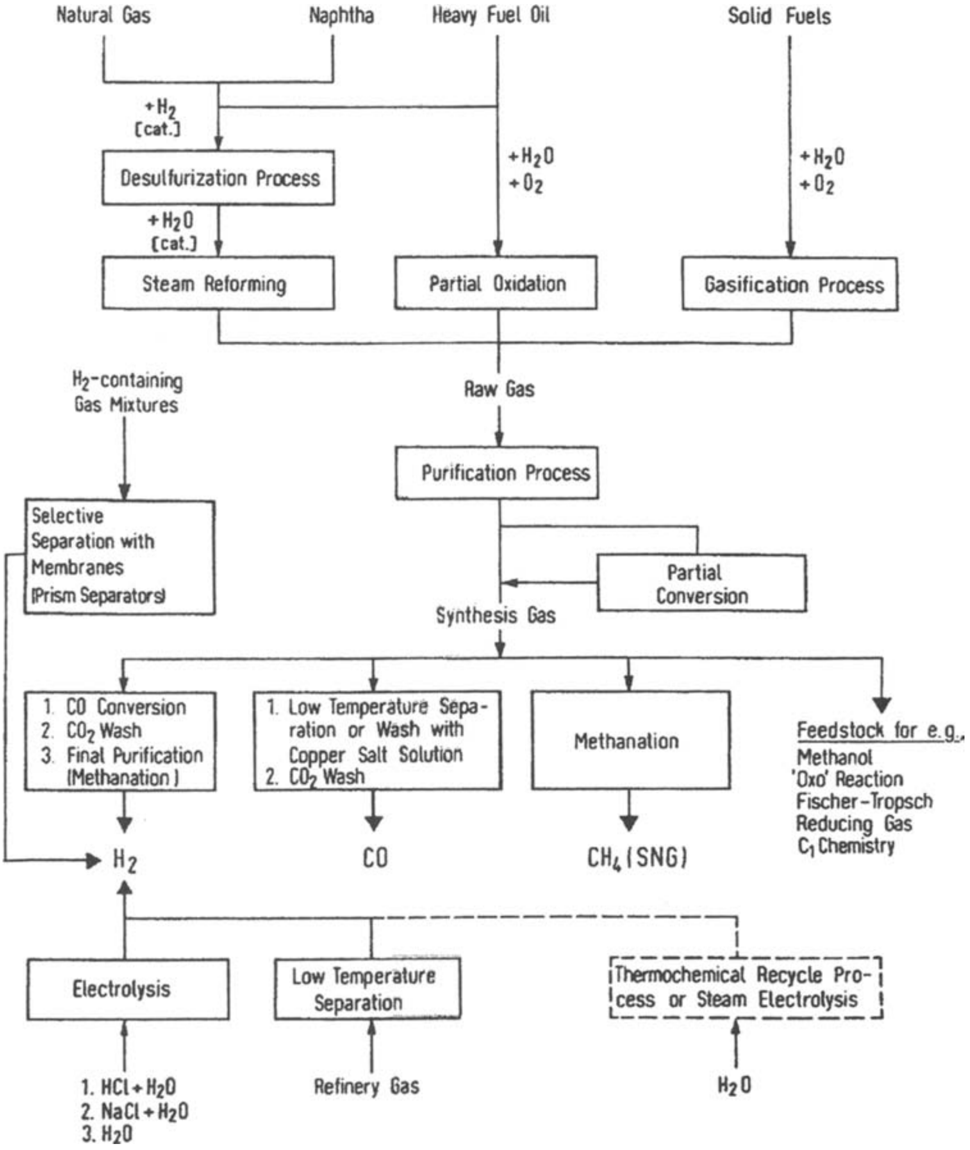


Fig. 22.3. Hydrogen manufacturing process steps.[46] (Copyright by VCH Publishers and reproduced by permission of the copyright owner.)

enough to favor the reforming reaction (22-1) and the water gas shift reaction (22-2a) over the reactions that form carbon.

In 2003 Synetix, a subsidiary of Johnson Matthey, offered for license a large-scale steam reforming process. In this process hydrocarbon feeds with boiling points up to 200°C can be treated. The process consists of three steps: feed pretreatment, catalytic reforming, and reforming of residual methane. The advantage of the Synetix process is that no soot forms, even with liquid crude oil fractions as feed. This makes catalyst regeneration unnecessary.[46] Because of these advantages, the Synetix technology is used in over 400 reformers in over 30 countries. When North Sea gas and other natural gas reserves around the world were developed, the use of naphtha as a feed stock declined and the need for this technology was reduced.

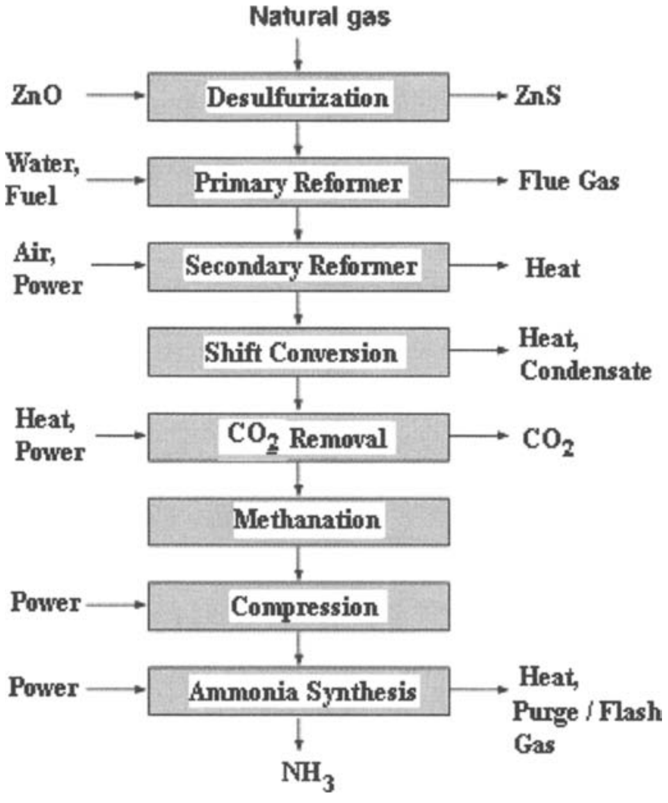


Fig. 22.4. Block diagram of the steam/air reforming process.[53] (Used by permission of European Fertilizer Manufacturers Association.)

Feed Pretreatment

The catalysts used in the steam reforming process are poisoned by trace components in the hydrocarbon feed – particularly sulfur, chlorine, and metal compounds. The best way to remove sulfur compounds is to convert the organic sulfur species to H_2S over a hydrodesulfurization catalyst. The next step is sulfur removal with an absorbent. The same catalyst can usually convert any organochloride species to give HCl and also act as an absorbent for most problematic metal species. A second absorbent is used for chloride removal.[70]

Prereformer

A prereformer partially completes the steam reforming reactions upstream of the main steam reformer at a much lower temperature by using a more active catalyst. One advantage in new plant designs is that the conventional steam reformer furnace can be smaller.[70] All the ethane, the heavier hydrocarbons, and some of the methane are decomposed endothermically and at temperatures below those in the main reformer. The product gas from the prereformer is an equilibrium mixture of hydrogen, methane, steam, and carbon oxides. The prereformer can reduce fuel consumption by up to 10 percent and increase throughput by up to 15 percent.[71]

Another advantage is that a prereformer may be preferred in flowsheets for processing heavier feedstocks. The prereformer converts heavier hydrocarbons to methane before they are fed to the steam reformer. This allows the steam reformer to be designed for methane service. The prereforming catalysts are very sensitive to poisons. Therefore a good feed purification section is essential.[70]

Reformers

Steam reforming refers to the endothermic catalytic conversion of light hydrocarbons in the presence of steam. Catalytic reforming takes place across a nickel catalyst that is packed in tubes in a fired furnace (the "primary reformer"), and in the refractory-lined chamber reactor (the "secondary reformer"). This is where hot process air is added to introduce nitrogen into the process. Typical reaction conditions in the primary reformer are 700°C to 830°C and 15 to 40 bar. Additional details about the primary reformer can be found in Reference 46. A portion of the primary reformer discharge gas is burned in the secondary reformer with added air or oxygen to give a gas mixture at a temperature of over 1200°C. Almost all of the methane reacts with steam at this temperature. The methane concentration depends upon the pressure, the temperature, and the quantity of nitrogen and steam present.[46]

Reformer Catalysts

The secondary reformer catalyst does not need to be as active as that in the primary reformer. The usual nickel concentration is about 15 percent in the secondary reformer and 25 percent in the primary reformer catalyst.

The steam reforming catalyst selection depends on furnace design, feedstock types, and the operating conditions. The main categories of catalyst are for (1) light duty reforming, (2) intermediate duty reforming, and (3) heavy duty reforming. The light duty catalysts are for natural gas, refinery off-gas, and preformed feeds.[70]

Intermediate duty catalysts are for feeds with a significant content of components from ethanes up to liquid petroleum gas (LPG). Heavy duty catalysts are primarily for naphtha feeds that have even more tendency for carbon deposition.[70]

Silica and silica-bearing materials cannot be used with the shift catalyst. This is because the silica volatilizes and migrates from the hotter zone to lower temperature zones downstream. Usually it deposits on the waste heat boiler tubes after the secondary reformer.

Normally, the nickel oxide is reduced to nickel and water by the hydrogen that is produced in the operation. In some cases the reduced nickel can be reoxidized to nickel oxide when large amounts of steam and small amounts of H_2 are present:[47]

$$Ni + H_2O \rightleftarrows NiO + H_2 \qquad (22\text{-}5)$$

The addition of H_2 to the natural gas feed keeps the nickel in the reduced state, which makes it more active. Also, the hydrogen will retard the formation of nickel sulfide and prevent or minimize poisoning of the catalyst:

$$NiS + H_2 \rightleftarrows Ni + H_2S \qquad (22\text{-}6)$$

Carbon can also reduce the effectiveness of the catalyst. When conditions are favorable for the following reactions, carbon will deposit on the catalyst:

$$CH_4 \rightleftarrows 2\,H_2 + C$$
$$\Delta H = +17.9 \text{ kcal/mol or } 75 \text{ kJ/mol} \qquad (22\text{-}3)$$

$$2\,CO \rightleftarrows CO_2 + C$$
$$\Delta H = -41.4 \text{ kcal/mol or } 173 \text{ kJ/mol} \qquad (22\text{-}4)$$

Thus, if insufficient steam is present, carbon will be deposited on the catalyst and reduce its effectiveness. Carbon will gasify with steam at 800°C or higher in the reformer:

$$C + H_2O \rightleftarrows H_2 + CO$$
$$\Delta H = +28 \text{ kcal/mol or } 119 \text{ kJ/mol} \qquad (22\text{-}2b)$$

Reformer operation and changes in operating rate should always be carried out in a way that ensures sufficient steam is over the catalyst. Thus, if the feed rate is to be increased, the steam rate should be increased first. Conversely, if the feed rate is to be decreased, the natural gas rate should be decreased first.

Reformer Materials of Construction

The primary reformer is a steam-hydrocarbon reforming tubular furnace that is typically externally fired at 25 to 35 bar and 780°C to 820°C on the process side. From the 1950s through the 1960s SS 304, SS 310, SS 347, HK 40 alloy, and HP 25/35 modified alloys were used as tube materials. However these materials developed various operating problems as rates increased and longer service lives were needed for economical operation.[88]

HP microalloys were developed during the 1990s. The microalloys enhanced carburization resistance and improved high-temperature creep-rupture resistance.[88]

For reformer outlet manifolds, the normal metallurgy choice is a wrought type of Alloy 800 H. Hot reformed-gas transfer lines are usually refractory-lined with an interior of Alloy 800 sheathing.[88]

In the secondary reformer air is added to the process stream at operating conditions of 28 to 30 bar and 955°C to 1025°C. The refractory-lined vessel has an outer shell of a low-alloy steel containing 0.5 Mo. Metal dusting occurs in the secondary reformer outlet sections. With hot gases containing a high CO content, carbon will diffuse into the Fe–Cr–Ni alloy. This phenomenon can lead to local mechanical fracturing of surface layers and failures by pitting.[88]

Materials such as SS 304 and Alloy 800 are very susceptible to metal dusting in the range of 500°C to 800°C. Besides temperature, carbon activity (the CO/CO_2 ratio in the gas) and CO partial pressure also affect metal dusting. Severe attacks occur when the carbon activity is in the range of 3 to 10. Recirculating CO_2 into the primary reformer along with feedstock can maintain a low CO/CO_2 ratio and avoid the severity of this attack. By maintaining a high steam-to-hydrogen ratio in the gas, the metal dusting can also be minimized.[88]

Hydrogen embrittlement is another important corrosion problem that is encountered in reformed-gas pipelines. The Nelson curves list the operating limits that should be followed to avoid decarburization and fissuring of steel in hydrogen service.[88]

Waste Heat Recovery

The waste heat recovery system is associated with flue gas from the reformer furnace and process gas from the secondary reformer. It generates high-pressure steam in specially designed boilers. Proper material selections and stringent water quality control are two proactive loss-prevention methods.[88]

Hydrogen Production Costs and Capital Costs

The theoretical energy requirement per mole of hydrogen produced for the overall steam reforming process is 40.75 kJ/mole of hydrogen.[60] The capital cost for a 60 million SCF per day hydrogen plant, based on steam methane reforming technology is US$ 1.00 to US$ 1.50 per SCF of hydrogen per day.[164]

The cost for making hydrogen by steam reforming of natural gas depends primarily on the cost of natural gas. Several sources estimate the hydrogen production cost, excluding capital charges (in $US per million BTU of H_2), to be 150 percent of the natural gas cost (in $US per million BTU).[164,170,175]

Other Reforming Processes

The RKN process uses steam reforming to make hydrogen from hydrocarbon gases. This process was developed by Haldor Topsøe in the 1960s. By 1974, 24 plants based on this technology were operating.[2]

The SMART (**S**team **M**ethane **A**dvanced **R**eformer **T**echnology) process makes hydrogen by the steam reforming of methane, and it houses the catalyst in a proprietary heat exchanger. The process was developed by Mannesmann KTI in 1996, and the first installation was started up in Maryland in 1998.[2]

The ATR (**Aut**othermal **R**eforming) process makes CO-enriched syngas. It combines partial oxidation with adiabatic steam-reforming. It was developed in the late 1950s for ammonia and methanol synthesis, and then further developed in the 1990s by Haldor Topsøe.[2]

The CAR (**C**ombined **A**utothermal **R**eforming) process is used to make syngas from light hydrocarbons, and the heat is provided by partial oxidation in a section of the reactor. It was developed by Uhde and commercialized in Slovakia in 1991.[2]

The KRES (**K**ellogg **R**eforming **E**xchanger **S**ystem) is a reforming process that provides syngas to the KAAP process. The KAAP (**K**ellogg **A**dvanced **A**mmonia **P**rocess) process is a high-pressure process that makes ammonia from its elements and does not use an iron-containing catalyst. MW Kellogg developed the process in 1990, and Ocelot Ammonia installed the first plant in British Columbia, in 1994.[2] Another KRES plant started up in 2003 at an NH_3 plant owned by Liaotong in Liaoning Province, China.[171]

The **H**aldor **T**opsøe **C**onvection **R**eformer (HTCR) is a relatively small piece of equipment that combines the radiant and waste heat sections of the conventional reformer. It uses PSA (pressure swing absorption) to make 99.9 percent hydrogen purity. It is best for small and medium-sized hydrogen plants (500 to 10,000 Nm^3/hr).[75]

Reliability and Revamps

Some of the revisions to conventional reforming are listed below.

Decreased Firing in the Primary Reformer. Decreased heat supply in the primary reformer means that the process outlet temperature is lowered to about 700°C, the firing efficiency increases, and the size and cost of the primary reformer are reduced. The milder operating conditions prolong catalyst life, catalyst tube life, and outlet header service life.[53]

Increased Process Air Supply to the Secondary Reformer. Decreased heat supply in the primary reformer means that increased internal firing is necessary to achieve approximately the same degree of total reforming. A somewhat higher methane slip (and thus a lower secondary reformer outlet temperature) is acceptable and preferable in this type of process. This is because methane is removed in the final purification.[53]

The process air requirement is about 50 percent higher than in the conventional process. This means increased compression capacity and energy. The process air compressor is usually driven by a gas turbine with the exhaust gas from the turbine being used as combustion air in the primary reformer. Some excess steam is available for export when using a gas turbine.[53]

Reformer. Where an increase of 10 to 50 percent of existing steam reforming capacity is required, revamping is often more cost effective than a new plant or the purchase of hydrogen over the fence. In most revamps the reaction area is only slightly affected by operating rate, and existing reactors are often able to operate at increased rate. Existing heat exchangers are often adequate as capacity is increased. However, air coolers in a CO_2 removal unit often need to be modified by adding surface area or increasing fan horsepower.[86]

Separation equipment tends to have fixed limits and can be costly to change. However, more capacity can often be obtained by changing column internals or the solvent composition.[86]

Radiant Section. Changes in the radiant section can be difficult to justify based on capacity alone. However, if the radiant tubes are near the end of their useful life, an upgrade to this section may provide more capacity. Changes in metallurgy since the mid-1970s have allowed changes in radiant section operating conditions.

Time Period	*Tube Material*	*Operating Pressure (psig)*	*Operating Temperature (°F/°C)*
1970s	HK-40	300	1450/790
1980s	HP	325	1550/845
1990s	Microalloy	450	1575/855

The microalloy tubes allow increased flux rates and higher reformer outlet temperatures. This in turn can make it possible to reduce the steam-to-carbon ratio while the hydrogen purity remains the same.[86]

Convection Section. The effects on the reformer of increased gas flow and temperature are multiplied in the convection section because additional load is placed on convection coils, fans, and the steam system. These areas commonly limit the operating rate of the reformer. The tube supports also need to be considered because they are exposed to hot flue gas without the cooling effect of process fluids.[86]

One of the most effective reformer modifications is to use heat from the convection section to preheat radiant section feed. This will reduce radiant section heat load, reduce radiant section firing rate, and potentially unload other areas such as steam generation. This option has been used to increase capacity by 10 percent without increasing the arch temperature in the radiant section.[86]

Combustion Air Preheat. Combustion air preheat reduces the fluegas flow through the furnace which unloads the fans and the entire convection section. The best known option is to use heat exchange with fluegas. For new units this can have the advantage of very high efficiency because the heat sink is ambient air. Another option is the use of steam to preheat air. This option was used to obtain a 12 percent increase in capacity at the same fuel firing rate and combustion air flow. A third option is to use circulating boiler feedwater to preheat the air.[86]

Heat Exchange Autothermal Reforming. A new development in the late 1980s was heat exchange autothermal reforming. In this process the heat content of the secondary reformer gas is used in a primary reformer with a new design. This reformer is a gas-heated, heat exchange reformer rather than the conventional fired furnace design. Surplus air or oxygen-enriched air is required in the secondary reformer to meet the heat balance in this autothermal concept.[53]

Emissions to the atmosphere are reduced significantly by eliminating the fluegas from the primary reformer. NOx emissions may be reduced by 50 percent or more compared to conventional steam. The level of NOx reductions depends on the extent of auxiliary combustion in the plant.[53]

Two processes of this kind are in operation, and some others are at the pilot stage. As of 1999, single train capacities have been limited to 1000 tonnes per day or less,[53] and four plants had been installed that use Synetix Gas Heated Reformer (GHR) technology.[72]

Synetix developed a modified design of the GHR known as the Advanced GHR or AGHR. BHP Petroleum of Australia became the first operator of an AGHR in 1998. The key difference in the AGHR is that it uses a single-pass tube arrangement whereas the GHR uses a bayonet tube reformer. Based on the experience at BHP Petroleum, the AGHR design results in a reformer that is lower in cost, easier to operate, easier to fabricate, and allows scale-up to capacities in excess of current world-scale throughputs (see Fig. 22.5).[72]

A hydrogen plant based on steam reforming with PSA was installed in Venezuela at the Compagnia Hidrogeno de Paraguana (CHP) plant to supply hydrogen to a refinery. The plant produces 50 million SCFD of hydrogen at 99.5 percent purity and 400 psig. The plant is a joint venture between BOC and Foster Wheeler and was started up in September, 1997. This plant uses 4 percent less in total fuel for firing, and has an installed cost that is approximately 23 percent below that of other plants of the same size.[87]

Small-Scale Reforming

Small-scale reforming systems are being pursued by a number of companies developing fuel cell electrical generation systems for home and automotive fuel cell applications. Before these systems become affordable and simple enough to be used as home electrical system components, they may be cost effective for industrial hydrogen supply systems.[48]

Small-scale reforming systems are relatively complex because they need fuel and air-feed systems, the reformer, a hydrogen purification system, and various cooling and water processing ancillary systems to make it all work. The systems also have to employ a specific hydrocarbon that is available at a reasonable cost at a customer's location. These systems probably work best for customers with hydrogen consumption rates in the 1500 scf/hr to 10,000 scf/hr range. They

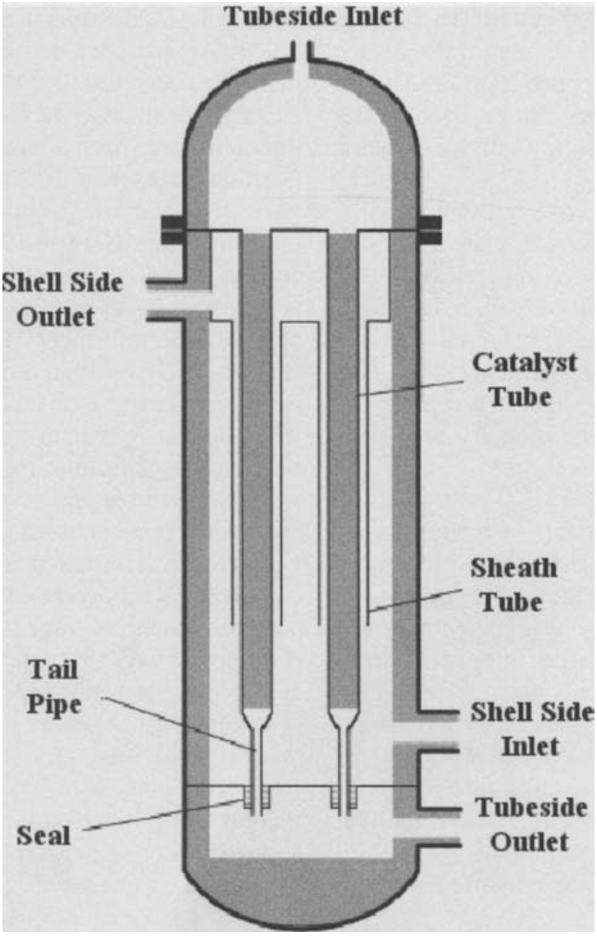


Fig. 22.5. Advanced Gas Heated Reformer (AGHR) from Synetix. (Reproduced by permission of Johnson Matthey Catalyst. Copyright Johnson Matthey PLC.)

are most cost effective when employed to produce hydrogen with a 99.9 percent or lower assay. As of 2007, small-scale reforming systems have not been commercialized. But they are in the advanced development stage.[48]

Technology Suppliers

Companies that provide technology to produce hydrogen via steam reforming are in the United States, Europe, and Japan. Many of these companies are listed in Reference 40.

Partial Oxidation. Noncatalytic partial oxidation processes (see Fig. 22.6) react hydrocarbons with gaseous oxygen at very high temperatures in a refractory-lined, pressurized reactor to produce synthesis gas. Although the process can handle a wide range of feedstocks, it was developed mainly to utilize the low-value "bottom of the barrel" and waste feedstocks that typically have high sulfur and high metal contents.[40]

Synthesis gas manufacture by partial oxidation or autothermal cracking of crude oil fractions was developed by BASF/Lurgi, Texaco and Hydrocarbon Research. Heat for the thermal cracking is supplied by partial combustion of the feed in the presence of water. Recycled CO_2 may also be added to the combustion to attain a desired CO/H_2 ratio. Shell developed a modified version (which does not

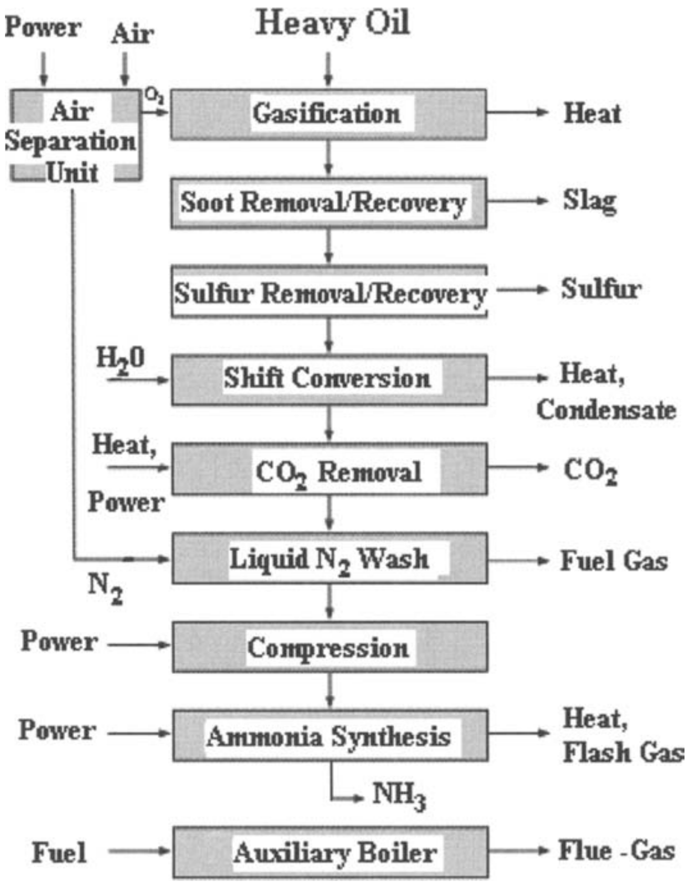


Fig. 22.6. Block diagram of partial oxidation process.[53] (Used by permission of the European Fertilizer Manufacturers Association.)

use a catalyst) that is referred to as the gasification process.[46]

As illustrated in Table 22.8, the H_2 to CO molar ratio in the synthesis gas product stream depends on the raw materials and the operating conditions. By burning natural gas with a limited quantity of oxygen, a synthesis gas that has a H_2 to CO molar ratio of approximately 2 to 1 can be produced:

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow 2 H_2 + CO \quad (22\text{-}7)$$

If steam is introduced into the reaction, the H_2 to CO molar ratio can be increased to over 2.0. This reaction is exothermic and can reach temperatures of 1200°C to 1500°C.[49] Typical operating costs are shown in Reference 40.

If fuel oil or crude oil is used as the raw material in partial combustion, care must be taken to provide for the removal of sulfur compounds and ash-containing materials in the crude oil (see Fig. 22.6). With crude-oil or fuel-oil partial combustion, the carbon content is much greater than in the case of natural gas, and special design considerations are necessary to produce a satisfactory gas.

Typical gas compositions from the partial combustion of various fuels are given in Table 22.9. The nitrogen that is needed to produce the desired H_2/N_2 ratio for ammonia production is usually introduced later in the processing sequence.

Partial Oxidation Processes

The MultiPurpose Gasification (MPG) process uses partial oxidation with oxygen to generate

TABLE 22.9 Product Gas Compositions from Various Feeds by Partial Combustion (percent by volume—dry)

Feedstocks & Gas Components	*Nat. Gas*	*Light Naphtha*	*Heavy Fuel Oil*	*Vacuum Resid.*	*Propane Asphalt*	*Coal*
Hydrogen	61.80	52.09	46.74	44.80	43.69	34.39
Carbon monoxide	33.75	42.59	48.14	49.52	50.09	44.22
Carbon dioxide	3.10	4.88	3.80	4.16	4.45	18.64
Methane	1.00	0.30	0.30	0.30	0.30	0.38
$N_2 + A$	0.27	0.13	0.23	0.18	0.30	0.68
H_2S	—	0.01	0.76	1.00	1.12	1.46
COS	—	—	0.03	0.04	0.05	0.10
NH_3	—	—	—	—	0.13	—
H_2/CO mol/mol	1.83	1.22	0.97	0.90	0.87	0.78

synthesis gas from different hydrocarbon feeds. These feeds include natural gas, tars, and other coal gasification residues, refinery residues, asphalts, coal and coke slurries, and chemical wastes. MPG is an updated development based on technology that Lurgi acquired in 1997 from SVZ.[179]

The MPG process preheats a gaseous feedstock with hot raw gas and an optional fired preheater. Preheat level and installation of the fired heater are determined by energy and cost optimization, which is based on the relative values of feed, fuel gas, and oxygen. Feed gas and oxygen enter the reactor with a minor amount of steam via the gas burner. Gasification occurs in a refractory-lined reactor at temperatures between 1200 and 1400°C.[179]

The noncatalytic partial oxidation of hydrocarbons by the Shell gasification process (SGP) takes place in a refractory-lined reactor that uses a specially designed burner. The oxidant is preheated and then mixed with steam before it is fed to the burner. The feedstock gasification conditions range from 1200 to 1400°C at a pressure of 50 to 70 bar, depending on the feedstock.[76,180]

The THGP (Texaco Hydrogen Generation Process) process makes pure, high-pressure hydrogen from various gaseous and light hydrocarbons. This process can be licensed from the Texaco Development Corporation.[1,51]

Technology Suppliers

The companies that license partial oxidation technology can be found in the United States and Europe. Some of these companies are listed in Reference 40.

Coal and Coke Gasification. In coal gasification the exothermic partial combustion of carbon and the endothermic water gas formation represent the actual gasification reactions:[46]

$$C + O_2 \rightleftarrows 2\,CO \quad \Delta H = -60 \text{ kcal/mol or } 246 \text{ kJ/mol} \qquad (22\text{-}8)$$

Partial Combustion

$$C + H_2O \rightleftarrows H_2 + CO \quad \Delta H = +28 \text{ kcal/mol or } 119 \text{ kJ/mol} \qquad (22\text{-}2b)$$

Heterogeneous Water Gas Reaction

Some other important reactions are:

$$C + CO_2 \rightleftarrows 2\,CO \quad \Delta H = +38 \text{ kcal/mol or } 162 \text{ kJ/mol} \qquad (22\text{-}9)$$

Boudouard Reaction

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad \Delta H = -10\ \text{kcal/mol or } 42\ \text{kJ/mol} \tag{22-2a}$$

Homogenous Water Gas Reaction (Water Gas Shift)

$$C + 2\,H_2 \rightleftarrows CH_4 \quad \Delta H = -21\ \text{kcal/mol or } 87\ \text{kJ/mol} \tag{22-10}$$

Hydrogenative Gasification

$$CO + 3\,H_2 \rightleftarrows H_2O + CH_4 \quad \Delta H = -49\ \text{kcal/mol or } 206\ \text{kJ/mol} \tag{22-11}$$

Methanation

Gasification processes can be characterized by the type of coal used and by the coal's physical and chemical properties.[46] Some processes use external heating and others use self-heating. The reactors may be fixed bed, fluidized bed, or entrained bed. The coal gasification processes are described in more detail under Coal Technology (Chapter 19).

Sasol (**S**uid-**A**frikaans **S**intetiese **O**lie) in South Africa has one of the largest coal gasification production operations in the world with the three plants.[1] One plant produces only chemicals and the other plants produce both liquid fuels and chemical feedstocks from coal. In 1994, Sasol's total ammonia capacity was over 500,000 tons per year.[54]

One of the first coal gasification plants in the United States was the Great Plains Synfuels plant that is operated by Dakota Gasification in Beulah, ND. This plant consumes over 5.5 million tonnes of coal per year and produces over 54 billion standard cubic feet (1.4 billion Nm^3) of natural gas, 365,000 tonnes per year of ammonia, 24 million gallons of liquid nitrogen per year (68 million kg or 150 million lb) plus several other chemicals.[89] (See www.dakota.com for more details.)

In 2000 Farmland Industries in Kansas started up a petroleum coke gasification plant to make ammonia. The plant uses Texaco's process to make 1000 tonnes per day of ammonia.[185, 186] In 2004 Rentech purchased an 830-tonne-per-day ammonia plant in Illinois and plans to convert it from natural gas to coal feedstock. Startup of the conversion is expected in 2007.[300]

Byproduct Hydrogen. Large volumes of byproduct hydrogen are generated from a variety of production processes. Some of these processes are listed in Reference 40. Some of the processes that can be used to obtain purified hydrogen are summarized below.

The HyTex (**Hy**drogen **Tex**aco) process makes pure hydrogen from waste gases in oil refineries in a three-step process.[1] The process was developed by Texaco and announced in 1991. The first commercial unit started up in Anacortes, WA in 1993.

Platforming operations make a gas that contains as much as 90 to 95 percent hydrogen. This gas is usually purified by low-temperature fractionation or washing with liquid nitrogen.

Kvaerner Oil & Gas, Norway, has introduced a process for manufacturing carbon black that generates substantial quantities of byproduct hydrogen. In 1998 the process was installed in Montreal, Québec (Canada) to produce 20,000 tonnes of carbon black and 50 million Nm^3 per year (5.2 million standard cubic feet per day) of hydrogen. The process appears to be economic only when the carbon black can also be sold as an end product.[40]

Air Products and Chemicals, Inc. has been selected to supply a hydrocarbon and nitrogen recovery system for a new polyethylene manufacturing plant in Baytown, TX. The plant will be owned by Chevron Phillips Chemical Company and Solvay Polymers, Inc. The recovery system uses partial condensation in conjunction with Air Products' pressure swing adsorption technology to recover hydrocarbons in the polyolefin plants, and recycle nitrogen with a purity of greater than 99 percent.[55]

A few ammonia plants have been located where a hydrogen off-gas stream is available from a nearby methanol or ethylene operation (e.g., Canadian plants at Kitimat, BC and Joffre, Alberta). The capital cost of such a plant is about 50 percent of the cost of a conventional plant of similar capacity because only the synthesis portion of the plant is required. However, byproduct carbon dioxide is not produced and downstream urea production is therefore not possible.[56]

Electrolysis. Electrolytic hydrogen production yields the highest-purity hydrogen (up to 99.999%), benefits from widespread raw materials availability (electricity and water), boasts simple system architecture, and can be scaled economically to serve applications ranging from the smallest hydrogen uses to the larger-volume uses. The main disadvantage of water electrolysis is that electricity is an expensive "fuel". As a result the technology generally is practical only for systems with hydrogen requirements of 2000 SCF per hour and less.[48]

By 2002 several manufacturers had introduced advanced water electrolysis systems that are standardized, compact in size, need minimal operator intervention, and require little maintenance. New cell designs, materials of construction, standardized designs, and manufacturing techniques have enabled manufacturers to decrease the fixed costs of electrolysis technology. In addition, these new systems operate automatically and require very little maintenance.[48,58]

Developing regions are the largest market for electrolysis systems. Electrolysis currently accounts for a very small portion of the hydrogen generated in developed countries that have a commercial hydrogen infrastructure. However, electrolysis can be economic for small-scale generation in areas with inexpensive electricity, and a few plants still produce hydrogen for small-volume ammonia production.[57] In 1997, Messer-MG Industries announced two hydrogen gas plants based on water electrolysis in the United States. In Canada, a portion of the capacity installed at HydrogenAl's merchant hydrogen plant in Québec is based on electrolytic cells.[40] Some of the companies that offer electrolysis technology are listed in Reference 40.

Other Processes.[1] The Hypro process makes hydrogen by catalytically decomposing hydrocarbons to carbon and hydrogen. The carbon is burned to provide the heat for the reaction. This process was developed by UOP.

The Lane process makes hydrogen by passing steam over sponge iron at approximately 650°C. The iron is converted to magnetite.

The MRH (**M**ethanol **R**eformer **H**ydrogen) process for generating hydrogen from methanol and separating it by PSA was developed by the Marutani CPE Company.

The Proximol process makes hydrogen by reforming methanol. This technology is offered by Lurgi.

The SBA-HT (**S**ociété **B**elge de l' **A**zote-**H**aldor **T**opsøe) process is a combination of both steam reforming and partial oxidation. The process converts liquid petroleum gas (LPG) to syngas that is rich in hydrogen. This process was operated in France and Belgium in the 1960s.

New Developments. Several research organizations are developing low-cost methods of hydrogen production. Much of this work is sponsored by the U.S. Department of Energy. Some of the research programs can be found in Reference 59.

The ITM Syngas process involves the direct conversion of methane to synthesis gas (see Fig. 22.7). The process utilizes a mixed, conducting ceramic membrane and partial oxidation to produce the synthesis gas.[40] The goal of this advanced reformer technology is to reduce the cost of hydrogen production by over 25 percent.[59,79]

Two projects were announced in the late 1990s to develop the ITM process and another related technology. Air Products will lead an eight-year, US$ 90 million research project that is supposed to culminate in the construction in 2005 of a 500 million SCFD ITM process development unit.[40] A separate

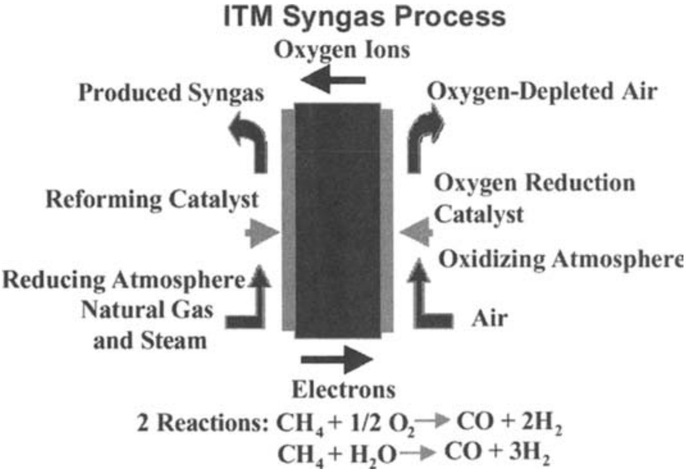


Fig. 22.7. ITM syngas process.

Oxygen Transport Membrane (OTM) Syngas alliance was formed in 1997 to develop ceramic membrane technology for conversion of natural gas to synthesis gas.[190]

Another process is the CO_2-free production of hydrogen via thermocatalytic decomposition of hydrocarbon fuels. The process involves a single-step decomposition of hydrocarbons over carbon catalysts in an air- and water-free environment. Preliminary assessments of the process indicated that hydrogen could be produced at a cost of US$ 5.00 per million BTU (if carbon sold at US$ 100/ton). This production cost is less than that for a steam reforming process coupled with CO_2 sequestration.[60]

Some additional new developments in hydrogen production are summarized below.

NGK Insulators of Japan received US. Patent 5,741,474 in 1998 for a Process for Production of High Purity Hydrogen. This process is a combination of reforming, partial oxidation, and membrane separation.

Northwest Power Systems obtained U.S. Patent 5,997,594 in 1999 for a Steam Reformer with Internal Hydrogen Purification.

BP and Kvaerner Process are finalizing the demonstration of their Compact Reformer Technology in 2001. This technology involves the integration of combustion, heat transfer, and catalytic reaction within a simple tubular module.[90]

Battelle Pacific Northwest National Laboratories are developing microreactors that produce synthesis gas. These reactors can be mass-produced to yield efficient, compact, and cost-effective systems.[61]

A related effort is FORSiM (**F**ast **O**xidation **R**eaction in **Si**-technology-based **M**icroreactors) which is funded by the Dutch Technology Foundation and is a cooperative venture between the University of Twente and the Technical University of Eindhoven. The objective of this work is to build and operate the first microreactor for catalytic partial oxidation for small-scale and on-demand hydrogen production.[61]

Initial Purification of Synthesis Gas

Synthesis gas from the gasification of fossil fuels is contaminated by several gaseous compounds that would affect its further use in different ways. The purification steps depend on the type of syngas process and the feedstock. Table 22.9 illustrates how the synthesis gas stream can vary with different feedstocks. Figure 22.8 illustrates the different process steps that may occur before ammonia synthesis takes place.[74]

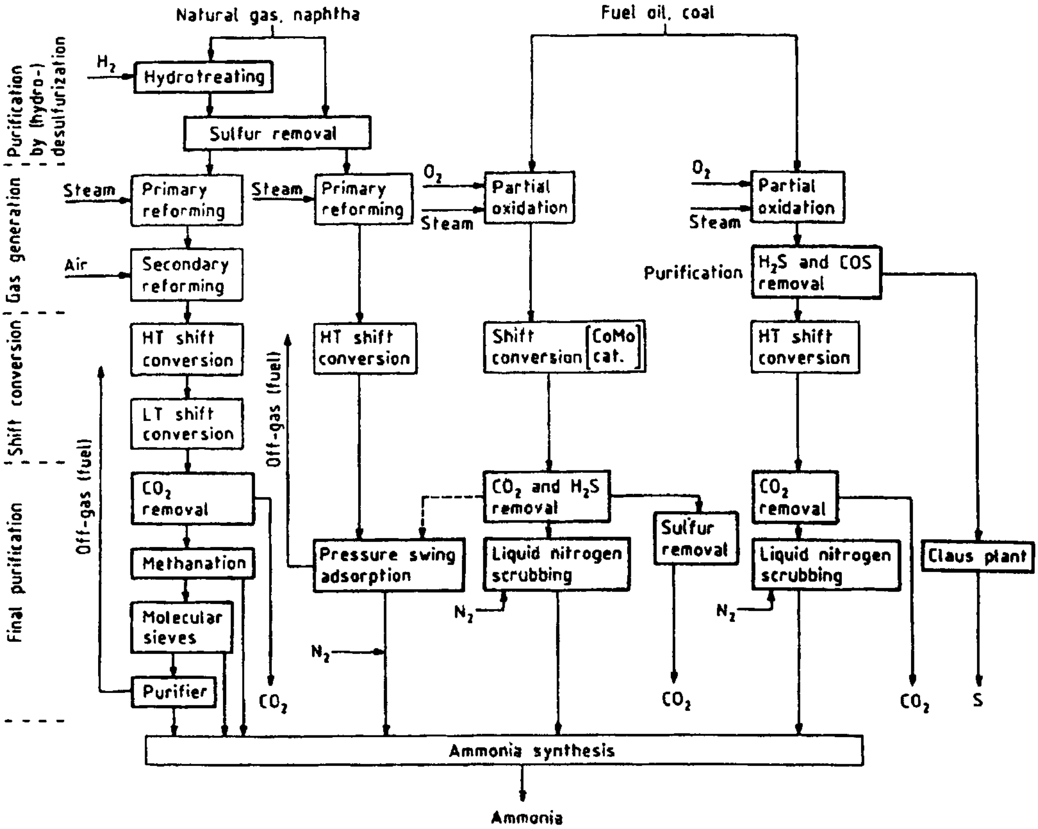


Fig. 22.8. Alternative process steps for generation and purification of synthesis gas. (Courtesy of Wiley-VCH. Bakemeier, H., Huberich, T., et al.: "Ammonia" in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 2, VCH Verlagsgesellschaft, Weinheim 1985, pp. 143–242.

If sulfur is present as H_2S or COS, it is a poison for many catalysts and will partly or completely inhibit the catalyst activity.[46] Carbon monoxide (CO) and carbon dioxide (CO_2) can poison the ammonia synthesis catalyst so both of these compounds must be removed.[53]

After the sulfur is removed, most traditional ammonia processes have employed the purification steps that are shown in Figs. 22.4 and 22.6. However, ammonia plants have been built that use hydrogen purification via PSA, membrane separation with polymeric membranes, and cryogenic separation. PSA achieves the greatest product purities (about 99.999% pure hydrogen), but it is capital-intensive. Polymeric membranes are the least capital-intensive, but they achieve the lowest purity (about 96 to 98%). In 1998 PSA was considered the standard process for high-purity hydrogen recovery from raw synthesis gas. It has replaced the traditional steps of the shift conversion of carbon monoxide followed by carbon dioxide removal by absorption and then final purification by methanation. Characteristics of these three purification technologies are outlined in Table 22.10.[40]

Purification with PSA and Polymeric Membranes. The PSA process is based on the selective adsorption of gaseous compounds on a fixed bed of solid adsorbent in a series of identical adsorption beds. The adsorbent is an active carbon or a carbon-molecular sieve. Each bed undergoes a

TABLE 22.10 Hydrogen Recovery Technology Characteristics[40,64]

Characteristic	*Membrane*	*Absorption*	*Cryogenics*
Hydrogen purity (%)	< 95	99.9+	95–99
Hydrogen recovery (%)	< 90	75–90	90–98
Hydrogen product pressure	< Feed pressure	Feed pressure	Variable
Byproducts available	No	No	Yes
Feed pressure (psig)	250 to 1800		250 to 500

repetitive cycle of adsorption and regeneration steps.[161,193] PSA provides the hydrogen at about the same pressure as the feed, but recoveries are typically lower than from other technologies.[170]

The first purification plant that used PSA was developed by Union Carbide Corporation (UCC) and was built at the Yokkaichi Plant of Mitsubishi Petrochemical Industries in 1971.[4] The process is now licensed by UOP, and more than 400 units were operating worldwide in 1992.[1]

The HYSEC Process was developed by Mitsubishi Kakoki K. and Kansai Coke & Chemicals. It has basically the same PSA unit as the UCC Process. After the main PSA beds, trace amounts of remaining oxygen are removed by a deoxo catalytic converter followed by a zeolitic dehumidifier.[4]

The LO-FIN (**L**ast **O**ut – **F**irst **In**) includes a unique gas-retaining vessel that preserves the concentration gradient in one stream before using it to repressurize another bed. This process was jointly developed by Toyo Engineering and Essex Corporation.[4]

The Sumitomo-BF PSA process uses carbon molecular sieves (CMS) as the selective adsorbent.[4]

Monsanto and Ube (Japan) developed membrane processes for purification of hydrogen gas mixtures. This process is based on the selective diffusion of hydrogen through semi-permeable membranes in the form of hollow fibers. The Monsanto PRISM® separator process (owned by Air Products as of 2004) uses a polysulfone fiber whereas Ube uses an aromatic polyimide fiber.[46]

Conventional polymeric hydrogen separation membranes yield hydrogen at low pressure. Air Products has demonstrated a carbon membrane on an alumina support that removes hydrocarbons from hydrogen/hydrocarbon mixtures and leaves the hydrogen at high pressure.[40]

For ultra-high-purity hydrogen (up to 99.9999% pure), high-pressure gas passes over heated palladium membranes. Johnson Matthey is believed to be the leading supplier of these membranes. In 1996, Generex (Tryon, NC) licensed newly developed palladium membrane technology from Los Alamos National Laboratories. In 1998 Wah Chang, an Allegheny Teledyne Company, purchased all patents and rights to the hydrogen metal membrane technology that Bend Research developed.[40]

US Patent 6,183,542 was issued in 2001 for a palladium membrane process. This process provides an apparatus that can handle high flow rates of gas while using a minimal amount of hydrogen-permeable material.

Proton Energy Systems (Rocky Hill, CT) received US Patent 6,168,705 in 2001 for an electrochemical gas purifier system that can purify and simultaneously compress hydrogen from a dirty gas stream without relying on moving parts. Final hydrogen gas pressures can exceed 2000 psig.

The companies that supply PSA and membrane separation systems are listed in Reference 40.

Carbon Monoxide Shift. The water gas shift conversion or the carbon monoxide shift reaction is one of the traditional purification steps that are found in many ammonia plants. The CO must be removed because it acts as a poison to the catalyst that is used in ammonia synthesis.

The carbon monoxide shift removes most of the CO from the synthesis gas and also produces more hydrogen.

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad \Delta H = -10\ \text{kcal/mol or } 42\ \text{kJ/mol} \qquad (22\text{-}2a)$$

Homogenous Water Gas Reaction (Water Gas Shift)

The "shift" from CO to CO_2 occurs in two steps. In the high temperature shift (HTS) conversion, the synthesis gas is passed through a bed of iron oxide/chromium oxide catalyst at around 400°C. The CO content of the gas is reduced to about 3 percent (on a dry gas basis). Additional details about the HTS step are given in References 53 and 70.

The gas from the HTS is cooled to increase the conversion, and then it is passed through the low temperature shift (LTS) converter. The LTS converter is filled with copper oxide/zinc oxide-based catalyst and operates at about 200–220°C. The residual CO content is about 0.2 to 0.4 percent (on a dry gas basis).[53]

In some plants the two shift reactions are combined in a medium temperature shift conversion. When the feed gas is not desulfurized, the CO conversion is called sour gas shift and a sulfur-resistant catalyst is used.[62,63,73,83,94,166]

Removal of Sulfur Compounds and Carbon Dioxide. If sulfur is present as H_2S or COS or if CO_2 is present, any of these compounds will be a poison for many catalysts and will partly or completely inhibit catalyst activity.

The point at which sulfur removal is employed depends on the synthesis gas process that is used. Table 22.11 lists many of the processes that are available.[46]

The Amine Guard is a corrosion inhibitor that was developed by Union Carbide. It is added to the MEA solvent and allows MEA concentration to be increased. The higher MEA concentration leads to a lower circulation flow rate and a lower energy demand during regeneration.[74]

As shown in Figs. 22.4, 22.6, and 22.8, the CO_2 removal step is normally after the shift conversion step. The process gas from the LTS converter contains mainly hydrogen, nitrogen, CO_2, and excess process steam. The gas is cooled and most of the excess steam is condensed before it enters the CO_2 removal system. This condensate normally contains 1500 to 2000 ppm of ammonia and 800 to 1200 ppm of methanol. Therefore it should be stripped or recycled.

The heat that is released during the cooling/condensation can be used: to regenerate CO_2 scrubbing solution, to drive an absorption

TABLE 22.11 Processes for Removal of Carbon Dioxide and Sulfur Compounds from Synthesis Gas

Process Name	*Key Chemical(s)*
• The Alkazid process:	Alkali salts of amino acids (N-Methylaminopropionic acid)
• The AMDEA process	Activated Methyl Diethanolamine
• The Benfield process	Hot potassium carbonate
• The Carsol process	Potassium carbonate
• The Catacarb process	Hot potassium carbonate
• The Fluor Solvent process	Propylene carbonate
• The Giammarco-Vetrocoke process	Potassium carbonate with arsenite
• The Hi Pure process	Two-stage hot potassium carbonate washing
• The Purisol process from Lurgi	N-Methyl-2-Pyrrolidone (NMP)
• The Rectisol process	Low temperature methanol
• The Selexol process	Dimethyl ethers of polyethylene glycol
• The Shell Sulfinol process	Di-isopropanolamine dissolved in sulfolane and water
• Pressurized washing	Monoethanolamine (MEA) or diglycolamine

refrigeration unit, or to preheat boiler feedwater. The amount of heat released depends on the process steam to carbon ratio (see Tables 22.8 and 22.9). If all this low-level heat is used for CO_2 removal or absorption refrigeration, then high-level heat has to be used for the feedwater system. An energy-efficient process should therefore have a CO_2 removal system with a low heat demand.[53]

The CO_2 is removed in either a chemical, a hybrid, or a physical absorption process. Residual CO_2 contents are usually in the range of 50 to 1000 ppmv, depending on the type and design of the removal unit. The physical absorption processes may be designed for zero heat consumption. But for comparison with the chemical processes, the mechanical energy requirements have to be considered.[53]

Alkazid Process

The Alkazid process removes sulfur compounds from gas streams. All the sulfur compounds are first catalytically hydrogenated to hydrogen sulfide (H_2S) using a cobalt/molybdena catalyst. The H_2S is then absorbed in an aqueous solution of a potassium salt of either methylamino propionic acid ("Alkazid M"), or dimethylamino acetic acid ("Alkazid DIK"). This solution is heated to regenerate the hydrogen sulfide as a concentrate. This concentrate is then treated by the Claus process to recover the sulfur.[1]

aMDEA Process

The aMDEA (**A**ctivated **M**ethyl **D**iethanolamine) process removes CO_2, H_2S, and trace sulfur compounds from natural gas and syngas via a pressurized wash with activated diethanolamine. This process was developed by BASF and in 2002 it was used in more than 140 plants.[1]

Benfield Process

The Benfield (**Ben**son and **Field**) process removes carbon dioxide, H_2S, and other acid gases from industrial gas streams by scrubbing with hot aqueous potassium carbonate that contains activators. The chemical reactions are:[1,46]

$$K_2CO_3 + CO_2 + H_2O \rightleftarrows KHCO_3 \qquad (22\text{-}13)$$

$$K_2CO_3 + H_2S \rightleftarrows KHS + KHCO_3 \qquad (22\text{-}14)$$

Process details are given in References 65 and 88. The process was invented in 1952 and is now licensed by UOP. More than 700 plants were operating in 2000.[1]

Catacarb Process

The Catacarb (**Cata**lyzed Removal of **Carb**on Dioxide) process removes carbon dioxide and hydrogen sulfide from gas streams by adsorption in a hot potassium carbonate solution that contains a proprietary catalyst. The process was developed and licensed by Eickmeyer and Associates based on work at the U.S. Bureau of Mines in the 1950s. More than 100 plants were operating in 1997.[1]

Fluor Solvent Process

The Fluor Solvent Process removes CO_2 from natural gas and various industrial gas streams by dissolving the CO_2 in a propylene carbonate solvent.[1] Additional details are given in References 67 and 68. The process was invented in 1958 by the Fluor Corporation and can be licensed from Fluor Daniel. By 1985, 13 plants were operating.[1]

Giammarco-Vetrocoke Process

Two processes are known by the Giammarco-Vetrocoke name. Both processes use an aqueous solution of sodium or potassium carbonate and arsenite to absorb acid gases. Some variations of the process use glycine instead of arsenite to activate the potassium carbonate solution. In one process, the solution is used to extract carbon dioxide from natural gas or synthesis gas. In the other, hydrogen sulfide is extracted from coke-oven or synthesis gas and yields elemental sulfur from a complex sequence of reactions. In 1992, more than 200 plants were operating.[1,66]

Hi Pure Process

The Hi Pure process is a variation of the Benfield process. It uses two stages of scrubbing by hot potassium carbonate solution to reduce the CO_2 content of gases to very low levels.[1]

Purisol Process

The Purisol process removes H_2S from gases by selective absorption in N-methyl-2-pyrrolidone (NMP). It was developed and licensed by Lurgi, particularly for desulfurizing waste gases from IGCC (Integrated Gasification Combined Cycle) coal gasification plants. However the technology might be applied to some synthesis gas processes. In 1996, seven Purisol units were either in operation or under construction.[1]

Rectisol Process

The Rectisol process was originally developed to remove sulfur and acid gas compounds from gas mixtures that are produced from the partial oxidation of hydrocarbons. It is based on pressurized washing with low-temperature methanol, which results in the physical absorption of the sulfur compounds in the methanol. The process was originally developed in 1951 by Lurgi for the SASOL coal gasification plant in South Africa. The process was further developed by Linde and is now offered for licensing by both companies for the removal of CO_2, H_2S, HCN, C_6H_6 (benzene), and gum-forming hydrocarbons from syngas and fuel gas. In 2003, over 70 units were in operation or under construction.[1]

Selexol Process

The Selexol process removes acid gases from hydrocarbon gas streams by selective absorption in polyethylene glycol dimethyl ether (DMPEG). It absorbs H_2S, CO_2, COS, and mercaptans. The process has been used to remove carbon dioxide from syngas, natural gas, and coal gas. The process was developed by Allied Chemical in the 1960s and is now offered for license by UOP. Over 55 units were operating in 2002.[1]

Shell Sulfinol Process

The Shell Sulfinol process removes H_2S, CO_2, COS, and organic sulfur compounds from natural gas by scrubbing with di-isopropanolamine dissolved in a mixture of sulfolane ($C_4H_8SO_2$) and water. It was developed in the 1960s by Shell. In 1997, over 200 commercial units were operating or under construction.[1]

Pressure Washing with Monoethanolamine (MEA)

In this process, a 15 to 30 percent solution of MEA in water is used to absorb the CO_2 under pressure. The solution is then regenerated by heating it in a stripper to release the CO_2. This process is characterized by good CO_2 absorption properties at low pressure. However high regeneration energy consumption limits its use.

If the Amine Guard corrosion inhibitor is used, the MEA concentration in the circulating solution can be increased to 30 percent from a normal 20 percent. Hence, the circulating rate can be decreased by 33 percent and the heat requirements are decreased by 43 percent.[69] The Amine Guard technology is licensed by UPO.[200]

Retrofits of CO_2 Removal System

In a CO_2 removal system that uses wet scrubbing, the existing towers are the major limit to more capacity because they are expensive to replace. In an amine system, absorption increases as amine concentration increases. But a higher amine concentration requires (1) more filtration to clean the solution and (2) the addition of corrosion inhibitors. Another option is to change from monoethanolamine (MEA) to methyl diethanolamine (MDEA).[86]

In a potassium carbonate system, different additives can be used to increase the CO_2 absorption rate. In any wet scrubbing system, a change from random to structured packing can lead to higher solvent circulation rates and improved mass transfer.[86]

Final Purification of Synthesis Gas

Before the synthesis gas enters the ammonia synthesis loop, essentially all of the oxygen compounds must be completely removed to (1) avoid poisoning the ammonia synthesis catalyst and (2) keep CO_2 from forming carbamates and ammonium carbonate in the synthesis loop. It is also advantageous to remove the inert gases (methane, argon, etc.) to achieve a higher synthesis conversion per pass.[74]

Methanation. In a steam reforming process that includes CO shift conversion and CO_2 removal, the synthesis gas still contains 0.1 to 0.2 mole percent CO and 100 to 1000 ppmv of CO_2. The following reactions are the simplest method for eliminating these small concentrations of oxygen compounds.

$$CO + 3\,H_2 \rightleftarrows H_2O + CH_4 \quad \Delta H = -49.27 \text{ kcal/mol or } 206 \text{ kJ/mol} \qquad (22\text{-}11)$$

$$CO_2 + 4\,H_2 \rightleftarrows 2\,H_2O + CH_4 \quad \Delta H = -39.44 \text{ kcal/mol or } 165 \text{ kJ/mol} \qquad (22\text{-}12)$$

Methanation

The normal methanation operating temperature is 250°C to 300°C, and a large excess of hydrogen is present. The equilibrium lies far to the right side of the above reactions so the CO and CO_2 impurities can be reduced to about 5 ppm.[70] Additional catalyst and process details are given in References 74, 75, 77, and 78.

Cryogenic Purification. In the cryogenic purifier all the methane and the excess nitrogen are removed from the synthesis gas as well as a part of the argon. The cooling is produced by depressurization and no external refrigeration is needed. The purified syngas is then practically free of all impurities, except for a small amount of argon. The cryogenic unit also receives the purge from the ammonia synthesis section and delivers an off-gas for fuel. The combination of higher conversion per pass and reduced purge flow result in a more efficient process.[53] The KBR Purifier is an example of this process.[81] Fifteen KBR Purifier plants have been built since 1966. These plants range in capacity from 680 to 1750 tonnes per day, and as of 2001 all fifteen plants are still operating.[81]

Dehydration. If the makeup gas to the ammonia synthesis loop is absolutely free of catalyst poisons, such as H_2O and CO_2, it can flow directly to the ammonia synthesis converter. This leads to the most favorable arrangement from a minimum energy point of view. This can be accomplished by allowing the gas that leaves the methanation step to pass through beds of molecular sieves to remove water and CO_2.[74]

Liquid Nitrogen Wash. In many partial oxidation syngas processes, liquid nitrogen scrubbing is used to remove the carbon monoxide that remains after the shift conversion step. The CO content may be as high as 3 to 5 percent in plants that have only a HTS conversion. The liquid nitrogen wash (1) delivers a gas to the ammonia synthesis loop that is free of all impurities (including inert gases) and (2) adds all or part of the nitrogen that is required for ammonia synthesis. The nitrogen is obtained from the air-separation plant that provides the oxygen for the partial oxidation process (see Fig. 22.6)[74].

Adjust Hydrogen to Nitrogen Ratio. The optimum ammonia synthesis reaction rate depends on several factors including pressure, temperature, H_2-to-N_2 molar ratio, and catalyst activity. Therefore the H_2-to-N_2 molar ratio is adjusted to suit the requirements in ammonia synthesis. This adjustment occurs before the compression step.

Compression

Ammonia synthesis is normally carried out at a pressure that is higher than that for synthesis gas preparation. Therefore the purified synthesis gas to the ammonia synthesis loop must be compressed to a higher pressure.[74]

Due to several major developments in ammonia process technology, ammonia plants with 1000 to 1500 tonne per day capacities have became the industry standard for new plant construction. In 2001 plants as large as 2000 tonnes per day have become common. These plants have much lower production costs than the earlier generation of smaller plants mainly because steam-driven, centrifugal compressors are used rather than electrically driven, reciprocating compressors.[57, 74]

AMMONIA SYNTHESIS

The ammonia synthesis reaction is:[74]

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

$$\Delta H_{298} = -45.72 \text{ kJ/mol or } 11.04 \text{ kcal/mol} \qquad (22\text{-}15)$$

The reaction normally takes place on an iron catalyst. The reaction pressure is in the range of 100 to 250 bar, and temperatures are in the range of 350°C to 550°C. At the usual commercial converter operating conditions, the conversion achieved per pass is 20 to 30 percent.[53] In most commercial ammonia plants, the Haber recycle loop process is still used to give substantially complete conversion of the synthesis gas. In this process the ammonia is separated from the recycle gas by cooling and condensation. Next the unconverted synthesis gas is supplemented with fresh makeup gas, and returned as feed to the ammonia synthesis converter.[74]

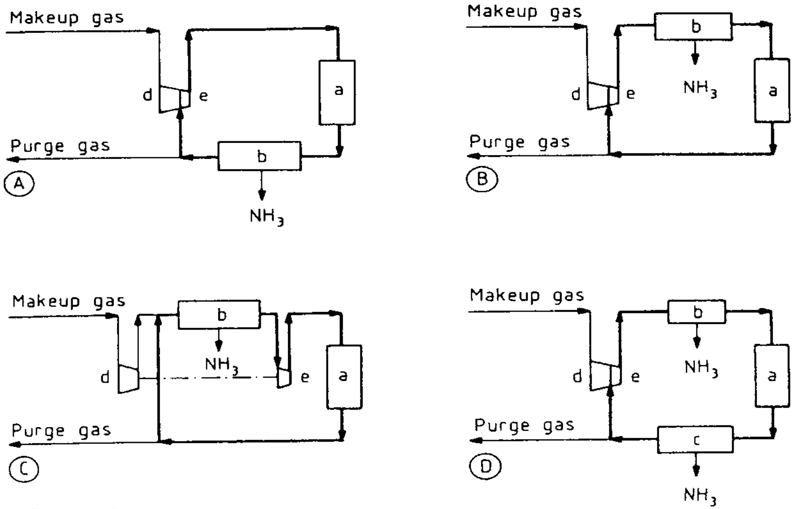
Synthesis loop arrangements differ with respect to (1) the points in the loop at which the makeup gas is delivered, (2) where the ammonia is taken out, and (3) where the purge gas is taken out[53] (see Fig. 22.9). The best arrangement is shown in Fig. 22.9A. After the gas leaves the ammonia synthesis converter, ammonia is condensed/removed by cooling and the recycle gas is returned to the recycle compressor. This represents the most favorable arrangement from a minimum energy point of view. It results in the lowest ammonia content at the entrance to the converter and the highest ammonia concentration for condensation.[74] The advantages and disadvantages of the other arrangements in Fig. 22.9 are described in Reference 74.

Conventional reforming with methanation as the final purification step produces a synthesis gas that contains inerts (CH_4 and argon) in quantities that do not dissolve in the condensed ammonia. Most of the inerts are removed by taking a purge stream out of the synthesis loop. The size of this purge stream controls the level of inerts in the loop at about 10 to 15 percent. The purge gas is scrubbed with water to remove ammonia and then it can be used as fuel or sent to hydrogen recovery. The best point at which to take the loop purge is discussed in Reference 53.

Reaction Rate

Knowledge of the macrokinetics is important for solving the industrial problem of designing ammonia synthesis reactors, for determining the optimal operating conditions, and for computer control of ammonia plants. Some of the considerations are: high pressure promotes a high rate of ammonia formation, high ammonia concentration in the synthesis gas (recycle gas) restricts ammonia formation (see Fig. 22.10), the rate of formation initially increases with rising temperature but then goes through a maximum as the system approaches thermodynamic equilibrium (see Fig. 22.11), and with lower temperatures, the maximum rate shifts to a lower hydrogen–nitrogen ratio (see Fig. 22.12).[74]

In 2001 Hyprotech and Synetix announced an ammonia plant simulation that can be used for modeling, online monitoring, and optimization of the plant. The simulation includes Synetix reactor models, customized thermo-



A) Synthesis Loop for Pure and Dry Makeup Gas
B) Product recovery After Recycle Compression
C) Product Recovery Before Recycle Compression (Four-Nozzle Compressor Design)
D) Two Stages of Product Condensation

a) Ammonia Converter with Heat Exchangers
b) Ammonia Recovery by Chilling and Condensation
c) Ammonia Recovery by Condensation at Ambient Temperature
d) Synthesis Gas Compressor
e) Recycle Compressor

Fig. 22.9. Schematic flow diagrams of typical ammonia synthesis loops.[74] (Courtesy of Wiley-VCH. Bakemeier, H., Huberich, T., et al.: "Ammonia" in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 2, VCH Verlagsgesellschaft, Weinheim 1985, pp. 143–242.

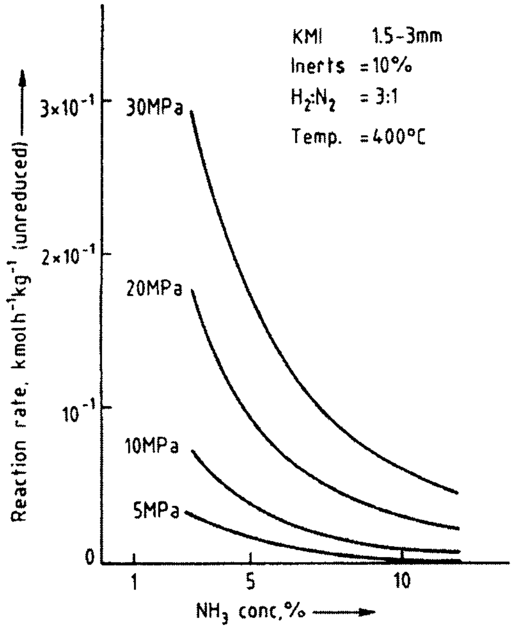


Fig. 22.10. Reaction rate for NH_3 synthesis. Dependence on the ammonia concentration at various pressures. (Courtesy of Wiley-VCH. Bakemeier, H., Huberich, T., et. al.: "Ammonia" in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 2, VCH Verlagsgesellschaft, Weinheim 1985, pp. 143–242.

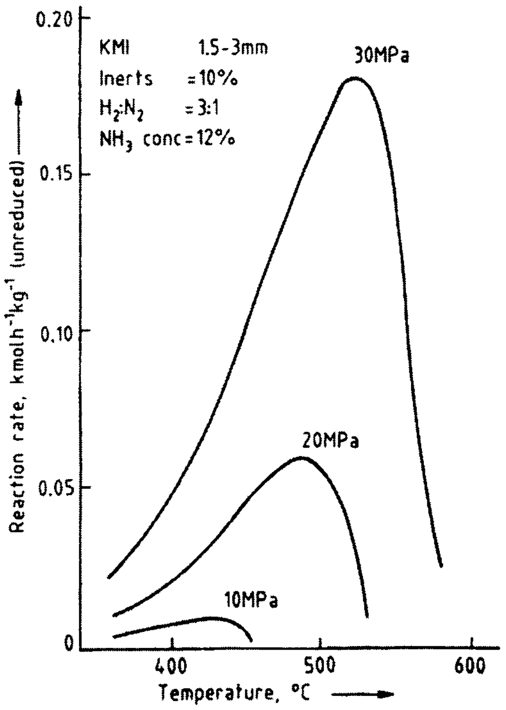


Fig. 22.11. Reaction rate for NH_3 synthesis. Dependence on the temperature at various pressures. (Courtesy of Wiley-VCH. Bakemeier, H., Huberich, T., et. al.: "Ammonia" in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 2, VCH Verlagsgesellschaft, Weinheim 1985, pp. 143–242.

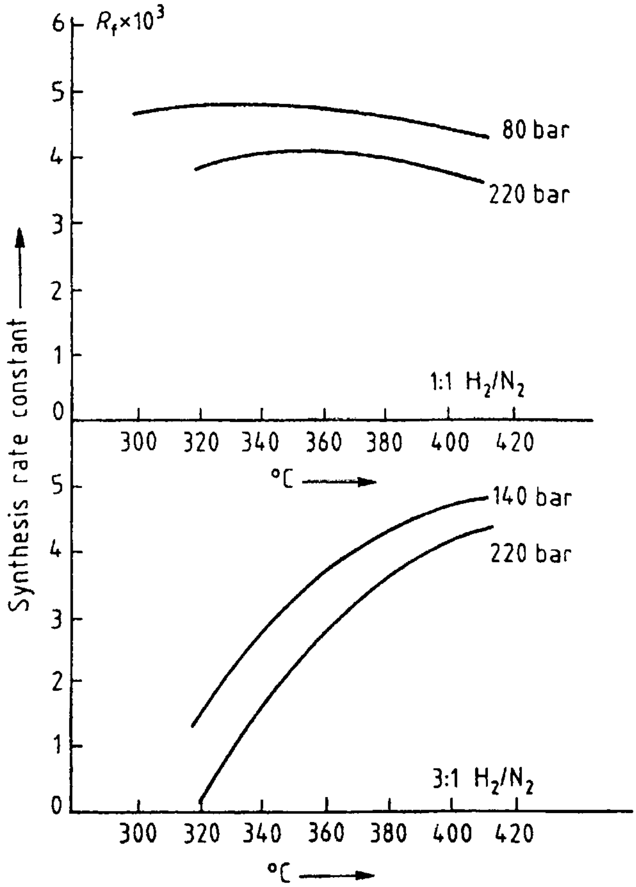


Fig. 22.12. Amonia synthesis rate constant dependence on hydrogen-nitrogen ratio. (Courtesy of Wiley-VCH. Bakemeier, H., Huberich, T., et. al.: "Ammonia" in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A 2, VCH Verlagsgesellschaft, Weinheim 1985, pp. 143–242.

dynamic data, and information to simulate the performance of a range of catalysts. The reactor models in the simulation include primary and secondary reformers, high-temperature shift converter, low-temperature shift converter, methanator, and ammonia synthesis converter.[80]

Catalysts

When ammonia is made from natural gas using the steam reforming process, several reaction stages are needed and catalysts are key to the economic operation of each stage. The chemistry of the process and the basic materials that make up the catalysts are shown in Fig. 22.13.[70]

For a given operating pressure and a desired production rate, the catalyst determines (1) the operating temperature range, (2) recycle gas flow, and (3) refrigeration requirements. It also indirectly influences the makeup gas purity requirements.[74]

Industrial catalysts for ammonia synthesis must satisfy the following requirements: (1) high catalyst activity at the lowest possible reaction temperatures, (2) the highest possible insensitivity to oxygen- and chlorine-containing catalyst poisons, (3) long life, and (4) mechanical strength.

The choice of particle size and shape of commercial ammonia catalysts is determined mainly by the catalyst performance and the pressure drop. From the standpoint of space–

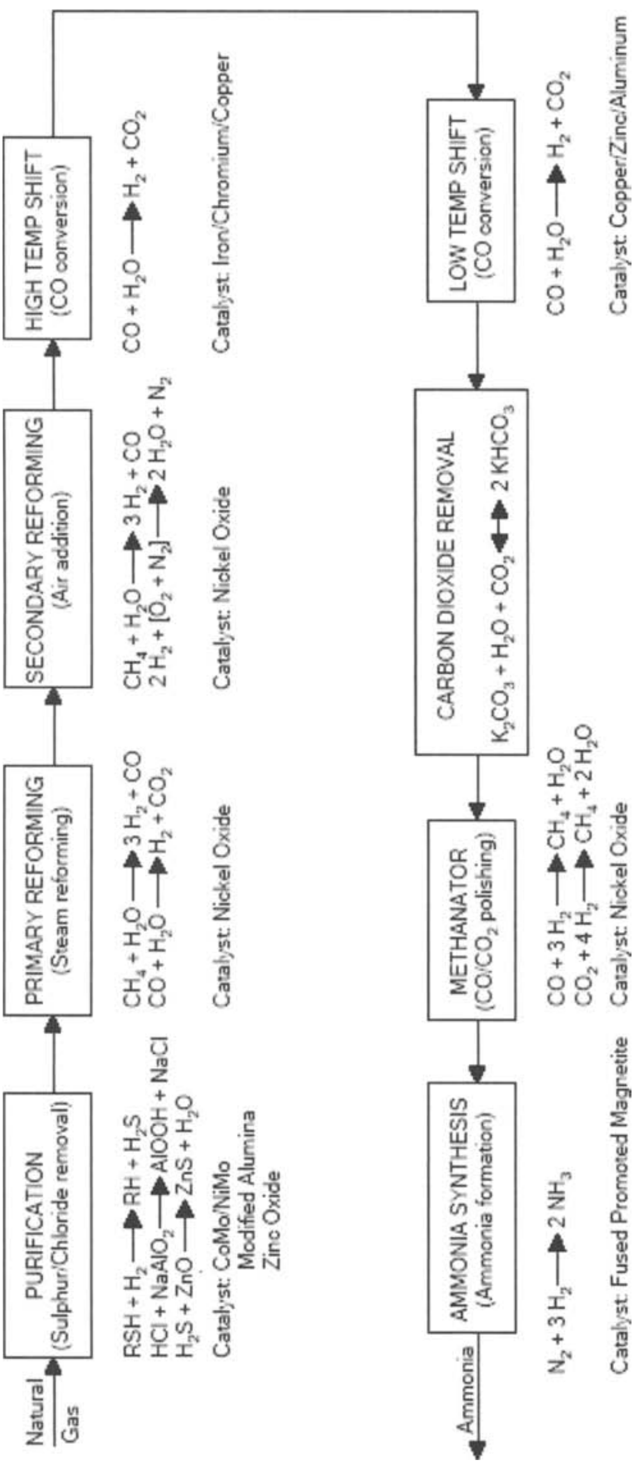


Fig. 22.13. Basic catalyses materials and chemistry of the ammonia process. (Copyright Johnson Matthey plc. Reproduced by permission of Johnson Matthey plc.)

time yield, it is desirable to use the finest possible particle, which is about 1–2 mm.[74]

For processes operating at pressures of 25 to 45 MPa (250 to 450 bar) and space velocities of 8000 to 20,000 m^3/m^3 h (STP), a grain size of 6 to 10 mm is preferred. (Space velocity is defined as the number of reactor volumes of feed—at specified conditions—that can be treated in unit time.) Larger granulations (8 to 15 mm or 14 to 20 mm), are used only in plants where the lowest possible pressure drop is essential because of very high gas velocities. In catalyst zones in which the ammonia formation rate is so high that the allowable temperature limits are exceeded, it may be advantageous as well to use coarse particles for suppressing the reaction.[74] Some of the poisons of ammonia catalysts are discussed in Reference 74.

The activity of damaged catalysts may be almost completely restored by reduction with clean synthesis gas at a relatively low temperature. It has also been found that the degree of poisoning rises as the partial pressure ratio, p_{H2O}/p_{H2}, increases and the degree of poisoning falls with increasing temperature.[74]

Energy Efficiency

Due to increased feedstock costs, some new ammonia plant designs use fuel more efficiently but their capital cost may be higher. The recovery of hydrogen and ammonia from the synthesis purge gas by a cryogenic unit or a membrane system results in an ammonia capacity increase of about 5 percent.[57]

Substantial improvements have been made in the energy efficiency of CO_2 removal systems. The first large-scale ammonia plants in the 1960s typically used monoethanolamine (MEA) as a solvent. Energy input was over 50,000 kcal/kg-mol of CO_2 removed. In 2001 plants use improved solvents and designs that can reduce the energy input to about 10,000 kcal/kg-mol of CO_2 removed.[57]

A typical world-scale plant that was built in the 1970s consumed about 42 billion BTU of natural gas per tonne of ammonia produced. Retrofitting such a plant to improve fuel efficiency can reduce gas consumption to about 36 million BTU per tonne. Ammonia plants that were built in the late 1990s use only about 30 million BTU per tonne of ammonia, are easier to operate and have slightly lower conversion costs. Some new plants also recover more than one million BTU per tonne by generating electricity from waste heat.[57]

Ammonia Plant Design

A simplified flowsheet for an ammonia plant that processes natural gas via steam reforming is shown in Fig. 22.14. A block diagram of this same plant is shown in Fig. 22.15. This diagram lists typical stream compositions, typical operating conditions, catalyst types (recommended by Synetix), and catalyst volumes.

The KAAP*plus*™ (**K**ellogg **B**rown & **R**oot **A**dvanced **A**mmonia **P**rocess—**Plus**) is an ammonia process design made up of commercially proven technologies: KBR Reforming Exchanger System (KRES), KBR Purifier, and KBR Advanced Ammonia Process (KAAP) for synthesis. This process uses a ruthenium-based catalyst that is 20 times more active than the iron-based catalysts and improves synthesis efficiency. This is because synthesis pressure is lowered from a typical pressure of 150 bar (2175 psig) to 90 bar (1305 psig).[57,81,203] Capital cost savings of 3 to 8 percent are achieved with KAAP*plus*.™ [81]

Haldor Topsøe's ammonia synthesis technology is based on the S-200 ammonia converter. This is a two-bed radial flow converter with indirect cooling between the beds. This converter concept has been used extensively to upgrade existing converters (Topsøe or other designs) in modification projects to achieve higher capacity (up to 20%) and/or better energy efficiency.[85]

Other companies that offer ammonia process technology are Linde,[208,214] ICI,[16,17] Ammonia Casale,[204,209,210,213] and Uhde.[211]

Ammonia Separation

The removal of ammonia product is accomplished via mechanical refrigeration or

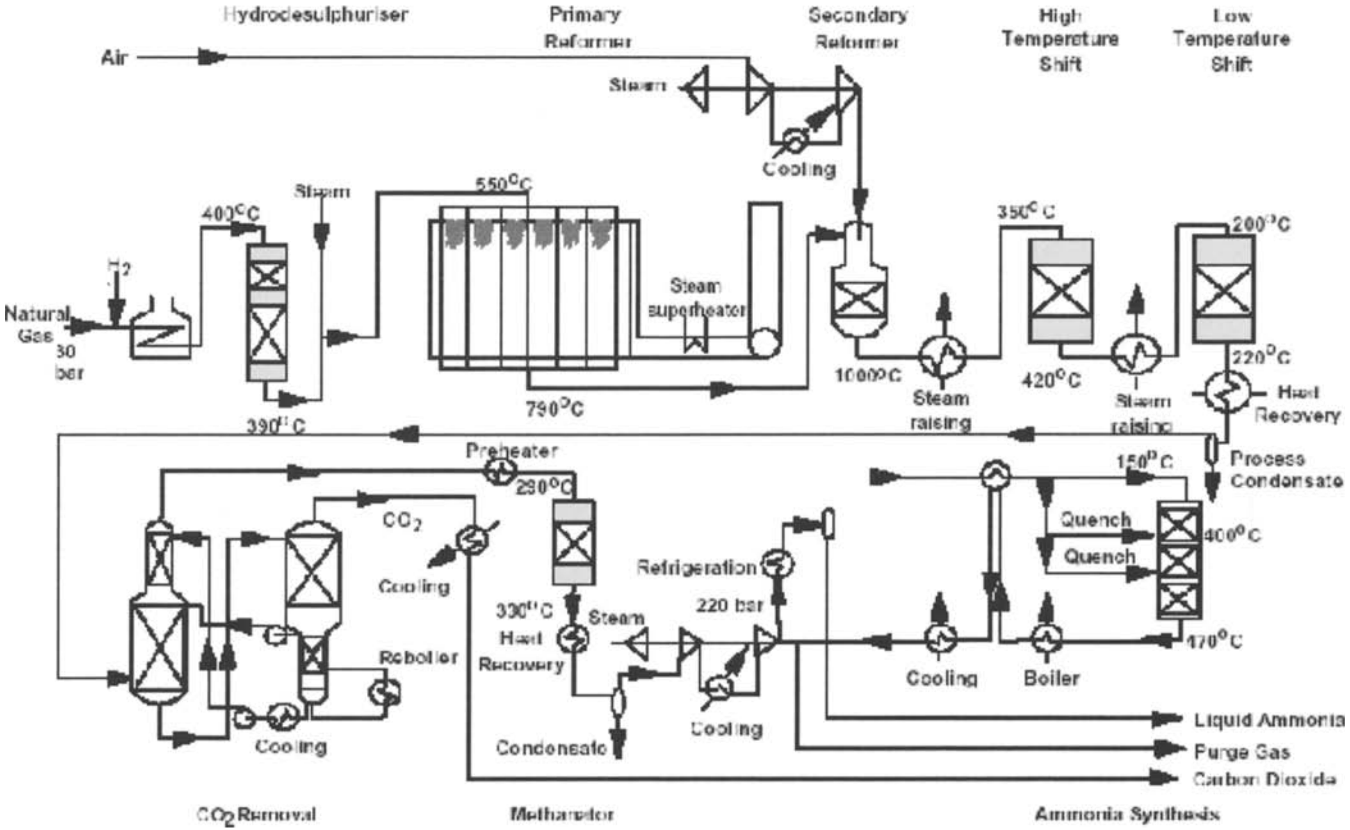
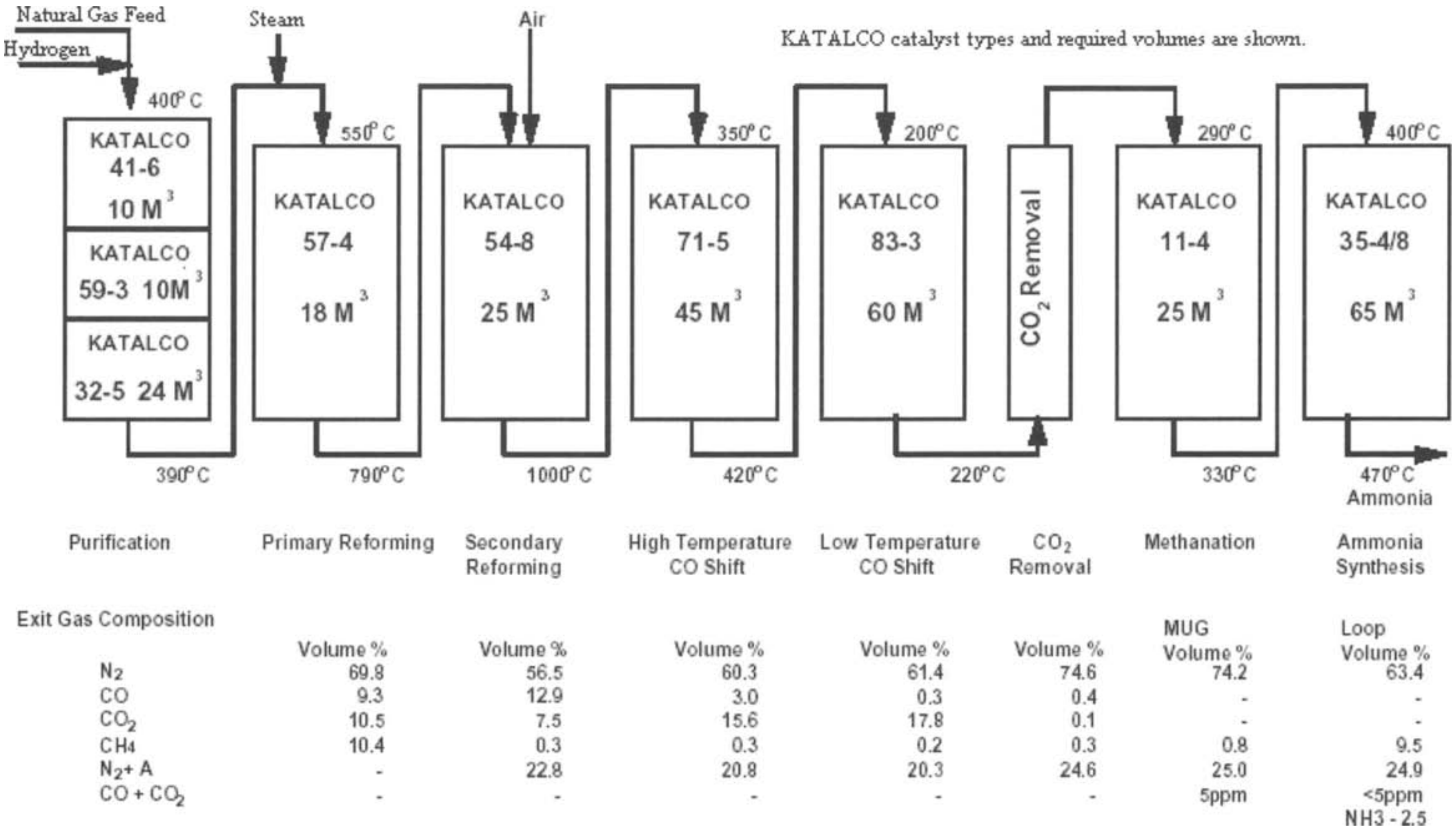


Fig. 22.14. Simplified ammonia plant flowsheet. (Copyright Johnson Matthey plc. Reproduced by permission of Johnson Matthey plc.)



Exit Gas Composition	Volume %	Volume %	Volume %	Volume %	Volume %	MUG Volume %	Loop Volume %
N_2	69.8	56.5	60.3	61.4	74.6	74.2	63.4
CO	9.3	12.9	3.0	0.3	0.4	-	-
CO_2	10.5	7.5	15.6	17.8	0.1	-	-
CH_4	10.4	0.3	0.3	0.2	0.3	0.8	9.5
N_2+ A	-	22.8	20.8	20.3	24.6	25.0	24.9
CO + CO_2	-	-	-	-	-	5ppm	<5ppm NH3 - 2.5

Fig. 22.15. Block diagram of 1000 tonne/day ammonia plant. (Reproduced by permission of Johnson Matthey Catalysts. Copyright Johnson Matthey plc.)

absorption/distillation. The choice is made by examining the fixed and operating costs. Typically, refrigeration is more economical at synthesis pressures of 100 atm (1470 psia) or more. At lower pressures absorption/distillation is usually favored.[212]

Ammonia Synthesis

If the synthesis gas contains traces of carbon oxides, ammonium carbamate will form upon mixing with the ammonia in the recirculating gas from the synthesis loop. The carbamate will clog and/or corrode downstream equipment. To avoid this condition, the carbon oxide levels in fresh makeup gas should be less than 5 ppm.[88]

Many ammonia synthesis converters are subject to nitriding and hydrogen embrittlement. The internal catalyst baskets are made of SS 321 material.[88] The nitriding effect is more pronounced in low-alloy steels above 450°C. Austinic steels with a high-nickel content offer considerably more resistance. Alloys of the Cr–Ni–Mo type are usually used for the gas side. Atomic hydrogen is absorbed in the metal by diffusion. The subsequent reaction with carbon in the steel results in blistering and cracking from decarburization[88].

Large Capacity Ammonia Plants

In 2002 the design and construction of ammonia plants with capacities of 3000 tonnes per day or more were underway. These large capacity plants will be at least 50 percent larger than the largest plants that were operating in 2002. The benefit of bigger plants is to realize economy of scale. Doubling the size of a single-train plant has the potential to reduce the capital-related cost of production by about 20 percent.[215]

The companies that are developing large capacity plants are KBR,[215] Haldor Topsøe,[215,217] Uhde,[215,218] plus Lurgi and Ammonia Casale.[291]

Ammonia Production Costs

Ammonia production costs are very dependent on feedstock cost, which is normally natural gas. Natural gas prices can vary significantly from region to region and by the cycles in the world energy market. Typical ammonia production costs are listed in Reference 57. The natural gas cost makes up 70 percent to over 85 percent of the cash production costs as the natural gas cost varies from $2.00 per million BTU up to $6.00 per million BTU. In general the ammonia cash production costs in $ per tonne are a factor of 40 to 50 times the natural gas price in US dollars per million BTU.

USES OF AMMONIA

Anhydrous ammonia was produced in about 80 countries in 2001. About 85 percent is used for nitrogen fertilizer production, including about 4 percent that is directly applied to the fields.[36,153]. In the United States the distribution of ammonia use differs slightly from the worldwide uses. In the United States only 80 percent of the ammonia is used to make fertilizers. Chemical intermediates account for 19 percent of the ammonia use and the remaining 1 percent is used in pulp and paper, metals, and refrigeration applications.[37]

Chemical Production and Other Uses

The uses of ammonia are in:

- *Acrylonitrile.* Acrylonitrile (ACRN) is used in the production of acrylic fibers and various resins. ACRN is produced by the catalytic oxidation of propylene and ammonia. About 0.48 tonnes of ammonia are needed to make one tonne of ACRN.[57]
- *Caprolactam.* Caprolactam is used principally in the production of nylon-6 fibers. In the production of caprolactam, ammonia is used to maintain a reaction pH of 7 in one step, and in another step it is used to neutralize sulfuric acid. Both of these steps result in the production of a low-grade ammonium sulfate fertilizer. In the classical process 5 kg of $(NH_4)_2SO_4$ are produced per kilogram of caprolactam. In 1992 about 33 percent of

the worldwide caprolactam capacity was based on DSM's caprolactam process that only produces 1.8 kg of $(NH_4)_2SO_4$ per kilogram of caprolactam.[46]

- *Miscellaneous Amines and Nitriles.* A small but significant amount of ammonia is consumed in the production of various amines and nitriles.[57]
- *Metallurgy.* In this application ammonia is cracked to produce a "dissociated ammonia" that consists of 75 percent hydrogen and 25 percent nitrogen. Dissociated ammonia is used in a number of metal treatment proceses.[57]
- *Refrigeration.* Anhydrous ammonia is used as a refrigerant in industrial, closed-circuit refrigeration systems. Ammonia's high latent heat, low vapor density, chemical stability, and low iron corrosivity promote its use. Ammonia is used in large industrial systems (rather than halocarbon refrigerants) because ammonia absorbs about six times as much heat per unit weight and energy costs of operation are substantially lower.[57]
- *Pulp and Paper.* In the production of ammonia-based sulfite pulp, the amount of ammonia used per ton of pulp varies from mill to mill. The industry average is 125 pounds of ammonia per ton of sulfite pulp. Ammonia is also used for stack gas scrubbing and wastewater treatment.[57]
- *Phosphate Ore Flotation.* A small amount of ammonia is used as a modifying reagent in the froth flotation of phosphate ores.
- *Household Cleaners.* Household ammonia, liquid window cleaners, liquid all-purpose cleaners, and various other household cleaning products constitute this small market for ammonia. Ammonia is also used to make surfactants that go into liquid dishwashing detergents.[57]
- *Air Pollution Control.* A number of processes use ammonia for scrubbing sulfur oxides (SO_x) and/or nitrogen oxides (NO_x) from industrial and electrical power plant stack gases.[57]
- *Uranium Concentrate Production.* Ammonia is used to precipitate the final uranium concentrate salt (yellowcake) prior to drying or calcination. It is generally economically preferred over sodium hydroxide or hydrogen peroxide.[57]
- *Water Purification.* Ammonia is combined with chlorine to purify some municipal and industrial water supplies.[57]
- *Waste Treatment.* Small amounts of ammonia are added when needed as the nitrogen source for the bacteria in industrial and municipal biological waste treatment systems. Other industrial plants use minor amounts of ammonia to neutralize acid in plant wastes.[57]
- *Duplicating Processes.* Ammonia is used as a process chemical in photographic copy machines.[57]
- *Fabric Treatment.* Permanent-press, 100 percent cotton fabrics are produced via a licensed process involving mercerization in a bath of liquid anhydrous ammonia. This Sanfor-Set process was commercialized in 1975.[57]
- *Semiconductor Industry.* High purity ammonia (99.99995%) is used in gallium nitride (GaN) manufacturing processes to provide high brightness blue and white LEDs (light emitting diodes), in high-performance optoelectronics (such as liquid crystal displays and flat panel displays), and in high-power electronic devices (such as lasers and laser diodes).

DISTRIBUTION AND STORAGE

Ammonia Toxicity

Ammonia is a strong local irritant, and the primary target organ is the pulmonary system. Ammonia or ammonium hydroxide can penetrate the cornea rapidly and lead to damage of the iris, cataract, and glaucoma. Oral ingestion of aqueous ammonia can corrode the mucous membranes of the oral cavity and constrictions of the esophagus may result.[74]

Ammonia is not considered to be carcinogenic nor is it mutagenic. The effects of different ammonia concentrations are summarized in Table 22.12.[74]

TABLE 22.12 Health Effects of Different Ammonia Concentrations

Ammonia Concentration (ppm)	*Health Effect*[a]
5	Threshold detection limit
50	Easily perceived
50–72	No significant impairment to respiration
100	Irritation to nose and throat Burning sensation in eyes
200	Headache and nausea
250–500	Rapid heart beating
700	Immediate onset of burning sensations in the eyes
1000	Immediate coughing

[a] The TLV has been set at 25 ppm (17 mg/m^3) as an 8 hour time-weighted average (TWA) with a short-term exposure limit (STEL) of 35 ppm (24 mg/m^3).

Ammonia Quality

Most industrial uses of ammonia require a higher-purity level of product than agricultural uses. Typical ammonia specifications are shown in Table 22.13.[74]

Commercial grade is produced by ammonia synthesis while refrigeration grade is normally made from industrial raw ammonia by distillation. For ammonia shipped or pipelined in the United States, water content must be at least 0.2 weight% to inhibit stress corrosion cracking of the carbon steel.[57]

Various concentrations and purities of aqueous ammonia are on the market. The typical concentration is 25 to 30 percent ammonia and the iron content is less than 10 ppm. If the ammonia content is above 25 percent, it must be shipped in a pressure vessel because of its elevated vapor pressure.[74]

Distribution and Storage

Ammonia production requires storage facilities to smooth over fluctuations in production, usage, and shipments. Ammonia is stored and distributed to point of use almost exclusively as a liquid.[74]

Three methods have been used for storing liquid ammonia.[74]

- Pressure storage at ambient temperature in spherical or cylindrical pressure vessels having capacities up to about 1,500 tonnes
- Atmospheric storage at −33°C in insulated cylindrical tanks for up to about 50,000 tonnes per vessel
- Reduced pressure storage at about 0°C; usually in insulated, spherical pressure vessels for quantities up to about 2500 tonnes per sphere

Ammonia is delivered in small containers, tank trucks, tank cars, barges, and via pipeline. The most common small containers are cylindrical steel bottles and pressurized flasks that contain about 20 to 200 kg and polyethylene canisters and metals casks.[74] Trucks have ammonia capacities up to 100 m^3 whereas jumbo rail cars hold up to 150 m^3. Liquid ammonia shipments by barge constitute a larger volume than by road or rail.

TABLE 22.13 Ammonia Quality Specifications

		Commercial Grade		*Refrigeration Grade*	
		USA	*Germany*	*USA*	*Germany*
Purity	wt%, minimum	99.5	99.5	99.98	99.98[a]
Water	wt%, maximum	0.5	0.2	0.015	0.02
Inerts[b]	mL/g, maximum	Not specified		0.1	0.08
Oil	ppm by weight	5.0	5.0	3.0	Not specified
Free of H_2S, pyridine and naphthenes					

[a] Allowable boiling point change on vaporization of 5 to 97% of the test sample, 0. 9°C.

[b] The noncondensable gases dissolved in ammonia are H_2, N_2, CH_4, and Ar. Their amounts depend on the methods of synthesis and storage. The inerts amount to about 50 mL/kg for atmospheric storage.

Additional guidelines about ammonia shipments are given in References 57 and 74.

Several ammonia pipeline systems were built in the United States in the 1960s. Their construction resulted from the construction of large plants near the sources of natural gas and from developing a large market for liquid anhydrous ammonia in direct fertilization. Pipelines are the lowest cost method to move ammonia over the long distances between the producers along the Gulf Coast and the consumers in the upper Midwest. Some pipelines are up to 3000 kilometers long and up to 10 in. in diameter.[74]

An integrated pipeline system has not been developed in Europe. Only a few pipelines with lengths of less than 50 kilometers have been installed. However in the former Soviet Union a 2424-km-long pipeline is in use.[74]

Ammonia Price

Direct sales by basic producers are generally at wholesale prices. Basic producers also sell to distributors and jobbers for resale to end users buying smaller quantities. Distributors of ammonia to industrial end users have their own storage facilities, packaging plants, and distribution networks. They are able to supply end users that buy in less than truckload quantities (a minimum of 1000 to 2000 pounds or 450 to 910 kilograms) or in cylinders or bottles.[57]

Another important aspect of the ammonia business is seasonality. The major end use for anhydrous ammonia is as a direct application fertilizer. The application season, particularly in Canada and the northern United States, is limited and significant storage capability is needed. As a result, it is normal to expect a plant to produce a downstream nitrogen product (such as urea) that is easier to store and handle and does not have such a limited application season. Industrial markets are normally nonseasonal.[57]

Long-term fixed-price contracts are not considered workable due to the volatility in the market and the uncertainty regarding future natural gas prices. The normal long-term contract simply guarantees continuity of supply and calls for prices to be negotiated every three to six months.[57] Historical prices are listed in Reference 57.

NITRIC ACID

Nitric acid is a strongly acidic, corrosive liquid that is produced by the oxidation of ammonia and subsequent reaction of the oxidation products with water. Pure nitric acid is colorless. The characteristic yellow-brown color generally associated with concentrated solutions is due to dissolved nitrogen dioxide.[91]

Nitric acid is an active compound and its salts are found in all fertile soils. The alchemists obtained nitric acid by heating alum and copper sulfate with nitrate in a retort. Owing to its powerful corrosive action, they named it aqua fortis or "strong water".[7]

Being a powerful oxidizing agent, nitric acid reacts violently with many organic materials and the reactions may be explosive. As a general rule, oxidizing reactions occur primarily with the concentrated acid and favor the formation of nitrogen dioxide (NO_2). The acidic properties tend to dominate the dilute acid and this results in the preferential formation of nitrogen oxide (NO).[53]

Nitric acid reacts with all metals except the precious metal series and certain alloys. Although chromium, iron and aluminum readily dissolve in dilute nitric acid, the concentrated acid forms a metal oxide layer that protects the metal from further oxidation.[53]

Physical Properties

Pure anhydrous nitric acid (100%) is a colorless liquid that solidifies at –41.6°C to form white crystals. It boils at 84.1°C. When it boils in light, a partial decomposition occurs with the formation of NO_2 via the following reaction.

$$HNO_3 \rightleftarrows H_2O + 2\,NO_2 + \tfrac{1}{2}\,O_2 \quad (22\text{-}15)$$

Anhydrous nitric acid should be stored below 0°C to avoid decomposition. The nitrogen dioxide remains dissolved in the nitric acid and creates a yellow color at room temperature and a red color at higher temperatures. The pure acid tends to give off white fumes when exposed to air, however, acid with dissolved nitrogen dioxide gives off reddish-brown vapors which leads to the common name "red fuming acid".[53]

Nitric acid is miscible with water and distillation results in an azeotrope with a concentration of 68.4 percent HNO_3 and a boiling temperature of 121.9°C at atmospheric pressure. Two solid hydrates are known the monohydrate ($HNO_3{\bullet}H_2O$) and the trihydrate ($HNO_3{\bullet}3H_2O$).[53]

Nitrogen oxides are soluble in nitric acid, and this property influences all the physical characteristics that depend on the concentration of the oxides. This mainly includes the vapor pressure above the liquid and the boiling temperature as well as the color. "Red Fuming Nitric Acid" is a term that, according to *Sax's Dangerous Properties of Industrial Materials* applies to nitric acid that contains more than 17 percent NO_2 and has a density of more than 1.48 g/cm.[3,53] White fuming nitric acid usually contains 90 to 99 percent by weight HNO_3, from 0 to 2 percent by weight dissolved NO_2, and up to 10 percent by weight water.

The TLV for nitric acid has been set at 2 ppm as an 8-hour time-weighted average (TWA) with a short-term exposure limit (STEL) of 4 ppm.

Some properties of nitric acid are given in Tables 22.14 and 22.15.

TABLE 22.14 Physical Properties of Nitric Acid Solutions[92–94]

wt. % HNO_3	*Density (at 20° C), g/cm³*	*Freezing point, °C*	*Boiling point, °C*	*Specific heat (at 20°C) J/(g•K)[a]*	*Partial press. (at 20°C) Pa[b]*		*Viscosity (@ 20°C) mPa•s (=cP)*	*Thermal conduct. (@ 20°C) W/(m•K)[c]*
					HNO_3	*H_2O*		
0.0	0.99823	0	100.0	4.19	—	2333	1.0	0.61
10.0	1.0543	−7	101.2	3.73	—	2266	1.1	0.57
20.0	1.1150	−17	103.4	3.39	—	2026	1.2	0.54
30.0	1.1800	−36	107.0	3.18	—	1760	1.4	0.50
40.0	1.2463	−30	112.0	3.01	—	1440	1.6	0.47
50.0	1.3100	−20	116.4	2.85	27	1053	1.9	0.43
60.0	1.3667	−22	120.4	2.64	120	653	2.0	0.40
70.0	1.4134	−41	121.6	2.43	387	347	2.0	0.36
80.0	1.4521	−39	116.6	2.22	1400	120	1.9	0.35
90.0	1.4826	−60	102.0	1.97	3600	27	1.4	0.31
100.0	1.5129	−42	86.0	1.76	6000	0	0.9	0.28

[a] To convert J/ (g•K) to cal/(g•°C), divide by 4.184.
[b] To convert Pa to atm, divide by 1.013 × 10^5.
[c] To convert W (m•K) to Btu (h•ft•°F), divide by 1.7307.

TABLE 22.15 Thermodynamic Properties of Nitric Acid and Its Hydrates[95]

	HNO_3	*$HNO_3{\bullet}H_2O$*	*$HNO_3{\bullet}3H_2O$*
Nitric acid, wt.%	100.0	77.77	53.83
Freezing point, C	−41.59	−37.62	−18.47
Heat of formation (at 25°C). kJ/mol[a]	−173.35	−472.07	−888.45
Free energy of formation (at 25°C). kJ/mol[a]	−79.97	−329.29	−810.99
Entropy (at 25 C), kJ/(mol•K)[a]	155.71	217.00	347.17
Heat of fusion, kJ/mol[a]	10.48	17.52	29.12
Heat of vaporization (at 20°C), kJ/mol[a]	39.48	—	—

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

Processes

The Birdeland-Eyde or Arc process made nitric acid by passing air through an electric arc, forming nitric oxide, oxidizing NO with air, and absorbing the resulting oxides of nitrogen in water. The reactions are:

$$N_2 + O_2 \rightarrow 2\,NO \qquad (22\text{-}16)$$

$$2\,NO + O_2 \rightarrow 2\,NO_2 \qquad (22\text{-}17)$$

$$2\,NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (22\text{-}18)$$

$$3\,HNO_2 \rightarrow HNO_3 + 2\,NO + H_2O \qquad (22\text{-}19)$$

The process was operated in Norway from 1905 to 1930, and it was first used in the United States in 1917.[1] It used hydroelectric power but was made obsolete by the ammonia oxidation process.

The Ostwald process is the basis for the modern processes that make nitric acid by the catalytic oxidation of ammonia. It was discovered in 1900 by Wilhelm Ostwald, a German physical chemist. The process was used by Germany during World War I to make explosives after the Allied blockade cut off the supply of nitrites from Chile and other places.[96]

Some of the processes that have been based on the Ostwald process are:

- The CNA (**C**oncentrated **N**itric **A**cid) process is a general name for processes that make nitric acid more concentrated than the 70 percent made in conventional processes.
- The CONIA process makes nitric acid simultaneously at two different concentrations.
- The DSN (**D**irect **S**trong **N**itric) process is a general name for processes that concentrate nitric acid from the 50 to 70 percent range up to the 98 percent range.
- The HOKO process also makes nitric acid simultaneously at two different concentrations.
- The Hycon process makes nitric acid at a range of concentrations. It was developed in 1968 and patented (U.S. Patent 3,542,510) by the Chemical Construction Corporation.
- The SABAR (**S**trong **A**cid **B**y **A**zeotropic **R**ectification) process makes nitric acid by the atmospheric oxidation of ammonia. Davy McKee developed the process and built plants based on this technology from 1974 to 1986.

Chemistry. In the Ostwald process ammonia is catalytically oxidized. The key steps in the process are: (1) oxidation of ammonia to nitric oxide (NO), (2) oxidation of NO to nitrogen dioxide (NO_2), and (3) absorption of NO_2 in water to produce nitric acid. Overall, the principal reactions may be summarized as follows.[91,97]

Ammonia reacts with air on platinum/rhodium alloy catalysts in the oxidation section of nitric acid plants.

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \quad \Delta H_{298} = -54\ \text{kcal/mol}\ (-226\ \text{kJ/mol}) \qquad (22\text{-}20)$$

Simultaneously N_2O, N_2, and H_2O are formed in side reactions according to Equations 21 and 22.

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \quad \Delta H_{298} = -75.8\ \text{kcal/mol}\ (-317\ \text{kJ/mol}) \qquad (22\text{-}21)$$

$$4\,NH_3 + 4\,O_2 \rightarrow 2\,N_2O + 6\,H_2O \qquad (22\text{-}22)$$

Some of the process energy recovery options are discussed in Reference 97. The yield of nitric oxide in Equation 22-20 depends on pressure and temperature as indicated in Table 22.16.[97]

TABLE 22.16 Effect of Reaction Pressure and Temperature on Nitric Oxide Yield

Pressure (bar)	*Temperature (°C)*	*Nitric Oxide Yield (%)*
Below 1.7	810 to 850	97
1.7 to 6.5	850 to 900	96
Above 6.5	900 to 940	95

Source: Reproduced by permission of European Fertilizer Manufacturers Association.

TABLE 22.17 Effect of Reactor Residence Time on Nitric Oxide Yield

Reactor Residence Time, Seconds	*Nitric Oxide Yield, Percent NH_3 Oxidized*
0.28	82.1
0.11	85.7
0.061	90.2
0.023	91.8

The space velocity in the ammonia oxidation reactor should be kept high to maximize yield and avoid decomposition of ammonia in the feed gas. Another potential yield loss is shown in Equation 22-23.

$$4\,NH_3 + 3\,NO_2 \rightarrow 7/2\,N_2 + 6\,H_2O \quad (22\text{-}23)$$

The effect of reactor residence time on nitric oxide yield is shown in Table 22.17.[98]

NO is oxidized to NO_2 as the combustion gases are cooled, but some side reactions (such as 22-24 and 22-25) may also occur.

$$2\,NO + O_2 \rightarrow 2\,NO_2$$
$$\Delta H_{298} = -13.6\text{ kcal/mol } (-57\text{ kJ/mol}) \quad (22\text{-}17)$$

$$4\,NO \rightarrow 2\,N_2O + O_2 \quad (22\text{-}24)$$

$$2\,NO_2 \rightleftarrows N_2O_4$$
$$\Delta H_{298} = -6.8\text{ kcal/mol } (-28.6\text{ kJ/mol}) \quad (22\text{-}25)$$

For the reaction in Equation 22-17, secondary air is added to the gas mixture obtained from the ammonia oxidation to increase the oxygen content to such a level that the waste gas leaving the plant has an oxygen content between 2 and 4 percent by volume. The rate of reaction is proportional to pressure cubed (see Reaction 22-26), and the volume or size of equipment needed to oxidize the nitric oxide is inversely proportional to pressure cubed:

$$d(P_{NO})/dt = -k\,(P_{NO})^2(P_{O2}) \quad (22\text{-}26)$$

The Absorption Reaction (22-27) is exothermic and continuous cooling is required within the absorber.

$$3\,NO_2 + H_2O \rightarrow NO + 2\,HNO_3$$
$$\Delta H_{298} = -6.8\text{ kcal/mol } (-28.6\text{ kJ/mol}) \quad (22\text{-}27)$$

The nitric acid produced in the absorber contains dissolved nitrogen oxides and is then bleached by the secondary air.

The overall reaction is:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$
$$\Delta H = -98.7\text{ kcal/mol} \quad (22\text{-}28)$$

Several process variations are described in Reference 91.

Catalysts. The catalyst typically consists of several woven or knitted wire gauze sheets with a composition of about 90 percent platinum, 5 percent rhodium, and 5 percent palladium. The primary functions of rhodium are to add mechanical strength to the gauze and to improve yield. The palladium is present to replace a portion of the more expensive rhodium.[91] Figure 22.16 shows that conversion efficiency does not improve if more than 5 percent rhodium is present in the catalyst.[143]

Catalyst life depends on several variables. High-pressure oxidation operations (which also operate at higher temperatures, per Table 22.16) require more frequent catalyst regeneration. The presence of trace amounts of iron, calcium, MoS_2 (lubricants), and phosphorus in the ammonia feed has been shown to shorten catalyst life. Deposits of iron oxides tend to catalyze the conversion of ammonia and oxygen to nitrogen and water, rather than to nitric oxide. These effects, as well as poor ammonia–air mixing and poor gas distribution across the catalyst, may reduce the yield by up to 10 percent.[91,97]

Some weight loss due to catalyst erosion and vaporization occurs and is more pronounced at the higher converter temperatures that are employed in the higher-pressure processes. Lost catalyst is usually recovered by "getter" systems that use palladium alloy gauzes and recover 60 to 80 percent of the lost catalyst. The "getter" gauze is placed as close to the platinum catalyst pack as possible so that the catalyst components can be recovered while they are in the vapor form. Although pure palladium is the most effective "getter", it becomes too brittle so a palladium alloy is used. Additional catalyst is recovered during periodic cleaning of the ammonia oxidation

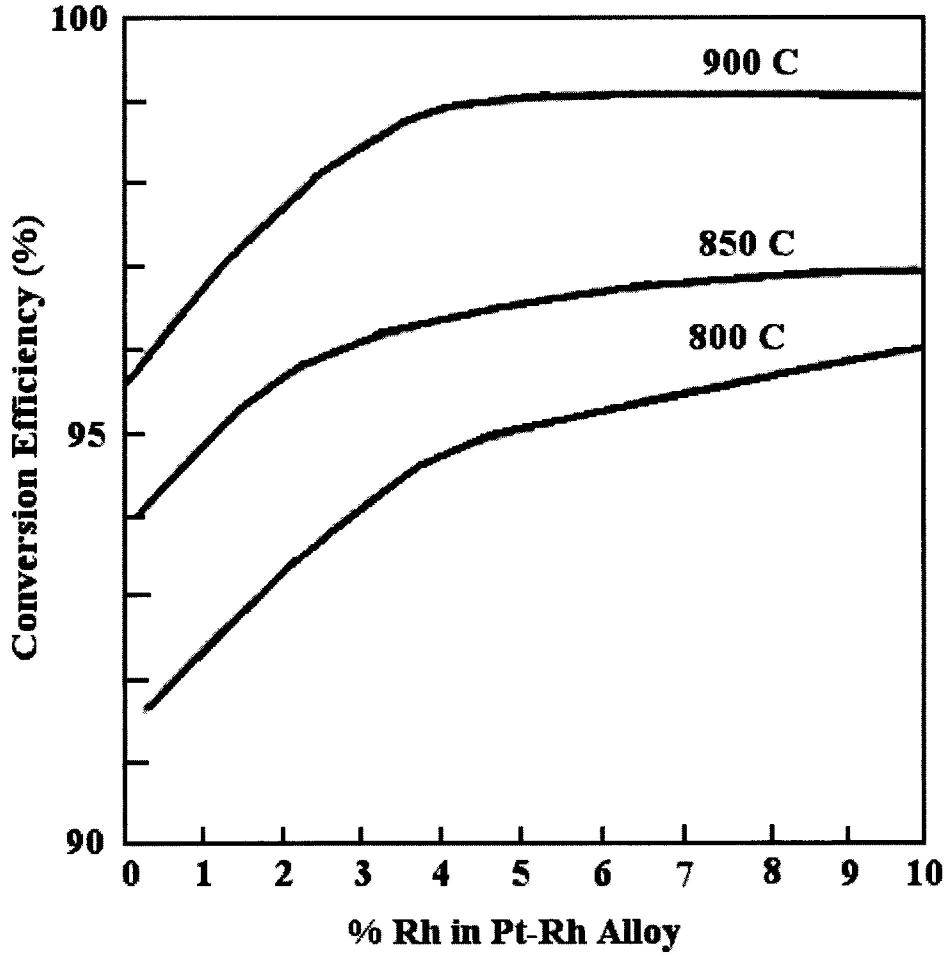


Fig. 22.16. Effect of rhodium content on catalyst efficiency.

reactor and during cleaning of downstream heat exchangers.[91,97]

When the catalyst pack no longer provides the desired reaction rates or product composition, new sheets of catalyst may be added to the old sheets. Or the old sheets may be replaced by a set of new sheets, and the old sheets sent back to the supplier to be refurbished. If any catalyst that is lost from the gauze is trapped in the downstream filter or recovered during equipment cleaning, it is also returned to be reprocessed.[91]

U.S. Patent 6,073,467 was issued in 2000 for a three-dimensional, knitted, noble metal gauze for nitric acid production. This catalyst design claims to provide elevated product yields and longer catalyst service life with the small noble metal losses.

Operating Pressure. All nitric acid plants are based on the same basic chemical operations: oxidation of ammonia with air to give nitric oxide, oxidation of the nitric oxide to nitrogen dioxide, and absorption in water to give a solution of nitric acid. The efficiency of the first step is favored by low pressure whereas that of the second step is favored by high pressure. Therefore both single-pressure and dual-pressure nitric plants are operating.[97]

In the single-pressure plant, the oxidation and absorption steps take place at essentially the same pressure. In dual-pressure plants, absorption takes place at a higher pressure than the oxidation stage. The oxidation and absorption steps can be classified as:[97] low pressure (below 1.7 bar), medium pressure (between 1.7 and 6.5 bar), and high pressure (between 6.5 and 13 bar).

The main unit operations in nitric acid plants are:[97] ammonia evaporation, ammonia filtration, air filtration, air compression, air/ammonia mixing, catalytic reaction of ammonia and air, energy recovery by steam generation and/or gas reheating, gas cooling, dual pressure only→NO_x compression, absorption with nitric acid production, and tail gas energy recovery.

Most new plants built in the 1990s have a dual-pressure design. Ammonia oxidation is operated at a medium pressure and absorption is operated at a high pressure. High-pressure systems offer the advantage of lower capital costs (as much as 30% lower than some lower-pressure processes) and are preferred in the United States for this reason. Relative disadvantages are higher catalyst loss and lower ammonia conversion. Lower-pressure oxidation designs have the best efficiencies in ammonia conversion and catalyst conservation. These plants have been preferred in Europe and other areas where ammonia has been relatively expensive and where allowable payout times have been longer.[91]

The single-pressure design (see Fig. 22.17) is generally used in smaller plants or in larger plants where minimization of capital is a critical design consideration. Ammonia oxidation and absorption of NO_2 occur at the same relative pressure. This reduces the complexity and capital cost compared to the dual-pressure plant. However, efficiency may be lower in both the front and back ends of the plant. Single-pressure plants can be designed to operate at low to medium pressure to favor the ammonia oxidation reaction, at high pressure to favor the absorption reactions, or at any operating pressure in between.[99]

The dual-pressure design (see Fig. 22.18) is generally use in larger plants, or in mid-size plants where higher utility/raw material costs dictate a minimization of operating expense. Ammonia oxidation occurs at low or medium pressure. The result is an increase in efficiency of the ammonia oxidation reaction and lower catalyst loss. Absorption of NO_2 occurs at high pressure to maximize the partial pressure of the gas reactants. A nitrous gas compressor boosts the pressure from the front end of the process (ammonia oxidation) to the back end (absorption).[91]

In Table 22.18 the raw material and utility consumption figures are given for both single- and dual-pressure processes.[99]

One type of NOx abatement system, the DCN (**D**estruction by **C**atalysis of **NO**$_x$) reactor is shown in Figure 22.19.[99]

Concentration of Nitric Acid. Most production of concentrated nitric acids (i.e., greater than the azeotrope of 68.4%) is based on weak acid hydration via extractive distillation with a drying agent. Common drying agents are sulfuric acid and magnesium nitrate.[91, 220]

A process exists that can directly produce concentrated nitric acid from dehydrated and concentrated nitrogen dioxide, weak acid, and oxygen. Generally the process operates at high pressure and follows these chemical reactions:[91]

$$2\,NO_2 \rightleftarrows N_2O_4 \qquad (22\text{-}25)$$

$$N_2O_4 + H_2O + \tfrac{1}{2}\,O_2 \rightarrow 2\,HNO_3 \qquad (22\text{-}28)$$

Few U.S. plants employ this method for production of concentrated acid. Most production of concentrated HNO_3 (i.e., concentrations above the azeotrope) is based on weak-acid dehydration via distillation with a drying agent. The most common dehydrators have been concentrated sulfuric acid and magnesium nitrite.[91]

An example of the dehydration process is the Kvaerner Chemetics process that uses concentrated sulphuric acid to eliminate the azeotrope and enable colorless, strong nitric acid up to 99 percent to be distilled from the mixed acids. The residual acid leaving the bottom of the processing tower is approximately 70 percent sulphuric acid.[101]

Alternative methods of integrated concentration have been developed that do not require separate dehydrating agents. These processes differ from the direct process in that weak acid reacts with concentrated nitrogen dioxide to produce an acid that is sufficiently

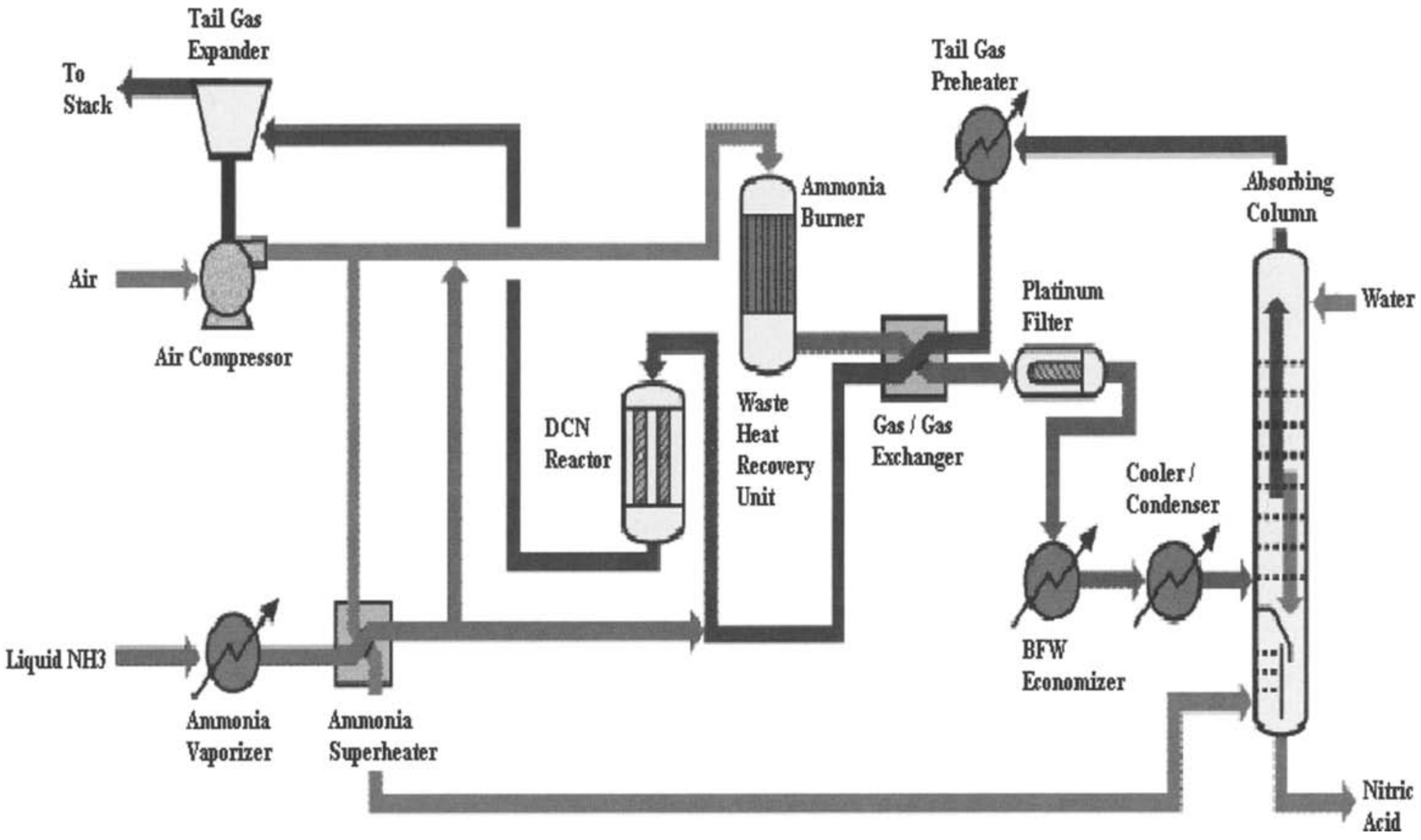


Fig. 22.17. Single pressure nitric acid plant, (Reproduced by permission of Monsanto Enviro-Chem Systems, Inc.)

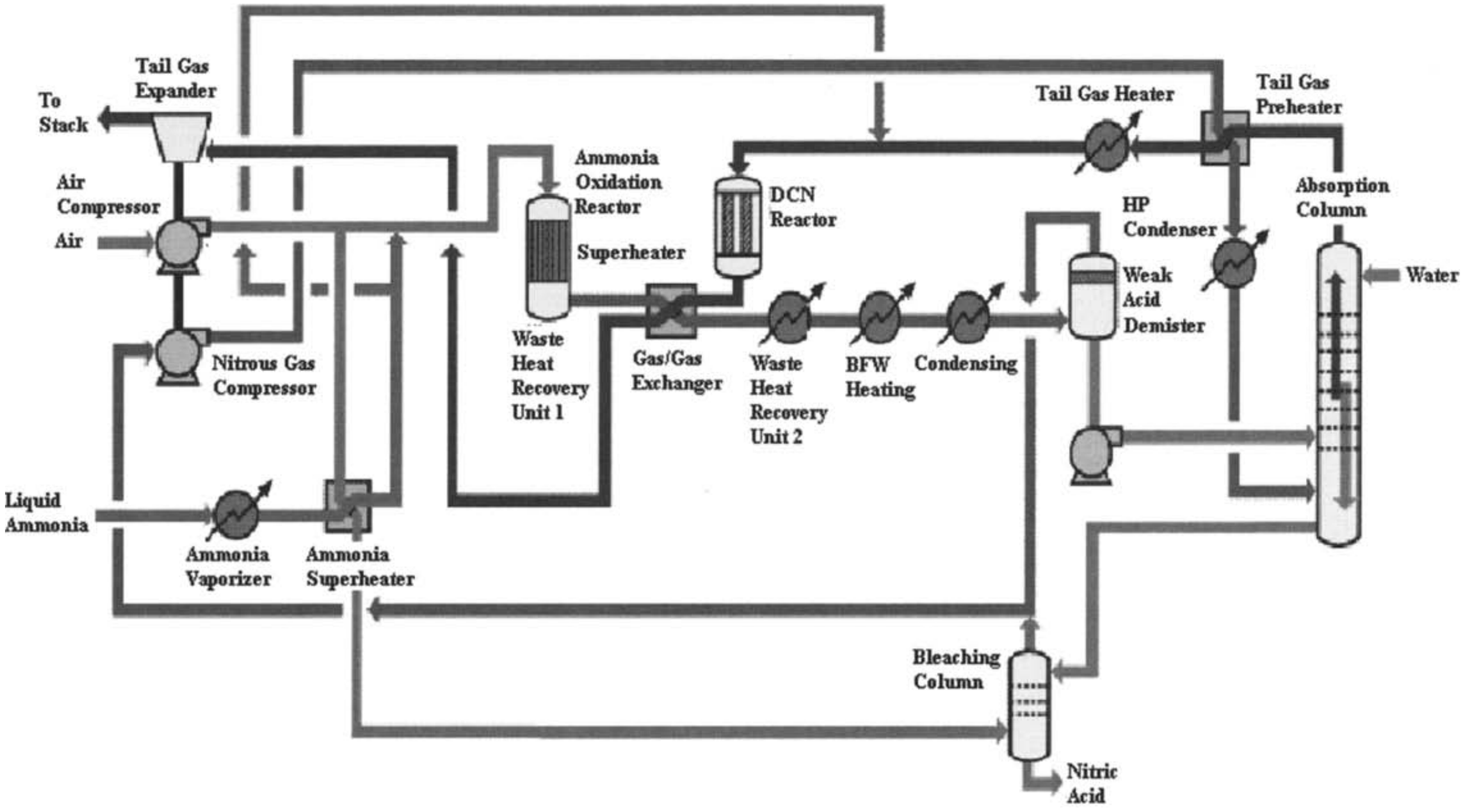


Fig. 22.18. Dual-pressure nitric acid plant. (Reproduced by permission of Monsento Enviro-Chem System, Inc.)

TABLE 22.18 Raw Material and Utility Consumptions in Different Nitric Acid Plant Designs

		H&H	*M&M*	*M&H*
Operating pressure	(Bar-a)	11	9	4.5/12
Typical run time	(Days)	70	120	210
Ammonia usage[a]	(ton/ton)	0.291	0.285	0.279
Platinum usage[b]	(mg/ton)	50	35	30
Power usage[c]	(kW-hr/ton)	1	2	2
HP steam export[d]	(ton/ton)	0.51	0.60	0.54
LP steam import[e]	(ton/ton)	0.27	0.21	−0.06
Cooling water[f]	(m^3/ton)	130	120	110

[a] Includes catalytic NOx abatement to 200 ppmv and average ammonia conversion efficiency over the entire gauze run length.

[b] Described as net of platinum recovery systems.

[c] Add 25 kW for HVAC, lighting and instrumentation.

[d] Steam conditions are 42 kg/cm^2 g and 400°C.

[e] Steam conditions are saturated at 3.5 kg/cm^2 g.

[f] At 11°C temperature rise and 2.5 kg/cm^2 pressure allowance.

Source: Reproduced by permission of Monsanto Enviro-Chem Systems, Inc.

superazeotropic that distillation into concentrated acid is economically feasible. The weaker azeotropic acid may be recycled for concentration or used as it is.[91] The magnesium nitrate process is described in Reference 104.

Uhde developed another process for the production of highly concentrated nitric acid (98 to 99%) that uses oxygen but no dehydrating agents. The NO from ammonia oxidation is converted to NO_2 by highly concentrated HNO_3. The NO_2 is cooled with brine, and after removal of the residual water, it is physically absorbed in chilled, highly concentrated nitric acid. Then the NO_2 is separated from the concentrated nitric acid in a distillation column and liquefied by refrigeration. The liquid NO_2 is dimerized in a $N_2O_4/HNO_3/H_2O$ mixture that reacts with supplemental oxygen at a pressure of about 720 psi to form highly concentrated nitric acid. The acid that leaves the reactor contains about 20 percent dissolved N_2O_4, which is separated in a distillation column and returned to the reactor. The concentrated nitric acid product is bleached and sent to storage, and a portion is recycled to the absorber.

Stabilizers. Over a period of time, concentrated nitric acids tend to decompose according to reaction (22-29) and pressure will build up in storage vessels:

$$HNO_3 \rightarrow 4\,NO_2 + H_2O + O_2 \qquad (22\text{-}29)$$

Because nitric acid is also very corrosive, some stabilizers and/or corrosion inhibitors are used.

Corrosion of aluminum by red fuming nitric acid is reduced by adding 4 percent by weight of hydrogen fluoride. Decomposition of concentrated acid is reduced by such substances as quaternary ammonium compounds, organic sulfones, inorganic persulfates, and organic sulfonium compounds.[102]

Pollution Abatement. The primary pollution problem in nitric acid plants is the abatement of NOx in tail gases. The processes that have been developed to reduce emissions at existing and new plants can be classified into four general categories: absorption, adsorption, selective catalytic reduction, and nonselective catalytic reduction.[91,104]

The main environmental factor that affects nitric acid process selection is the concentration of NOx in the tail gas. In the United States, gaseous emissions from newly constructed nitric acid plants are limited to 1.5 kilograms NOx per tonne of nitric acid produced with a maximum opacity of 10 percent.

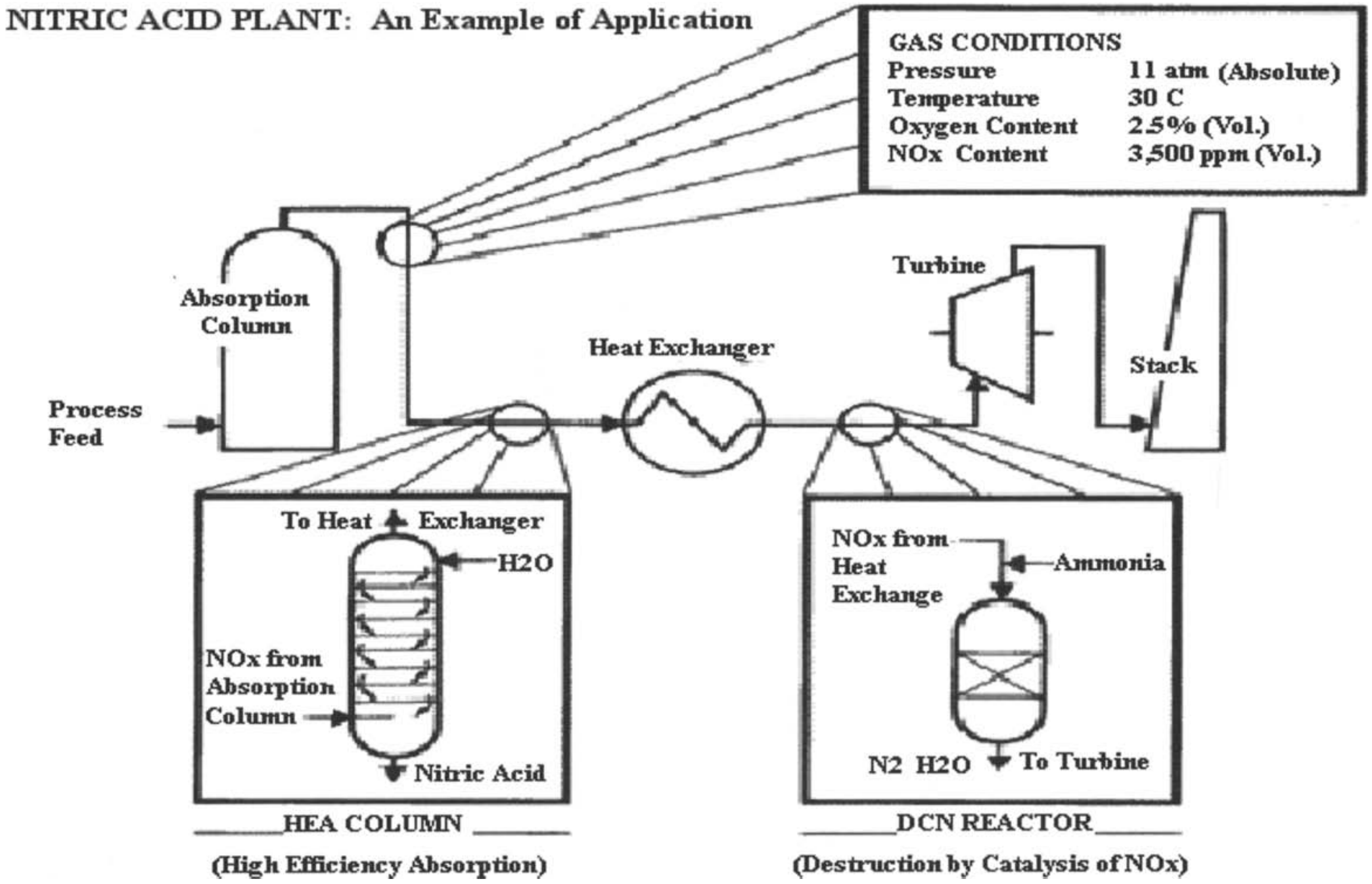


Fig. 22.19. NO_x abatement system with DCN (Destruction by Catalysis of NO_x). (Reproduced by permission of Monsanto Enviro-Chem System, Inc.)

In Western Europe, NOx emissions are limited by EU regulations to 200 ppm.[91]

Absorption abatement refers to modifications that involve the addition of increased absorption capacity or optimization of the existing absorption system.[91]

Adsorption abatement uses acid-resistant molecular sieves to absorb the NOx from the tail gas. The adsorbant is periodically regenerated and the NOx recovered, converted to NO_2 and recycled for recovery as nitric acid.[91]

Selective catalytic reduction is normally used in new nitric acid plants. In this process ammonia reacts with nitric oxide and nitrogen dioxide but to a lesser extent with oxygen to selectively reduce the NOx compounds to N_2[97, 104] as shown below:

$$6\,NO + 4\,NH_3 \rightarrow 5\,N_2 + 6\,H_2O \qquad (22\text{-}30)$$

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O \qquad (22\text{-}31)$$

$$3\,O_2 + 4\,NH_3 \rightarrow 2\,N_2 + 6\,H_2O \qquad (22\text{-}32)$$

Nonselective abatement uses a catalyst and fuel (usually a gaseous hydrocarbon) to reduce nitrogen oxides to nitrogen and combust any remaining free oxygen in the tail gas. This process consumes significantly more fuel than a selective reduction system, but the energy from burning the fuel is mostly retrieved as power in an expander.[104]

The gas at the outlet of the absorber may vary within the following limits during stable operation: NOx = 100 to 3500 ppmv, N_2O = 300 to 3500 ppmv, O_2 = 1.5 to 4 percent by volume, H_2O = 0.3 to 2 percent by volume, flow = 3100 to 3400 Nm^3/tonne of HNO_3.

The minimum emission levels achieved in 2001 without added pollution abatement are:

- Medium Pressure Absorption: 1000 to 2000 ppmv
- High Pressure Absorption: 100 to 200 ppmv

Whereas a dual-pressure plant or a high-pressure, single-pressure plant (with high pressure absorption) may give acceptable emission levels, the medium-pressure absorption plant must be followed by an abatement system.[97]

Monsanto Enviro-Chem offers NOx abatement technology that is licensed from Rhodia of France. It includes a high efficiency absorption (HEA) section for extended absorption and a catalytic reduction section (SCR) for catalytic destruction of NOx (i.e., the DCN technology).[99] Additional process details are given in Reference 99. The operating conditions for the steps in the Monsanto technology are compared in Table 22.19.

Production. An estimated 65 percent of the worldwide nitric acid production is used to make ammonium nitrate (AN) for use in fertilizers. Other AN uses (mainly explosives) account for about 15 percent of the market. The balance is consumed in a variety of non-AN industrial applications. The production of AN fertilizers and most industrial explosives require acid concentrations less than the azeotropic concentration of 68.4 percent.

TABLE 22.19 Operating conditions in NOx Abatement Systems

		DCN[a] Only	*HEA Plus DCN*	*HEA[b] Only*
NOx gas to HEA	ppmv	N/A	3,500	3,500
NOx gas to DCN	ppmv	3,500	700	N/A
NOx gas to turbine	ppmv	200	200	200
Nitric acid recovered	kg/ton–HNO_3	N/A	27	31
Ammonia consumed	kg/–HNO_3	8.5	1.3	N/A
Gas temperature rise	°C	43	6.5	0
Pressure drop	kg/cm^2	0.07	0.2	0.35
Capital cost	Ratio	1.0	2.5	3.5

[a] DCN: Destruction of Catalysis of NO_x.
[b] HEA: High efficiency absorption.
Source: (Reproduced by permission of Monsanto Enviro-Chem Systems, Inc.)

World nitric acid production in 1999 is estimated to be 53 million tonnes per year. Captive use consumes most of the production, and the merchant market probably involves only about 10 percent of the total.[91]

World demand for nitric acid will continue to be largely dependent upon demand for solid ammonium nitrate fertilizer and nitrogen fertilizer solutions that incorporate ammonium nitrate. Since the 1980s urea has been replacing solid ammonium nitrate as a fertilizer. This has been partially offset by increased use of AN in explosives, polyurethane foams, and nylon 6,6. World nitric acid production declined by about 5 percent between 1987 and 1999, but it is projected to increase marginally by 2005. The major producing regions are Western Europe, the United States, the former Soviet Union (FSU), and Eastern Europe.[91,104]

Nitric acid is sold commercially in various concentrations that are expressed in degrees Baumé (Be) which is an alternate specific gravity scale. Various grades of concentrated or fuming nitric acid (95% or more HNO_3/NO_2) are available.[91,104]

Storage and Distribution. Nitric acid is normally stored in flat-bottomed, roofed tanks that are made from low-carbon, austenitic stainless steel. Most concentrations of nitric acid are transported in tank cars and by truck. Stainless steel is necessary for concentrations up to 80 to 85 percent. Stronger solutions are less corrosive and may be stored in aluminum.

In the United States the Department of Transportation (DOT) defines three categories of nitric acid: nonfuming, more than 70 wt.% acid; nonfuming, less than 70 wt.% acid; and red fuming nitric acid. All must be labeled "corrosive".

Nitric acid is subject to self-decomposition, depending on the concentration and temperature. The general rule is: the higher the concentration or the temperature, the faster the decomposition rate. Nitric acid must be transported from the manufacturer to the user within the shortest possible time, particularly in the summer months.[97]

Uses of Nitric Acid

Some of the major uses for nitric acid are:

- *Ammonium Nitrate (AN):* Production for fertilizers and explosives.
- *Adipic Acid:* Nitric acid oxidizes cyclohexanone-cyclohexanol mixtures to adipic acid, which goes into nylon 6,6, other resins and plasticizers.
- *Nitrobenzene:* Nitrobenzene is made by the direct nitration of benzene with nitric/sulfuric acid mixtures.
- *Toluene Diisocyanate (TDI):* Toluene diisocyanates (2,4- and 2,6 isomers) are produced from toluene diamine derived from dinitrotoluene, which is produced by the nitration of toluene with nitric/sulfuric acid mixtures. TDI is used mainly in polyurethane foams.
- *Potassium Nitrate:* Production for tobacco fertilizer and industrial markets.
- *Sodium Nitrate:* Production for fertilizers, explosives, and as a heat transfer medium.

Some of the other uses for nitric acid are: other metal nitrates, in the steel industry, in the electronics industry, to make nitrochlorobenzene, cellulose nitrate, in several nitrate paraffins (e.g., nitromethane, nitroethane, and nitropropane), in non-military explosives, to digest crude uranium concentrates, in mixed fertilizers, and in concentrated nitric acid.

AMMONIUM NITRATE

Ammonium nitrate (AN) was first prepared in the sixteenth century. Its early industrial development was primarily for use in explosives. However, after 1940 its use as a fertilizer developed rapidly. It is made by the reaction of gaseous ammonia with aqueous nitric acid:

$$HNO_3(l) + NH_3(g) \rightarrow NH_4NO_3(aq) \qquad \Delta H = +26 \text{ kcal/g-mol} \qquad (22\text{-}33)$$

The resulting AN solution may be handled in various ways.[103] It can be stored as a solution, used in downstream plants or sold as a solution; it can be formed into solid AN by prilling or granulation; or it can be mixed with a solid filler. The most common filler is calcium carbonate in the form of ground limestone, dolomite, or byproduct calcium carbonate. This product is known as calcium ammonium nitrate (CAN) and can be prilled or granulated.

Processes

As shown in Figure 22.20,[295] the typical AN production process has three main unit operations: neutralization, evaporation, and solidification (prilling and granulation).[103,105] Additional details about AN production are given in Reference 107.

Neutralization. The exothermic neutralization of nitric acid with ammonia gas produces AN solution and steam. The nitric acid is commonly preheated if the available concentration of nitric acid is in the lower end of the 50 to 70 percent range.[103]

Neutralization can be performed in a single stage or in two stages. A two-stage neutralizer operates with a low pH in the first stage and a neutral pH in the second stage. In most neutralizers the pressure, temperature, and concentration are linked by the boiling point characteristics of AN solutions with only two of these variables being independent.[103]

Neutralizers may be free-boiling vessels, circulating systems, or pipe reactors. The water in the nitric acid is evaporated by the heat of reaction (550 to 620 BTU/lb of AN, depending on the acid strength). At least ten different types and designs of neutralizers are used in Europe. The factors that influence the choice of neutralizer design are described in Reference 103. Different neutralizer designs are discussed in References 226, 227, and 295.

Steam Purification. The steam that leaves the neutralizer can be purified, or it can be condensed and then purified. Some steam purification techniques are described in Reference 103. The steam may be used in the evaporator; be used to preheat and evaporate ammonia, or be used to preheat the nitric acid.[103]

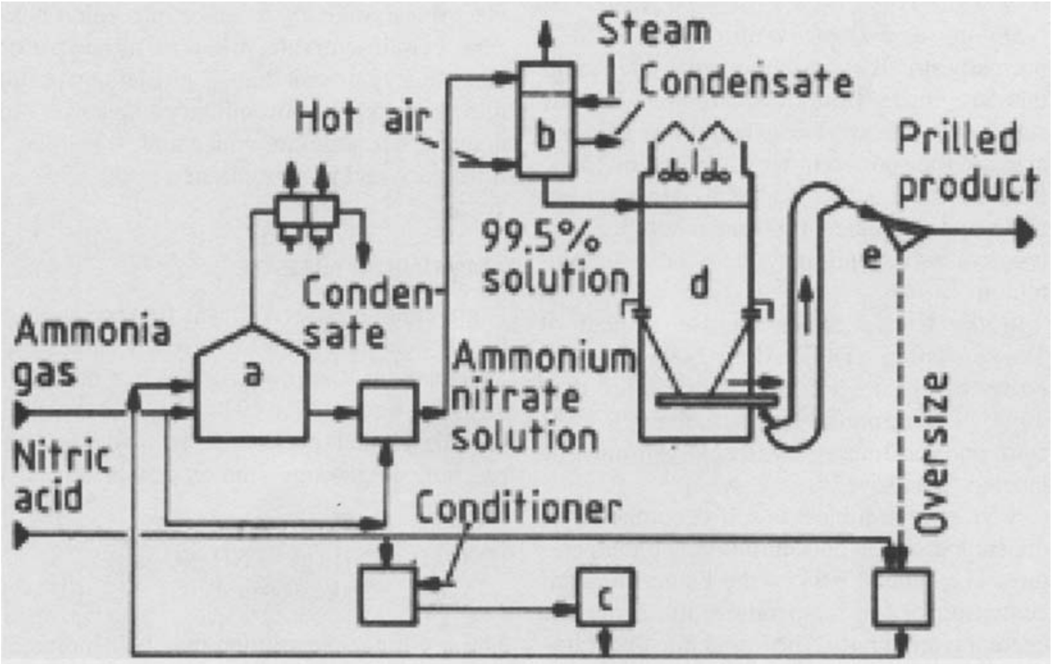


Fig. 22.20. Ammonium nitrate process sketch. (Courtesy of Wiley-VCH. 295. Zapp, K.H.., Ammonium Compounds, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., Weinheim, Germany, June 15, 2000.)

Evaporation. The evaporator is normally needed to remove water from the AN solution. It must produce a solution with the required concentration at a temperature that avoids crystallization. The acceptable water content is normally below 1 percent for a prilled product and up to 8 percent for the feed to some granulation processes. Evaporators in commercial use include circulatory systems, shell and tube heat exchangers, and falling film-type evaporators.[103]

Prilling. Prilling refers to the formation of granules by the solidification of droplets of AN. The AN solution is concentrated to 96 to 99 percent at a pH above 4.5 to form a "melt". The melt may be mixed with an additive or nucleating agent that stabilizes the prills against temperature cycling through the crystal transition phases. Then the melt is transported to the top of the prilling tower and sprayed through a system of fixed orifices or dropped through a rotating perforated bucket into a rising air stream. The droplets crystallize into hard spherical "prills" that are dried, cooled, and sized for shipment. If calcium ammonium nitrate (CAN) is made, ground calcium carbonate (limestone or dolomite) is added to the melt prior to the formation of the droplets.[103,105,240]

SASOL in South Africa produces a porous, prilled ammonium nitrate (PPAN) that finds its widest application in a mix with fuel oil. This mixture is used as an explosive and is commonly known as ANFO (**A**mmonium **N**itrate **F**uel **O**il). Additional details about PPAN are given in Reference 106.

Granulation. Granulation refers to techniques using processes such as agglomeration, accretion, or crushing to make a granular fertilizer. In contrast to the prilling technique, granulation requires a more complicated plant and a variety of equipment is used: rotating pans and drums, fluidized beds, and other equipment. Granular products can be made in a wider choice of particle sizes than prills.[103]

The AN is added in the granulator as a spray of hot concentrated solution. No further drying of the granules will normally be required. The granules are screened and the fines and crushed oversize returned to the granulator.[103]

Typical CAN granulators include drums and pugmills. The calcium carbonate may be mixed with the AN solution before granulation or in the granulator itself. Granules from this process will normally require drying in a fluidized bed or rotary drier.[103]

Air Abatement Equipment. Emissions from the prilling and granulation sections of AN and CAN plants can be treated by a range of abatement equipment. Particulate material from some granulation plants is relatively coarse in particle size, whereas the prill tower emissions contain very fine particles. Candle filters are normally required for prill tower emissions. They can abate particulate emissions down to 15 mg/m^3 of air. For coarser material dry devices such as bag filters or dry cyclones are used. Particulate emissions can have higher concentrations, perhaps up to a range of 30 to 50 mg/m^3, but the recovered material is a solid that can more readily be recycled.

Production

Production of fertilizer grade AN is concentrated mainly in Europe and North America. In 2001 U.S. production was 7.1 million tons, which was 18 percent lower than the peak production in 1998. U.S. plants were operating at 70 percent of nameplate capacity in 2001.[240] International trade amounts to about 4 million tonnes (on a nitrogen equivalent basis) per year. Additional information can be found in Chapter 24, "Fertilizers."

Some of the physical and chemical properties of ammonium nitrate are given in Table 22.20.[103]

Storage and Distribution. Solid AN in packages must be stored in a general warehouse that has been approved for AN duty. Bulk AN and CAN must be protected from moisture as both products are hygroscopic. Large bulk warehouses may be air-conditioned

TABLE 22.20 Ammonium Nitrate Physical and Chemical Properties

Property		
Appearance	White or off-white granules or prills	
Odor	Odorless	
pH (10 g/100 ml)	>4.5	
Melting point	160°C to 170°C (depending on moisture content)	
Decomposition point	>210°C	
Molecular weight	80.05	
Solubility in water		
	0°C	118.3 g/100 g
	20°C	190.0 g/100 g
	80°C	576.0 g/100 g
Bulk density		830 to 1100 kg/m³
Nitrogen content	35% (100% ammonium nitrate)	

due to the local climate. Some additives can also reduce the water uptake. The anticaking agents may be used that are internal to the finished particle or applied as a coating.[103,240]

AN solution must be stored at a temperature above the crystallizing temperature of the solution. Gaseous ammonia is normally added in small quantities to maintain the solution at the correct pH because AN solutions lose ammonia during storage.[103] Steps should also be taken to avoid contamination by decomposition catalysts such as chlorides and organic materials.

Ammonium nitrate decomposes in two ways. Controlled decomposition with careful heating is the commercial process for producing nitrous oxide:

$$NH_4NO_3 \xrightarrow{200°C-260°C} N_2O + H_2O$$
$$\Delta H = -6.7\ \text{kcal/g-mol} \qquad (22\text{-}34)$$

Explosive decomposition by heating or by explosive shock is the basis for its use as an explosive:

$$2\,NH_4NO_3 \rightarrow 2\,N_2 + 4\,H_2O + O_2$$
$$\Delta H = -28.2\ \text{kcal/g-mol} \qquad (22\text{-}35)$$

The oxygen that is released in Reaction (22-35) can be used to more than triple the explosive effects by mixing an organic, such as fuel oil, with AN. This mixture, known as ANFO, is much cheaper and much safer to handle than dynamite:

$$3\,NH_4NO_3 + (CH_2)_n \rightarrow 3\,N_2 + 7\,H_2O + CO_2$$
$$\Delta H = -102.5\ \text{kcal/g-mol} \qquad (22\text{-}36)$$

UREA

Urea was discovered in 1773, and it was first synthesized from ammonia and cyanic acid in 1828.[108] In the early 1900s urea was produced on an industrial scale by the hydration of cyanamide, which was obtained from calcium cyanamide:[109]

$$CaCN_2 + H_2O + CO_2 \rightarrow CaCO_3 + CNNH_3 \qquad (22\text{-}37)$$

$$CNNH_3 + H_2O \rightarrow CO(NH_2)_2 \qquad (22\text{-}38)$$

After development of the ammonia process by Haber and Bosch in 1913, the production of urea from ammonia and CO_2 developed rapidly. In 2001 urea is prepared on an industrial scale exclusively by this method.[109]

$$\underset{\text{Ammonia}}{2\,NH_3} + \underset{\substack{\text{Carbon}\\ \text{Dioxide}}}{CO_2} \rightleftarrows \underset{\substack{\text{Ammonium}\\ \text{Carbamate}}}{NH_2COONH_4} \qquad (22\text{-}39)$$

$$\underset{\substack{\text{Ammonium}\\ \text{Carbamate}}}{NH_2COONH_4} \rightleftarrows \underset{\text{Urea}}{CO(NH_2)_2} + \underset{\text{Water}}{H_2O} \qquad (22\text{-}40)$$

Reaction (22-39) is fast and exothermic and essentially goes to completion under the high pressure reaction conditions. Reaction (22-40) is slower, is endothermic, and does not go to completion. The conversion (on a CO_2 basis) is usually 50 to 80 percent. The conversion increases with increasing temperature and NH_3/CO_2 ratio. It decreases with increasing H_2O/CO_2 ratio.[110]

When urea melt is subjected to heat, some biuret is formed.

$$\underset{\text{Urea}}{2\,CO(NH_2)_2} \rightleftarrows \underset{\text{Biuret}}{NH_2CONHCONH_2} + \underset{\text{Ammonia}}{NH_3} \qquad (22\text{-}41)$$

Biuret is undesirable for some industrial and fertilizer applications. Prilled urea normally contains more biuret (0.8–1.5%) than granular

TABLE 22.21 Physical Properties of Urea[108]

Chemical formula	NH_2CONH_2
Molecular weight	60.06
Freezing/melting point	132.6°C
Boiling point	Decomposes
Density, d_4^{20}	1.3230 g/cm^3
Heat of solution in water	+251 J/g (60 cal/g)
Bulk density	0.74 g/cm^3
Specific heat (J/(kg-K)	
0°C	1.439
50°C	1.661
100°C	1.887
150°C	2.109

Properties of Saturated Aqueous Solutions of Urea

Temperature (°C)	*Solubility in Water (g/100 g Solution)*	*Density (g/cm^3)*	*Viscosity (mPa-s = cP)*	*Water Vapor Pressure (kPa)*
0	41.0	1.120	2.63	0.53
20	51.6	1.147	1.96	1.73
40	62.2	1.167	1.72	5.33
60	72.2	1.184	1.72	12.00
80	80.6	1.198	1.93	21.33
100	88.3	1.210	2.35	29.33
120	95.5	1.221	2.93	18.00
130	99.2	1.226	3.25	0.93

urea because prilled urea goes through an extra evaporation step.

Urea is an odorless white solid that contains 46.65 percent nitrogen. It is not flammable, but it will melt and decompose in a fire to give off ammonia. When it is dissolved in water, it hydrolyzes very slowly to ammonium carbamate and eventually decomposes to ammonia and carbon dioxide. Some of the other properties of urea are given in Table 22.21.[108,110]

Processes

In 2001 most new urea plants are licensed by Snamprogetti (SNAM), Stamicarbon (STAC), or Toyo. SNAM utilizes thermal stripping whereas STAC and Toyo use CO_2 Stripping. At the end of 1996, about 70 SNAM plants, 125 STAC, and 7 Toyo plants had been built. STAC will design plants for over 3000 tonnes per day; SNAM designs plants for about 2800 tonnes per day; and Toyo designs plants for about 2300 tonnes per day as single train units.[108]

Because urea is made from ammonia and carbon dioxide, all urea plants are located adjacent to or in close proximity to an ammonia plant. Figure 22.21[111] shows an example of an ammonia plant and a urea plant that are part of the same complex.

The Snamprogetti (SNAM) process, the synthesis section of the Stamicarbon (STAC) process and the synthesis section of the Toyo-ACES (**A**dvanced **P**rocess for **C**ost and **E**nergy **S**aving) process are described in References 108 and 110. An updated version of the STAC process, Urea 2000plus, is offered by DSM (Stamicarbon's parent company).[108,110]

The **I**sobaric **D**ouble-**R**ecycle (IDR) urea process was developed by Montedison. In this process most of the unconverted material leaving the reactor is separated by heating and stripping at synthesis pressure using two strippers in series. The unconverted ammonia, CO_2, and carbamate in the urea solution are recycled to the synthesis loop.[108,110]

The **H**eat **R**ecycle **U**rea **P**rocess (HRUP) was developed by Urea Technologies in the 1970s and is offered by Monsanto Enviro-Chem. This

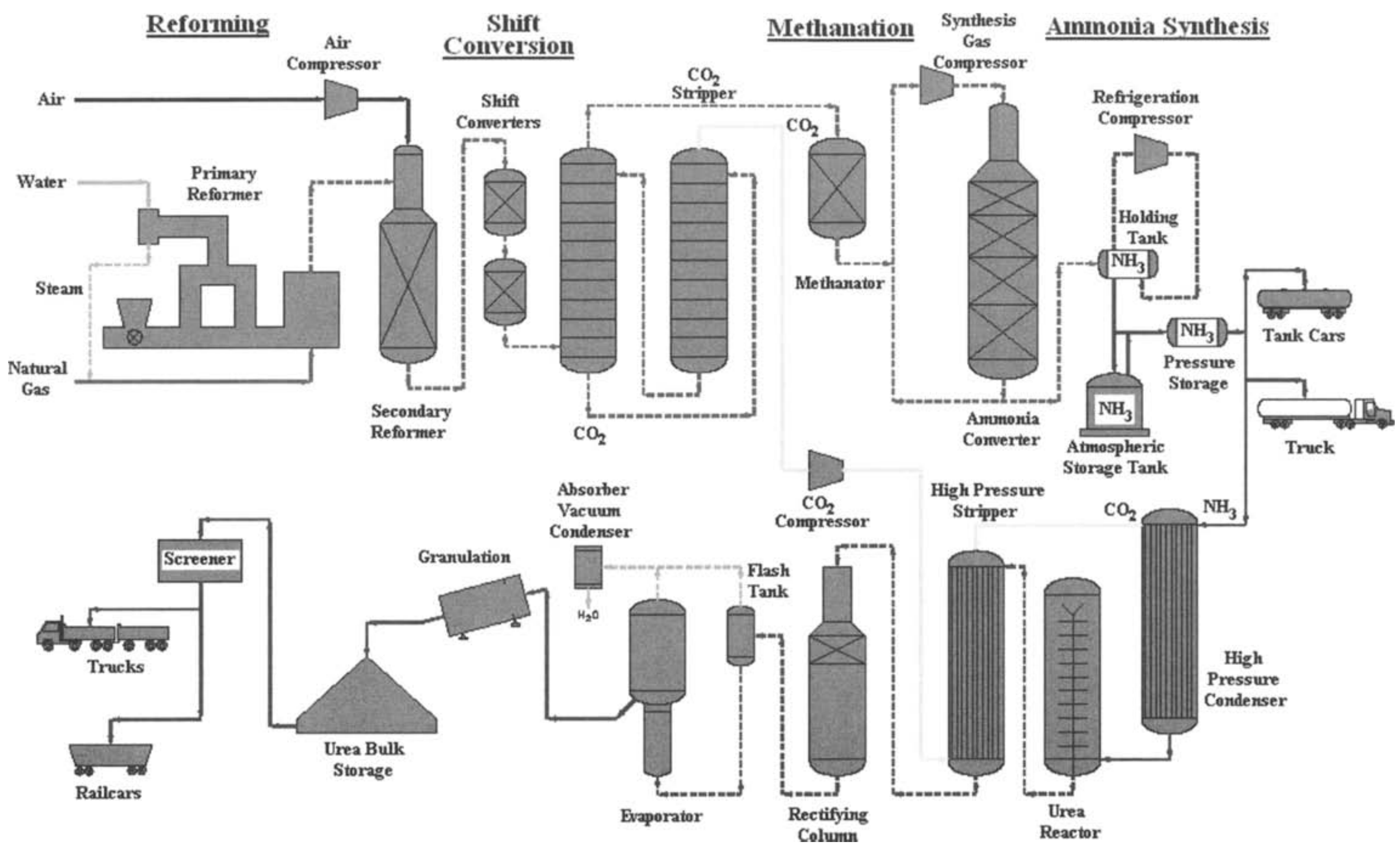


Fig. 22.21. Agrium's Carseland nitrogen operations: ammonia and urea production. (Agrium Carseland Nitorgen Operation, Carseland Alberta, Canada, 3/01. Image may not be duplicated or reproduced without the written permission of Agrium.)

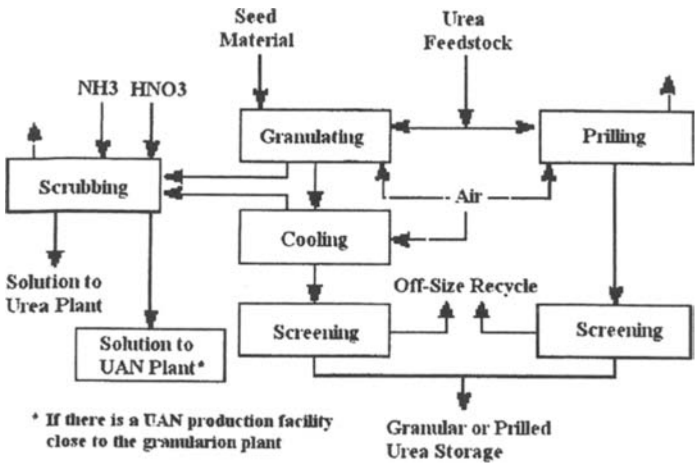


Fig. 22.22. Block diagram for urea granulation and prilling processes.[110] (Reproduced by permission of European Fertilizer Manufacturers Association.)

process is described in References 110 and 112. Several urea-producing reactors have been updated with Casale high efficiency trays. These trays increase conversion, which increases plant capacity and reduces energy use.[209]

Prilling. A prilling plant is show in Fig. 22.22 and is described in References 108 and 110.

Granulation. Almost all new plants that make granules use the Hydro-Agri process, which can be built to make over 3000 tonnes per day. The basic principle of the process involves the spraying of the melt onto recycled seed particles or prills circulating in the granulator. The process is described in more detail in References 108, 109 to 110.

Another process is the C&I Girdler drum system, but it cannot compete in today's market because of capacity restrictions. Toyo has developed a spouting-fluid bed technology and by 1996 three plants were in operation. Stamicarbon will also license a fluid-bed plant that is similar to the Hydro-Agri design.[108]

Production

The ammonia cost makes up 62 to over 70 percent of the cash production costs of urea as the natural gas cost varies from \$2.00 per million BTU up to \$6.00 per million BTU. In general urea cash production costs in dollars per tonne are a factor of 1.4 to 1.6 times the ammonia price in US dollars per tonne.[113] See References 36, 145, and 230 for details about urea production.

Storage and Distribution

Urea may be supplied as a solid or in a solution, and solid urea is classified as granular or prilled products. Prilled products have less desirable qualities than granules and are usually marginally cheaper than granulated product.[109]

The majority of urea is designated as fertilizer grade. Technical grade does not contain any additives. Low-biuret grade contains less than 0.3 percent biuret and is used on citrus crops. Feed grade is fed directly to cattle. It is free of additives and is supplied as microprills with a diameter of about 0.5 mm. Slow-release grades use coatings and additives to increase the amount of nitrogen absorbed by crops. Urea supergranules have diameters up to 15 mm and are used in wetland rice and forest fertilization.[109]

The shift from bagged to bulk transport and storage of prilled and granulated urea has called for warehouse designs in which large quantities of urea can be stored in bulk. Caking and subsequent product degradation at unloading are the result of water absorption.

To avoid these problems the warehouse should be airtight and thoroughly insulated. The caking can also be reduced by adding small amounts of formaldehyde (up to 0.6 wt%) to the urea melt or by adding surfactants to the solid product.[109]

Uses

Urea is used in:[113] liquid and solid fertilizers, urea-formaldehyde resins that make adhesives and binders mostly for wood products, livestock feeds, melamine for resins, and NOx control for boilers and furnaces.

MELAMINE

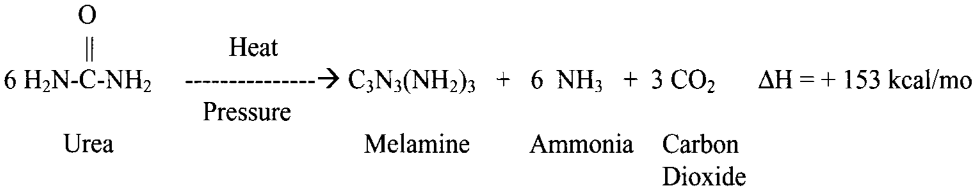
Melamine is characterized by its three amino ($-NH_2$) groups and by its 66.6 percent nitrogen content. Its chemical formula can be written as $C_3H_6N_6$ or $C_3N_3(NH_2)_3$. It was first prepared in 1834, but it was not until 1937 that it was produced commercially.

Some of the properties of melamine are listed in Table 22.22.[114]

Processes

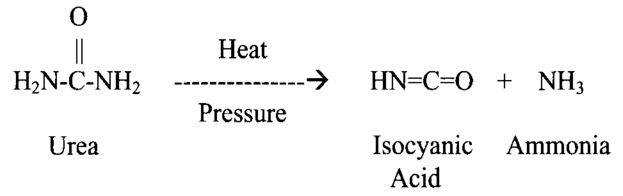
Melamine can be produced from urea, dicyandiamide, or hydrogen cyanide, but in 2001 all commercial-scale production is based on urea.[114]

Melamine is produced from urea by either a high- or a low-pressure process, and either process can consist of one or two stages. The net reaction is.[114]



$$6\,\underset{\text{Urea}}{H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2} \xrightarrow[\text{Pressure}]{\text{Heat}} \underset{\text{Melamine}}{C_3N_3(NH_2)_3} + \underset{\text{Ammonia}}{6\,NH_3} + \underset{\text{Carbon Dioxide}}{3\,CO_2} \quad \Delta H = +153\text{ kcal/mole} \qquad (22\text{-}42)$$

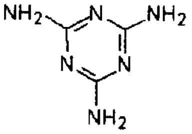
The reactions in the two-stage process are shown in Equations (22-43) and (22-44). The products are quenched with water or an aqueous mother liquor. This stream is then processed by filtration, in centrifuges, or by crystallization.[114]



$$\underset{\text{Urea}}{H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2} \xrightarrow[\text{Pressure}]{\text{Heat}} \underset{\text{Isocyanic Acid}}{HN{=}C{=}O} + \underset{\text{Ammonia}}{NH_3} \quad \Delta H = \sim 800\text{ kcal/kg Urea (endothermic)} \qquad (22\text{-}43)$$

$$\underset{\text{Isocyanic Acid}}{6\,HN{=}C{=}O} \xrightarrow{\text{Catalyst}} \underset{\text{Melamine}}{C_3N_3(NH_2)_3} + \underset{\text{Carbon Dioxide}}{3\,CO_2} \quad \Delta H = -1{,}100\text{ kcal/kg Urea (exothermic)} \qquad (22\text{-}44)$$

TABLE 22.22 Properties of Melamine

Appearance	Fine white crystalline powder
Molecular weight	126.13
Specific density (g/cc)	1.573
Melting point	354°C
Boiling point	Decomposes above 300°C and releases ammonia vapors
Bulk Density	750 kg/m^3
Toxicity	Mild/low
Stability	Stable
Solubility	Insoluble in most inorganic compounds Very soluble in water
Melamine structure	

In a typical high-pressure process such as the one licensed by Eurotecnica (see Figure 22.23 and www.eurotecnica.it/melamine.htm), the reaction is carried out in the liquid phase (without a catalyst) at 90 to 150 bar and 380°C to 450°C. Under these conditions, urea forms cyanuric acid which then reacts with ammonia to form melamine. The first step is the same as Equation (22-43) and the second step is shown in Equations (22-45) and (22-46).[46,114]

$$\underset{\text{Isocyanic Acid}}{3\,HN{=}C{=}O} \rightarrow \underset{\text{Cyanuric Acid}}{C_3N_3(OH)_3} \qquad (22\text{-}45)$$

$$\underset{\text{Cyanuric Acid}}{C_3N_3(OH)_3} + \underset{\text{Ammonia}}{3\,NH_3} \rightarrow \underset{\text{Melamine}}{C_3N_3(NH_2)_3} + 3\,H_2O \qquad (22\text{-}46)$$

In a typical low-pressure process, the reaction is carried out in the vapor phase at 1 to 10 bar and 350°C to 400°C. This process uses a catalyst such as modified aluminum oxide or aluminosilicate. Under these conditions urea forms isocyanic acid as shown in Equation (22-43). On the catalyst the isocyanic acid is converted to cyanamide or carbodiimide which is subsequently converted to melamine [see Equations (22-47) and (22-48)].[46,114]

$$\underset{\text{Isocyanic Acid}}{2\,HN{=}C{=}O} \rightarrow (\underset{\text{Carbodiimide}}{HN{=}C{=}NH} \text{ or } \underset{\text{Cyanamide}}{H_2N{-}C{\equiv}N}) + \underset{\text{Carbon Dioxide}}{CO_2} \qquad (22\text{-}47)$$

$$(\underset{\text{Carbodiimide}}{HN{=}C{=}NH} \text{ or } \underset{\text{Cyanamide}}{H_2N{-}C{\equiv}N}) \rightarrow \underset{\text{Melamine}}{C_3N_3(NH_2)_3} + \underset{\text{Carbon Dioxide}}{CO_2} \qquad (22\text{-}48)$$

Carbon dioxide and ammonia are obtained as byproducts in both the low- and high-pressure processes and are usually recycled to the urea process to improve process economics. With recycling, about 1.5 pounds of urea are used to produce one pound of melamine which corresponds to a yield of 95 percent (compared to a yield of only 49% without recycle).[114]

DSM Melamine started up a new 30,000-tonne per year melamine plant in 2004 and reached design capacity in 2006. This plant will use the high-pressure shortened liquid phase (SLP) process developed by DSM. The SLP process is expected to increase efficiency by 25 percent and have the same costs as a 100,000 tonne/year production facility. The new process requires only 3 or 4 processing steps, in contrast to the 10 steps in conventional processes.[115]

The major melamine process technologies and the suppliers of these technologies are listed in Reference 114.

Production

In 2001 worldwide capacity was 1.1 million tons per year.[234] In 1998, Western Europe accounted for 35 percent of world capacity, followed by Asia (excluding Japan) with 24 percent and both the United States and Japan with 16 percent each.[114] Demand for melamine is heavily influenced by construction and auto manufacture.[114]

Uses

Melamine is supplied in bags, carlots, and truckloads. Some of the melamine uses are: surface coatings, laminates, paper treating, molding compounds, textile treating, wood adhesives, and other uses such as ceiling tiles, tire cord, flame retardants, and many other small-volume applications.[114,236]

ALIPHATIC AMINES

Amines are derivatives of ammonia in which the hydrogen atoms in the ammonia have been displaced by monovalent hydrocarbon radicals. Depending on the number of hydrogen atoms displaced, amines are classified as primary (RNH_2), secondary (R_2NH), or tertiary (R_3H). The amines can be categorized further according to the type of hydrocarbon radicals that substitute for the hydrogen atoms:

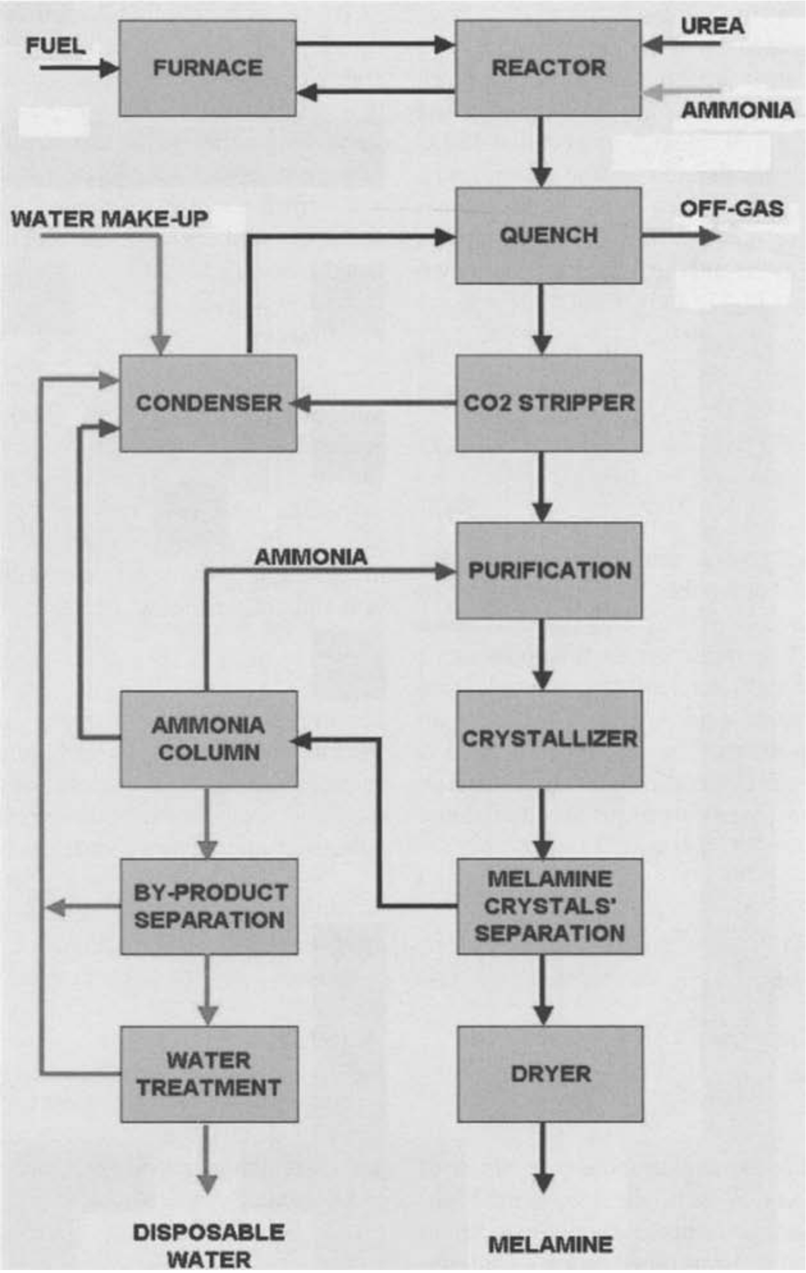


Fig. 22.23. Eurotecnica high-pressure melamine process. (Reproduced by permission of Eurotecnica.)

aliphatic (saturated or unsaturated), aromatic, heterocyclic, alicyclic, or any combination of these.

Imines are one group of compounds that are similar to amines. Imines contain an ammonia molecule in which two hydrogen atoms are displaced by bivalent hydrocarbon radicals (R = NH). Another group of compounds that are similar to amines is nitriles. In nitriles all the hydrogen atoms in ammonia are displaced by a trivalent hydrocarbon radical (RC ≡ H).

Methylamines

Methylamines are colorless liquids that are volatile at normal atmospheric conditions. They have threshold odor limits of less than 10 ppm, and at low concentrations they have a fishy smell. At high concentrations they smell like ammonia. The physical properties are given in Tables 22.23 and 22.24.

Conventional Processes. The reaction of an alcohol with ammonia provides the most common commercial routes to alkylamines. Capacities of many plants depend on the product mix of mono/di/tri products as well as the variety of amines (ethyl, propyl, and butyl).[116]

In alcohol amination, methanol and excess ammonia react at 350°C to 500°C and 15 to 30 bar in the presence of aluminum oxide, silicate, or phosphate catalysts according to the following reactions.[46]

Although companies can produce a range of C_2 to C_6 amines on a campaign basis in a higher alkylamine plant, methylamine plants are usually designed and dedicated solely for production of a given chain-length product. The methylamine plants also use a different catalyst from that in a higher amines plant.[116]

Mitsubishi Rayon has operated a process since 1984 in which the equilibrium of methylamine formation is shifted to make more dimethylamine by use of an acid zeolite catalyst. The product stream contains 7 mol% MMA, 86 mol% DMA, and 7 mol% TMA, and the investment as well as the operating costs are lower than the conventional Leonard process that is used by most companies. Because DMA has the highest sales volume, the process might be appealing.

Aldehyde–Amine and Ketamine Hydrogenation Process. Imines can be produced by the addition of ammonia to a carbonyl compound, and the imines are hydrogenated to make amines per Reaction (22-55):[116]

$$NH_3 + CH_3OH \xrightarrow{Cat} CH_3NH_2 + H_2O \quad \Delta H = -5.358 \text{ kcal/mol} \tag{22-49}$$

$$CH_3NH_2 + CH_3OH \xrightarrow{Cat} (CH_3)_2NH + H_2O \quad \Delta H = -9.598 \text{ kcal/mol} \tag{22-50}$$

$$(CH_3)_2NH + CH_3OH \xrightarrow{Cat} (CH_3)_3N + H_2O \quad \Delta H = -14.098 \text{ kcal/mol} \tag{22-51}$$

$$NH_3 + (CH_3)_3N \xrightarrow{Cat} CH_3NH_2 + (CH_3)_2NH \quad \Delta H = +8.740 \text{ kcal/mol} \tag{22-52}$$

$$NH_3 + (CH_3)_2NH \xrightarrow{Cat} 2\ CH_3NH_2 \quad \Delta H = +4.240 \text{ kcal/mol} \tag{22-53}$$

$$CH_3NH_2 + (CH_3)_3N \xrightarrow{Cat} 2\ (CH_3)_2NH \quad \Delta H = +4.500 \text{ kcal/mol} \tag{22-54}$$

Reactions (22-49) to (22-51) are known as the alkylation reactions. They are exothermic and highly irreversible, except for Reaction (22-51). Reactions (22-52) through (22-54) are known as disproportionation reactions. They are reversible and are endothermic. The alkylation reactions dictate the rate of consumption of methanol and are somewhat faster than the disproportionation rates that govern the selectivity of the three amines. Guidelines for optimizing the reactions are discussed in References 46 and 116.

Figure 22.24 shows a typical methylamines process diagram.[117] The raw material and utility use are summarized in Table 22.25.[17]

$$RCHO + NH_3 \longrightarrow RCH = NH \xrightarrow{H_2} RCH_2NH_2 \tag{22-55}$$

Nitrile Reduction. The choice of catalyst and variations of the temperature, pressure, and concentration of ammonia can control the product mix of amines from hydrogenation of a nitrile. The reaction is shown in Reaction (22-56):

$$RC{\equiv}N + H_2 \rightarrow RCH_2NH_2 + (RCH_2)_2NH_2 + (RCH_2)_3N \tag{22-56}$$

TABLE 22.23 Physical Properties of Anhydrous Methylamines

	MMA[a]	*DMA*[b]	*TMA*[c]
Chemical formula	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Molecular weight	31.06	45.08	59.11
Freezing point, °C	−93.5	−92.02	−117.3
Boiling point, °C	−6.3	6.9	2.9
Vapor density (1 atm, 25°C) g/liter	1.3	1.9	2.5
Specific gravity, air = 1	1.1	1.6	2.0
Liquid density (25°C), g/ml	0.6562	0.6496	0.6270
lb/gal	5.48	5.42	5.23
Liquid viscosity (25°C), cP	—	0.190	0.175
Critical temperature, °C	156.9	164.5	160.1
Critical pressure, atm	73.6	52.4	40.2
Enthalpy of formation, ΔH°_f (25°C), kcal/mol			
Gas	−5.49	−4.41	−5.81
Liquid	−11.3	−10.5	−11.0
Solution (1000 moles H_2O)	−16.78	−17.3	−18.6
Vapor pressure, psia			
25°C	50	30	32
100°C	400	230	205
Heat capacity, C_p (25°C), cal,/ °C•mol			
Gas	12.7	16.9	21.9
Liquid	—	32.9	32.31
Heat of fusion (m.p.), cal/g	47.20	31.50	26.46
Heat of vaporization (b.p.), cal/g	198.6	140.4	92.7
Autoignition temperature, °C	430	400	190
Flammable limits, vol. %			
Lower	4.9	2.8	2.0
Upper	20.7	14.4	11.6

Source: Du Pont Methylamines Bulletin
[a] MMA = Monomethylamine
[b] DMA = Dimethylamine
[c] TMA = Trimethylamine

TABLE 22.24 Physical Properties of Aqueous Methylamines

Properties	*40% MMA*	*40% DMA*	*60% DMA*	*25% TMA*
Boiling point (°C)	48	54	36	43
Freezing Point (°C)	−38	−37	−74.5	6
Liquid density (25°C)				
g/ml	0.897	0.892	0.829	0.930
lb/gal	7.49	7.44	6.92	7.76
Vapor pressure (25°C)				
psia	5.8	4.2	9.7	6.6
mm Hg	300	215	500	340
kPa	40	29	67	45
Flash point, closed cup (°C)	−12	−18	−52	6

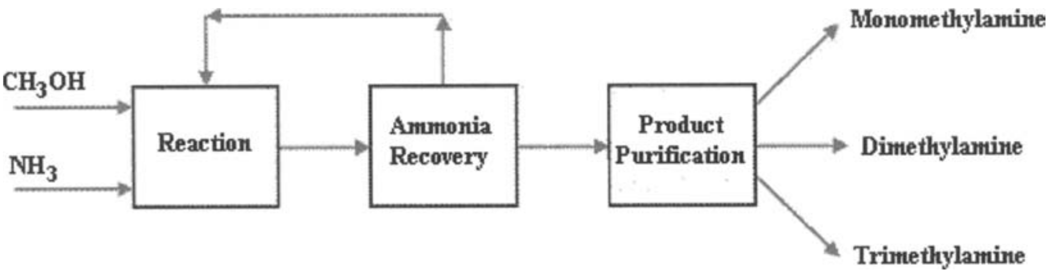


Fig. 22.24. Typical methylamines process.

TABLE 22.25 Methyl Amine Production: Raw Material and Utility Use (Tonne per Tonne of Product Leaving the Reactor)

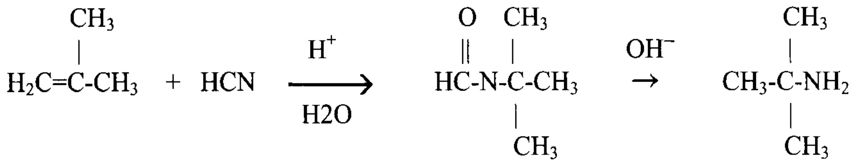
	MMA	*DMA*	*TMA*
Methanol	1.053	1.451	1.660
Ammonia	0.559	0.385	0.294
Steam	3.0		
Cooling Water (m^3)	150		
Electricity (kWh)	150		

Source: Reproduced by permission of Hydrocarbon Processing.

A large excess of ammonia suppresses formation of di- and trialkylamines. Reference 116 describes the process in more detail.

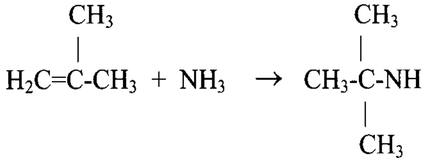
Other Alkyl Amines

Ritter Reaction. Mitsubishi Rayon and Sumitomo Chemical in Japan make t-butylamine Reaction (22-57). Average yields are about 85 percent based on isobutylene. Rohm and Haas in the United States makes t-octylamine from hydrogen cyanide and diisobutylene by a similar route.[116]



$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 + HCN \xrightarrow[\text{H2O}]{H^+} \overset{\overset{\displaystyle O}{\|}}{HC}{-}N{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3 \xrightarrow{OH^-} CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}NH_2 \quad (22\text{-}57)$$

Direct Amination. Direct amination of olefins is a special case and has been successfully developed for only a few amines. BASF has developed a process for the direct amination of isobutylene to yield t-butylamine [see Reaction (22-58)], and has operated a commercial plant in Western Europe since 1993.[116]



$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 + NH_3 \rightarrow CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}NH_2 \quad (22\text{-}58)$$

Hydrogenation of Anilines. A manufacturing process that is specific for cyclohexylamines is the catalytic hydrogenation of anilines or phenols in the presence of ammonia. Process details are given in Reference 116.

Manufacturing Costs. Manufacturing costs for alkylamines depend on the specific amine and the process. Reference 116 gives the estimated production costs for two different processes.

Production

Methylamines are commonly sold as anhydrous gases or as 25, 40, 50, and 60 percent aqueous solutions. The other alkylamines are usually sold on a 100 percent basis although some are also marketed as aqueous solutions. In 1997 MMA and TMA prices increased to \$0.73 per pound and DMA went up to \$0.77

per pound. Since that time, market prices have declined somewhat as methanol prices have receded.[116, 247] From 1995 to 2003 the price of cyclohexylamine has varied from a low of \$0.70 per pound to a high of \$1.35 per pound. High benzene prices have increased the price of aniline and are putting pressure on cyclohexylamine prices.[118]

Methylamine growth should remain strong as applications in the largest market segments are growing two to three times quicker than GNP.[119] However, worldwide growth in alkylamines should average a modest 2 to 3 percent annually from 2005 through 2009.[116] From 1998 to 2003 cyclohexylamine production has been constant at 15.5 million pounds per year.[118]

In the United States growth is expected to increase at 3.3 percent per year between 2003 and 2006.[247]

The major world producers of methylamines include BASF, Air Products, DuPont, and UCB. The major producers of C_2 to C_6 alkylamines include Air Products, BASF, and Celanese.[116]

The largest consumer of alkylamines are the United States, followed by Western Europe (at ~70% of the United States consumption) and Japan (at ~25% of the United States consumption).[116]

Uses

The three methylamines are important intermediates for the manufacture of solvents, insecticides, herbicides, pharmaceuticals, and detergents. DMA is the most important due to its use in the manufacture of N,N-dimethylformamide and N,N-dimethylacetamide, which find wide application as solvents.[46,116]

MMA ranks second in terms of demand. It is mainly used to make dimethyl urea and N-methylpyrrolidone, as well as for methyltaurine which is employed in CO_2 washes or as a raw material for detergents.[46,116]

TMA plays only a minor role. It is used in the manufacture of choline chloride, quaternary salts and epichlorohydrin.[46,116]

Some of the other alkyl amines and their uses are:

- Ethylamines: Pesticides and catalysts
- Propylamines: Herbicides, detergents, catalysts
- Butylamines: Pesticides, plasticizers, insecticides, catalysts, herbicides
- Cyclohexylamines: Corrosion inhibitors, catalysts, antibiotics, herbicides, cyclamate sweeteners in Asia

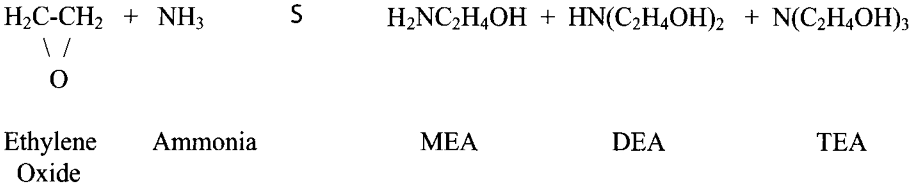
ETHANOLAMINES AND SECONDARY PRODUCTS

The main use of ethanolamines (EOA) is for the manufacture of detergents by reaction with fatty acids. The principal secondary products of ethanolamines are morpholine, ethylenimine, and ethylenediamine.

EOAs are corrosive and will attack some plastics and rubbers. They are a moderate fire hazard. MEA and TEA are clear viscous liquids with a mild ammonialike odor. DEA is crystalline or a viscous liquid. All are soluble in water and ethanol. Vapor is irritating to the eyes, skin, and respiratory tract and depression of the central nervous system can occur. They can also be absorbed by the skin in toxic amounts.[120]

Ethanolamine Process

Ethylene oxide reacts exothermically with 20 to 30 percent aqueous ammonia at 60 to 150°C and 30 to 150 bar in a tubular reactor to form the three possible ethanolamines (mono-ethanolamine: MEA, di-ethanolamine: DEA and tri-ethanolamine: TEA) with high selectivity.



$$\underset{O}{H_2C\text{-}CH_2} + NH_3 \quad \mathrm{S} \quad H_2NC_2H_4OH + HN(C_2H_4OH)_2 + N(C_2H_4OH)_3 \qquad (22\text{-}59)$$

TABLE 22.26 Effect of Excess Ammonia on Ethanolamine Selectivity[46]

Molar Ratio (NH_3 to EO)	*Selectivity Ratios*		
	Mono-	*Di-*	*Tri-ethanolamine*
10:1	75	21	4
1:1	12	23	65

Source: Copyright © Wiley-VLN and reprinted by permission of the copyright owner.

The composition of the reaction product stream can be influenced by temperature and pressure. Higher ratios of excess ammonia lead to a higher monoethanolamine content as shown in Table 22.26. The high triethanolamine content that results from an equimolar mixture of reactants indicates that the primary reaction with ammonia is slower than the secondary reactions.[46]

A typical ethanolamine flowsheet is shown in Fig. 22.25.[117] Nippon Shokubai has developed technology that uses a zeolite catalyst that suppresses the formation of TEA and produces more MEA and DEA.[120] Another process flowsheet is described in Reference 121 along with detailed process conditions.

Himtek Engineering in St. Petersburg, Russia offers ethanolamine (EOA) technology that operates at 40 to 70°C and 15 to 35 atmospheres. The ammonia and part of the MEA are recycled. Three vacuum stills are used to separate the three products. This technology is described in Russian patents No. 2,141,475 and No. 2,063,955.[122]

Production. All EOA plants make a mixture of products. The most important is MEA, which accounts for about half of total production. It is followed by DEA with 30 to 35 percent of production. In 2001 Ineos was the largest global producer followed by BASF and Huntsman. EOA demand is growing between 4 and 6 percent annually with MEA and DEA growth rates substantially exceeding that for TEA. In 2001 EOA supply exceeded demand and the oversupply situation continued through 2002 with startups of more new plants. About 50 percent of EOA capacity is in the Americas, more than 30 percent is in Europe, and the balance is in the Pacific Rim and the Middle East. Table 22.27 summarizes world consumption and growth rates for EOA.[38,120]

Uses. EOA production is consumed in the following areas: detergents (32%), ethyleneamines (20%), gas purification

TABLE 22.27 World Consumption of Ethanolamines and Growth Rates[120] Consumption (Thousands of Tonnes)

Region	*1995*	*2000*	*2005*
Americas	279	358	418
Western Europe	260	329	385
Asia	99	157	197
Other	27	60	90
Totals	665	904	1,090
		Growth Rates (%)	
Americas	—	5.1	3.1
Western Europe	—	4.8	3.2
Asia	—	9.7	4.6
Other	—	17.3	8.4
Totals	—	6.3	3.8

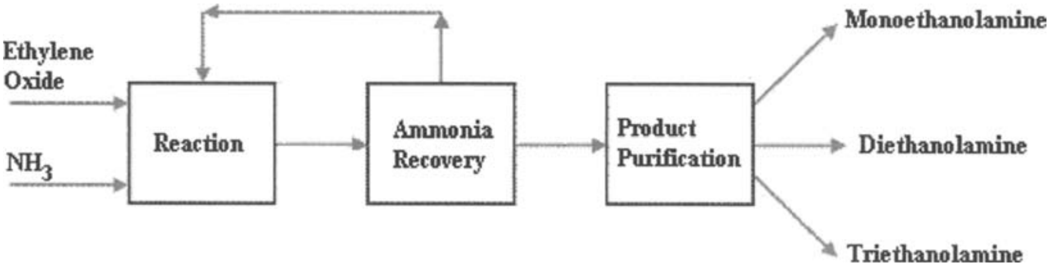
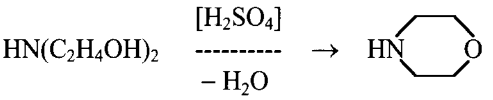


Fig. 22.25. Typical ethanolamine process.

(17%), metal cleaning (10%), herbicide intermediates (10%), textiles (5%), and miscellaneous (6%).[249] The specific uses of MEA, DEA, and TEA are listed in Reference 123.

Secondary Products of Ethanolamine

Morpholine. Morpholine is a solvent and intermediate for optical brighteners and rubber chemicals. In one process it is obtained from DEA by dehydration with 70 percent H_2SO_4 to close the ring:

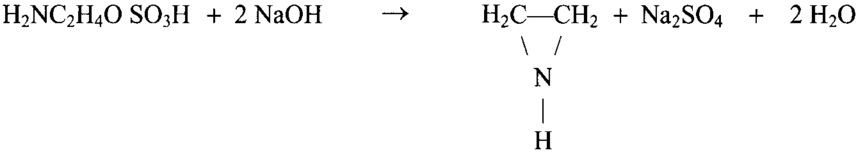


(22-60)

In the United States a newer production route is used in which diethylene glycol, ammonia, and hydrogen react at 150°C to 400°C and 30 to 400 bar over a catalyst containing Ni, Cu, Cr, or Co to give morpholine.[46]

Ethylenimine. Ethylenimine can be made from MEA via a two-step process that BASF and Hoechst developed.[46]

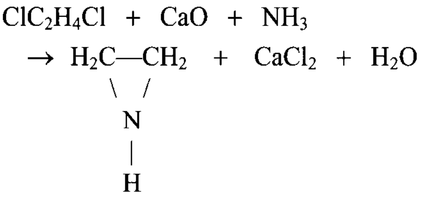
$$H_2NC_2H_4OH + H_2SO_4 \rightarrow H_2NC_2H_4OSO_3H + H_2O \qquad (22\text{-}61)$$



$$H_2NC_2H_4O\,SO_3H + 2\,NaOH \rightarrow H_2C\text{—}CH_2\,(NH) + Na_2SO_4 + 2\,H_2O$$

(22-62)

Dow makes ethylenimine by reacting 1,2-dichloroethane with ammonia in the presence of CaO at about 100°C:



$$ClC_2H_4Cl + CaO + NH_3 \rightarrow H_2C\text{—}CH_2\,(NH) + CaCl_2 + H_2O$$

(22-63)

Most ethylenimine is converted into polyethylenimine, a processing aid in the paper industry. It also serves as a reaction intermediate when ureas are formed with isocyanates.[46]

Ethylenediamine. Commercial ethylenediamine (EDA) is produced by two different routes:

- From 1,2-dichloroethane (EDC) and ammonia by Cl/NH_2 substitution
- From MEA and ammonia by OH/NH_2 substitution

The reaction in the first process is shown below, and the process details are given in Reference 46.

$$ClC_2H_4Cl + 2\,NH_3 \rightarrow NH_2C_2H_4\,NH_2 + \text{Higher Amines} + NH_4Cl + \text{Amine Chlorides} \qquad (22\text{-}64)$$

In 1969 BASF developed a process to make EDA by the reaction of MEA and ammonia:[46]

$$NH_2C_2H_4OH + NH_3 \xrightarrow[H_2]{Ni} NH_2C_2H_4NH_2 + H_2O \qquad (22.65)$$

The properties of EDA and some of the higher amines are given in Table 22.28.

Ethylenediamine Production

In 1999 the EDA capacity in the United States was 390 million pounds per year of ethyleneamines. Demand was expected to grow from 310 million pounds per year in 1998 to 370 million pounds per year in 2003. These estimates include exports that average 70 to 80 million pounds per year and imports that total about 10 to 12 million pounds per year. From 1989 to 1998 growth averaged 4 percent per year, but it is expected to slow to 3 percent per year through 2003.[124] Prices are kept confidential, but the 2001 US EDA price is estimated to be \$0.80 to \$0.85 per pound.[118]

TABLE 22.28 Properties of Ethylenediamine and Higher Amines

	EDA[a]	*DETA*[b]	*TETA*[c]	*TEPA*[d]	*PEHA*[e]
Molecular wt.	60.11	103.17	146.24	189.31	232.36
Melting point, °C	11-39	-35	-30	-26	—
Boiling point, °C	117	207	277	decomp @ 340°C	
Density, lb/gal	7.67	7.96	8.19	8.33	8.39
Flash pt. (O.C.), °C	38 102	143	185	185	—
Specific gravity	0.898	—	—	—	—
pH	11.9 (25% solution in water)	—	—	—	—
Vapor Density	2.07	—	—	—	—
Nitrogen content, wt%.	46.6	—	—	—	—
Viscosity, mPa-s	2.0 (at 20°C)	—	—	—	—
Autoignition temp, °C	385	—	—	—	—
Physical State	Colorless liquid with aminelike odor	—	—	—	—

[a]EDA: Ethylenediamine.
[b]DETA: Diethylenetriamine.
[c]TETA: Triethylenetetramine.
[d]TEPA: Tetraethylene pentamine.
[e]PEHA: Penta-ethylenehexamine.

Ethylenediamine Uses

Ethylenediamines are used in the following products: lube oil and fuel additives (20%), chelating agents (16%), wet-strength resins (15%), epoxy curing agents and polyamides (13%), surfactants (10%), oil field chemicals (7%), and miscellaneous (19%).

HEXAMETHYLENETETRAMINE (HEXAMINE)

Hexamine was first prepared in 1859. It is a white crystalline powder with a slight amine odor. It is soluble in water, alcohol, and chloroform, but it is insoluble in ether. However, the aqueous solutions exhibit inverse solubility, i.e., less hexamine dissolves as the temperature increases. The hydrate, $(CH_2)_6N_4 \cdot 6H_2O$ can be crystallized from the aqueous solution at temperatures below 14°C. Additional properties are listed in Table 22.29.

Hexamine Processes

Hexamine is made by the liquid phase reaction of ammonia and formaldehyde:

$$4\,NH_3 + 6\,HCHO \rightarrow CH_2)_6N_4 + H_2O \qquad \Delta H = -55\ \text{kcal/mol Hexamine} \quad (22\text{-}66)$$

Process details are given in References 125 and 252.

TABLE 22.29 Properties of Hexamine/Hexamethylenetetramine

Molecular weight	140.19
Sublimation temperature	285–295°C
Flash point	250°C
Density of solid @ 20°C	1.33 g/cm^3
Bulk density	700 to 800 g/L
Particle Size	700 micron, maximum
Specific heat	36.5 cal/°C
Heat of formation @ 25°C	28.8 kcal/mol
Heat of combustion @ 25°C	1003 kcal/mol
Solubility in water	
20°C	874 g/L
25°C	867 g/L
60°C	844 g/L
pH of 10% aqueous solution	8 to 9
Vapor Pressure @ 20°C	0.0035 mbar

Production. Production has declined from 48 million pounds in 1995 to 32 million pounds in 2001. The decline is mainly due to a decline in the use of phenolic resins that contain hexamine.[252] Hexamine is produced as a granular and free-flowing powder as well as a 42.5 percent solution. The solution is shipped in tank trucks, railcars, and drums. Solids are packed in bags, fiber drums, and super sacks. Hexamine is sensitive to moisture. Therefore it should be stored in an atmosphere with a relative humidity below 60 percent.[126]

Uses. Hexamine is used as a stabilizer and surface treatment in numerous applications and industries. Specific applications are described in Reference 127.

HYDRAZINE

Hydrazine, NH_2-NH_2, is the simplest diamine. Anhydrous hydrazine was first prepared in 1894. In 1953 Arch Hydrazine (formerly Olin Chemical) pioneered U.S. production of hydrazine to fuel the first Titan rocket.

Hydrazine is a clear, hygroscopic fuming liquid with the odor of ammonia. It is a mild base that is miscible in polar solvents such as water, ammonia, amines, and alcohols. Additional properties are shown in Table 22.30.[135]

Processes

Five processes are available for the commercial production of hydrazine: the Raschig process, the Raschig/Olin process, the Hoffmann (urea) process, Bayer ketazine process, and the peroxide process from Produits Chimiques Ugine Kuhlmann (of France).

TABLE 22.30 Physical Properties of Hydrazine

Molecular weight	
Anhydrous	32
Hydrate	50
Boiling point (°C)	113.5
Melting point (°C)	1.4
Specific gravity (g/ml)	
0°C	1.025
15°C	1.014
25°C	1.004
50°C	0.982
Critical temperature (°C)	380
Critical pressure (atm)	145
Vapor pressure (mm Hg)	
25°C	14
31°C	20
36°C	100
Viscosity (cp)	
5°C	1.2
25°C	0.9
Heat of vaporization (kcal/mol)	9.6
Heat of solution (kcal/mol) @ 25°C	−3.9
Heat capacity (J/mol °K) @ 25°C	98.87
Heat of combustion (kcal/mol)	−146.6
Heat of formation (kcal/mole)	
Liquid	12
Gas	23
Flash point (°C)	52
Explosive limits in air by vol. (%)	4.7 to100
Azeotrope	
Boiling point (68% hydrazine) (°C)	120.5

	Hydrazine Concentration (wt %)132					
	100	*64*	*51.2*	*35.2*	*22.4*	*15.4*
Melting Point, °C	2.0	−51.7	−59.8	−64.6	−26	−14
Boiling point, °C	113.5	120.5	117.2	108	107	103
Density (25°C), g/ml	1.0045	1.0320	1.0281	1.0209	1.0132	1.0083
Viscosity (20°C), μPa – s	0.974	1.5	1.44	1.10	1.08	1.04
pH	—	12.75	12.10	—	—	10.5

Raschig Process. The Raschig process was discovered in 1907 and then modified into the Olin process. The chemical reactions take place in the liquid phase and involve three steps:

$$NaOH + Cl_2 \rightarrow NaOCl + HCl \quad (22\text{-}67)$$

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH \quad (22\text{-}68)$$

$$NH_2Cl + NH_3 + NaOH \rightarrow NH_2\text{-}NH_2 \cdot H_2O + NaCl \quad (22\text{-}69)$$

Hydrazine is produced in the hydrated form with one mole of water added. Although a significant fraction of hydrazine is used as the hydrate, numerous applications (such as rocket propulsion) require anhydrous hydrazine. Because of the azeotrope at 68 percent hydrazine, reactive distillation or extractive distillation must be used to produce pure hydrazine.

Additional process details are given in Reference 132. The Raschig process is shown in Fig. 22.26.

The Raschig process can also be used to react amines with chloramine to make monosubstituted or unsymmetrical disubstituted hydrazines.

$$NH_2Cl + RNH_2 \rightarrow RNHNH_2 \quad (22\text{-}70)$$

$$NH_2Cl + R_2NH \rightarrow R_2NNH_2 \quad (22\text{-}71)$$

Raschig/Olin Process. The Raschig/Olin process is used to make anhydrous hydrazine. In this process Reactions (22-67) through (22-69) also occur. However the refining area has a different design from the Raschig process. Additional details are given in Reference 132.

The refining area has five steps: ammonia removal, NaCl concentration and removal, hydrazine–water distillation to reach azeotropic concentration, extractive distillation with aniline to break the azeotrope and distillation to separate hydrazine from aniline. Sometimes 50 percent caustic replaces aniline in the extractive distillation. If ultra-pure hydrazine is needed, freeze crystallization is used to remove the

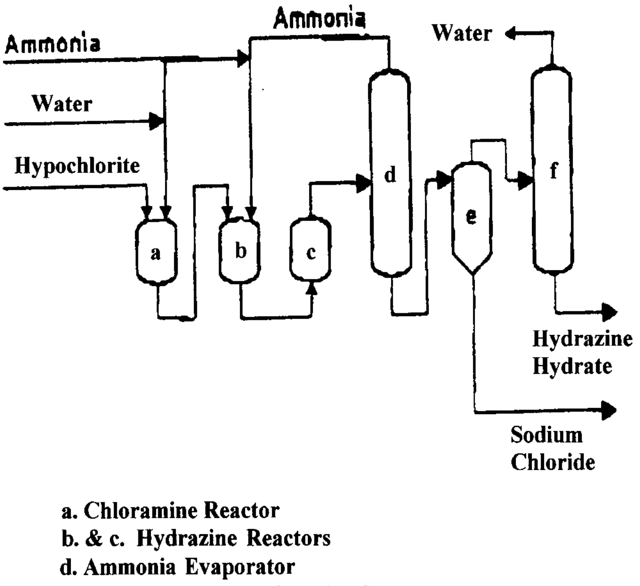


Fig. 22.26. Raschig process for hydrazine production. (Courtesy of Wiley-VCH. Schirmann, J.P, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, pp. 177–190, Reinhold Publishing, New York, 1996.)

supernatant fluid. Assays between 99.5 and 99.99 percent have been achieved.

The overall yield based on chlorine is 65 percent. The combined yield for Reactions (22-67) and (22-68) is about 95 percent, whereas the yield for Reaction (22-69) is 70 percent. Japanese patent SHO-62-83308 claims to increase hydrazine yield by almost 10 percent by high-frequency heating immediately after the reactants are mixed in Reaction (22-68). A sketch of the Raschig/Olin process is shown in Fig. 22.27.[132]

Hoffman (Urea) Process. The overall reaction for the Hoffman process is:

$$\underset{\text{Urea}}{CO(NH_2)_2} + \underset{\text{Hypochlorite}}{NaOCl} + 2\,NaOH \rightarrow \underset{\text{Hydrazine}}{NH_2\text{–}NH_2} + NaCl + Na_2CO_3 + H_2O \qquad (22\text{-}72)$$

Process details are given in Reference 132.

This process was not being operated in 2001 although it has operated commercially in the past. Compared with the standard Raschig process, it was the most economical method for low production levels. However, rapid growth in plant size made it obsolete.[132]

Bayer Ketazine Process. The Bayer Ketazine process is based on the reaction of chloramine with ammonia in the presence of acetone at pH 12 to 14. NaOCl, acetone and a 20 percent aqueous solution of ammonia (at a mole ratio of 1:2:20, respectively) are fed to a reactor at 35°C and 200 kPa to make the aqueous dimethyl ketazine solution. Excess ammonia and acetone are removed in a series of columns and recycled to the reactor. The ketazine solution is distilled to make a hydrazine hydrate containing 64 percent hydrazine.[132]

Peroxide Process. This process (see Fig. 22.28) was invented by PCUK and is operated by AtoFina in France. The reaction is carried out in the presence of methyl ethyl ketone (MEK) at atmospheric pressure and 50°C. The molar ratio in the feed of hydrogen peroxide (H_2O_2), MEK, and NH_3 is 1:2:4. Additional process details are given in Reference 132.

Production. Hydrazine is marketed as anhydrous hydrazine, as the monohydrate (64% hydrazine), and as a 54.5 percent aqueous solution (85% hydrazine monohydrate). The largest U.S. producers of hydrazine-based on a 2000 report[134] are: Arch Chemical (23 million pounds per year), Bayer (17 million pounds per year), and Fairmont Chemical (1 million pounds per year).

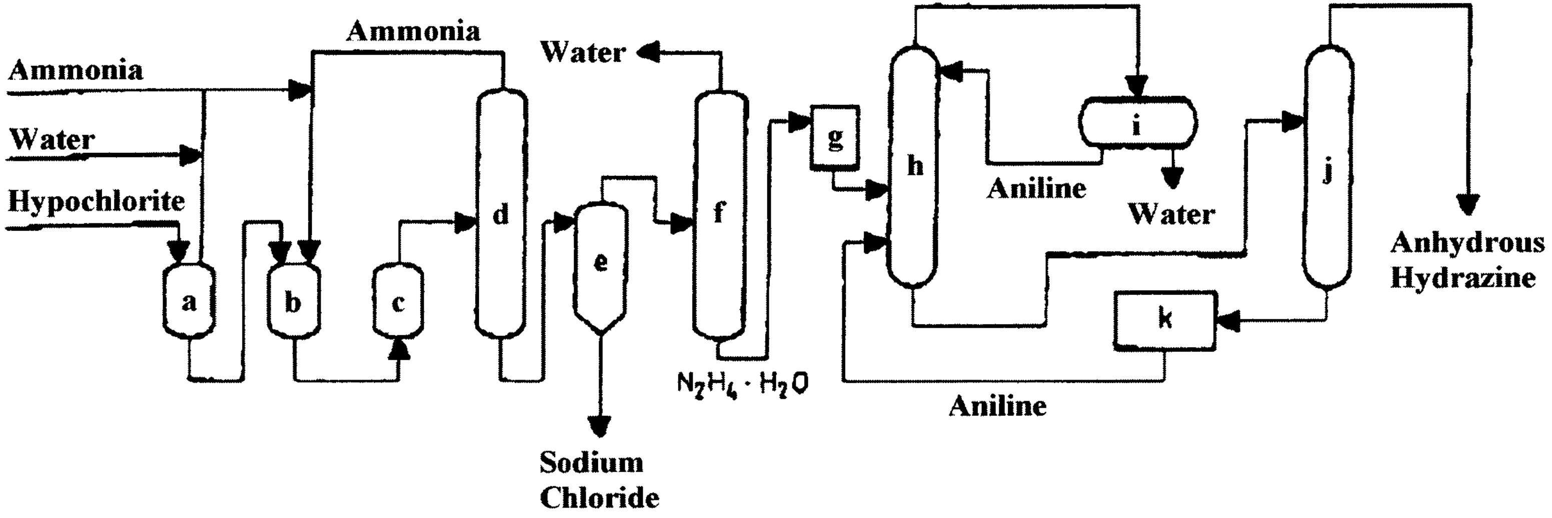
About 29 million pounds are sold in the United States and the manufacturers retain about 7 million pounds for internal use. The space industry uses only 5 percent of all hydrazine produced in the United States.[134] Total capacity in the western world in 1988 was estimated to be about 130 million pounds per year.[132]

The permissible exposure limit (PEL) for hydrazine hydrate on an 8-hour, time-weighted average (TWA) is 0.1 ppm. The ammonia like odor of hydrazine hydrate normally cannot be detected until the concentration is above 3 to 5 ppm.[135]

Uses. Hydrazine is used directly as an oxygen scavenger and as an energy source. Hydrazine is consumed in the following applications: blowing agents (33%), pesticides (32%), water treatment (18%) and miscellaneous (17%).[128]

HYDROGEN CYANIDE

HCN is a colorless liquid. However, some iron cyanides are blue (prussian blue) and their presence as a slight contaminant usually gives HCN a bluish tint that led to the German name Blausäure – blue acid. Selected physical properties of hydrogen cyanide are shown in Table 22.31.



a. Chloramine Reactor
b. & c. Hydrazine Reactors
d. Ammonia Evaporator
e. Hydrazine-Sodium Chloride Separator
f. Hydrazine Hydrate Concentration
g. Hydrazine Hydrate Storage
h. Hydrazine Hydrate Dehydration
i. Aniline-Water Decantation
j. Anhydrous Hydrazine Distillation
k. Aniline Storage

Fig. 22.27. Raschig/Olin process for hydrazine production. (Courtesy of Wiley-VCH. Schirmann, J.P, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, pp. 177–190, Reinhold Publishing, New York, 1996.)

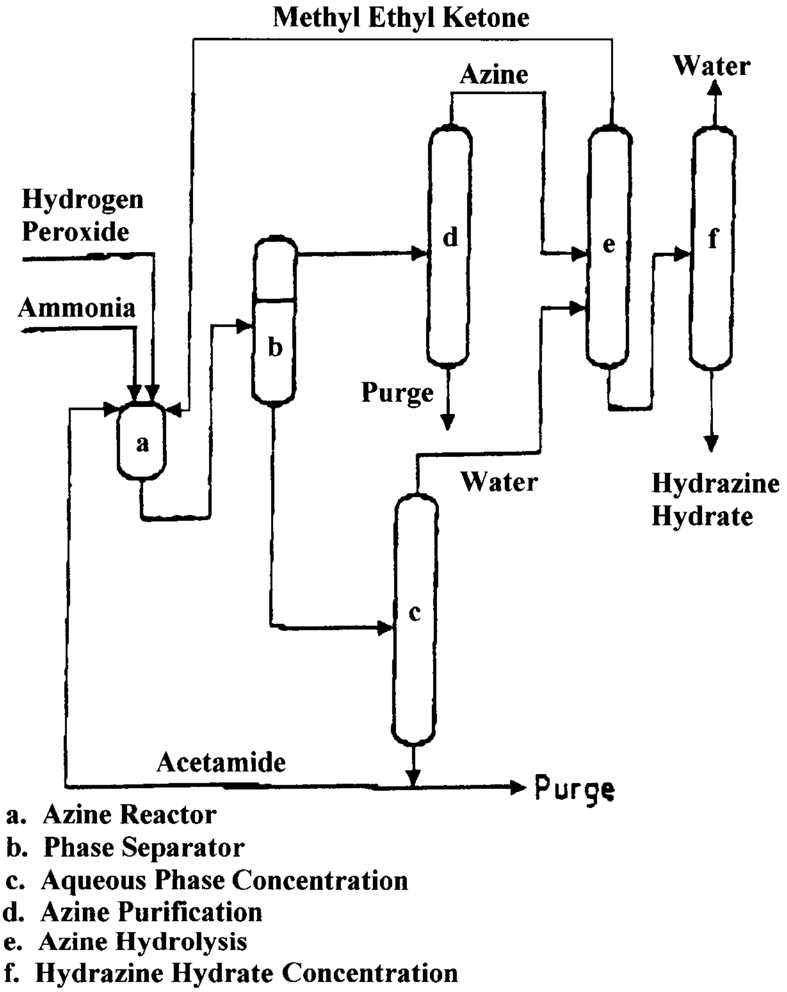


Fig. 22.28. Peroxide process for hydrazine production.[132] (Courtesy of Wiley-VCH. Schirmann, J.P, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, pp. 177–190, Reinhold Publishing, New York, 1996.)

Safety

Many people can detect hydrogen cyanide by odor or taste sensation at a concentration of 1 ppm in air whereas most people can detect 5 ppm. OSHA has set 4.7 ppm as the maximum, average safe exposure limit for a 15-minute period. Exposure to 20 ppm of HCN in air causes slight warning symptoms after several hours; 50 ppm causes disturbances within an hour; 100 ppm is dangerous for exposures of 30 to 60 minutes; and 300 ppm can be rapidly fatal unless prompt, effective first aid is administered. A small concentration of cyanide always exists in a person's body, and the body has a mechanism to continuously remove small amounts of cyanide.[129]

HCN may also present some processing hazards. HCN undergoes an exothermic polymerization at a pH of 5 to 11 to form solid black compounds. This polymerization can become explosively violent, especially if it is confined. To avoid polymerization, stored HCN should contain less than 1.0 wt.%

TABLE 29.31 Physical Properties of Hydrogen Cyanide

Molecular formula	HC≡N
Molecular weight	27.03
Melting point	−13.24°C
Triple point	−13.32°C
Boiling point (1 atm)	25.70°C
Density, g/ml	
0°C	0.7150
10°C	0.7017
20°C	0.6884
Specific gravity of aqueous solutions (@18°C compared to water @ 18°C)	
10.04%	0.9838
20.29%	0.9578
60.23%	0.8290
Vapor specific gravity (@31°C, air = 1)	0.947
Vapor pressure, kPa	
−29.5°C	6.697
0.0°C	35.24
27.2°C	107.6
Liquid viscosity @ 20.2°C	0.2014
Specific heat, J/mol	
−33.1°C, liquid	58.36
16.0°C, liquid	70.88
27.0°C, gas	36.03
Heat of formation (@ 25°C, 1 atm), ΔH_f, kJ/mol	
Gas @ 25°C	−130.5
Liquid @ 25°C	−105.4
Heat of fusion @ −14°C, kJ/mol	7,100
Latent heat, kJ/mol	23.8
Heat of combustion, net, kJ/mol	642
Conductivity, S/cm	3.3 × 10 − 6
Heat of vaporization, kJ/mol	25.2
Heat of polymerization, kJ/mol	42.7
Flash cup, closed cup, °C	−17.8
Explosive limits in air at 100 kPa & 20°C, vol.%	6 to 41
Autoignition temperature, °C	538

water; it should be kept cool; and it should be inhibited with sulfuric, phosphoric, or acetic acid.[129]

Explosively violent hydrolysis can occur if an excess of a strong acid (H_2SO_4, HNO_3, or HCl) is added to HCN. The reaction is fastest at or near stoichiometric ratios, e.g., 1 to 2 moles H_2SO_4 per mole HCN and can cause severe equipment damage if confined.[129]

An important environmental issue is the fate of cyanide. HCN, if spilled, evaporates quite readily. That which does not evaporate is soon decomposed or rendered nonhazardous by complexing with iron in the soil, by biological oxidation or by degradation from photolysis.[129] Several methods for treatment and disposal of cyanide compounds are described in References 129 and 133.

Manufacture

Six processes are presently of economic significance: the Andrussow process is currently the principal HCN manufacturing process in the world, the BMA process is practiced by two companies and provides high yield and selectivity by using a complex reaction system, the Fluohmic process is of interest in locations where electricity is inexpensive, the formamide process is useful for sites with inexpensive carbon monoxide, the BP (British Petroleum) acrylonitrile process produces HCN as a byproduct, and the methanol process.

Andrussow Process. The Andrussow process was patented in Germany by Dr. L. Andrussow in 1933. Its main advantages are low converter investment, low maintenance costs and high natural gas yields. The Andrussow process produces HCN by the reaction of ammonia, air and natural gas at 1000°C to 1200°C in the presence of a platinum/rhodium catalyst. The reaction is:

$$NH_3 + CH_4 + 1.5\ O_2 \xrightarrow[\text{Pt/Rh}]{1200^\circ C} HCN + 3\ H_2O \quad \Delta H = -115.2\ \text{kcal/mol HCN} \qquad (22\text{-}73)$$

More reaction details are given in Reference 129. The heat of reaction is recovered in the waste-heat boiler to generate about 5 pounds of steam per pound of HCN produced.

The precious metal catalyst is usually 90 percent platinum and 10 percent rhodium in gauze form. The catalyst life can range from 4000 hours to as much as 10,000 hours. A catalyst pack is usually replaced because it has been contaminated by minor impurities in the feed gases. Very little catalyst metal is consumed or lost during the life of a catalyst.

The reaction takes place under fuel-rich conditions to maintain a nonflammable feed mixture. Typical feed composition is 13 to 15 percent ammonia, 11 to 13 percent methane and 72 to 76 percent air on a volumetric basis. Control of feed composition is essential to guard against deflagrations as well as to maximize the yield. The yield from methane is approximately 60 percent of theoretical.

The reactions in the Andrussow process are more complex than that shown in Equation 22-72.[130] Most of the heat required for HCN formation is supplied by combustion of methane. This results in an overall reaction that is exothermic.[129] The converter off-gas typically has the following molar composition: HCN = 6 − 12%, NH_3 = 1.5 − 3%, H_2 = 7 − 11%, N_2 = 50 − 55%, H_2O = 20 − 25%, CO = 3 − 4%, CO_2 = 0.3%, and CH_4 = 0.1%.

Two processes can be used to remove NH_3 from the converter off-gases. Figure 22.29 shows a process that recovers unreacted ammonia for recycle to the converter and the process in Fig. 22.30 uses sulfuric acid to produce ammonium sulfate as a byproduct. Ammonium sulfate can create a disposal problem, but the recycle system is capital and energy intensive. Ammonia must be removed from the off-gas before HCN can be recovered because the ammonia promotes polymerization of the HCN.[129] Additional process details are given in Reference 129.

BMA Process. The BMA (Blausäure-Methan-Ammoniak, or HCN-methane-ammonia) process was developed by Degussa around 1949. In the process, ammonia reacts with methane in the absence of oxygen in a gas-fired tubular reactor. U.S. patent 5,785, 942 describes the BMA process and improvements

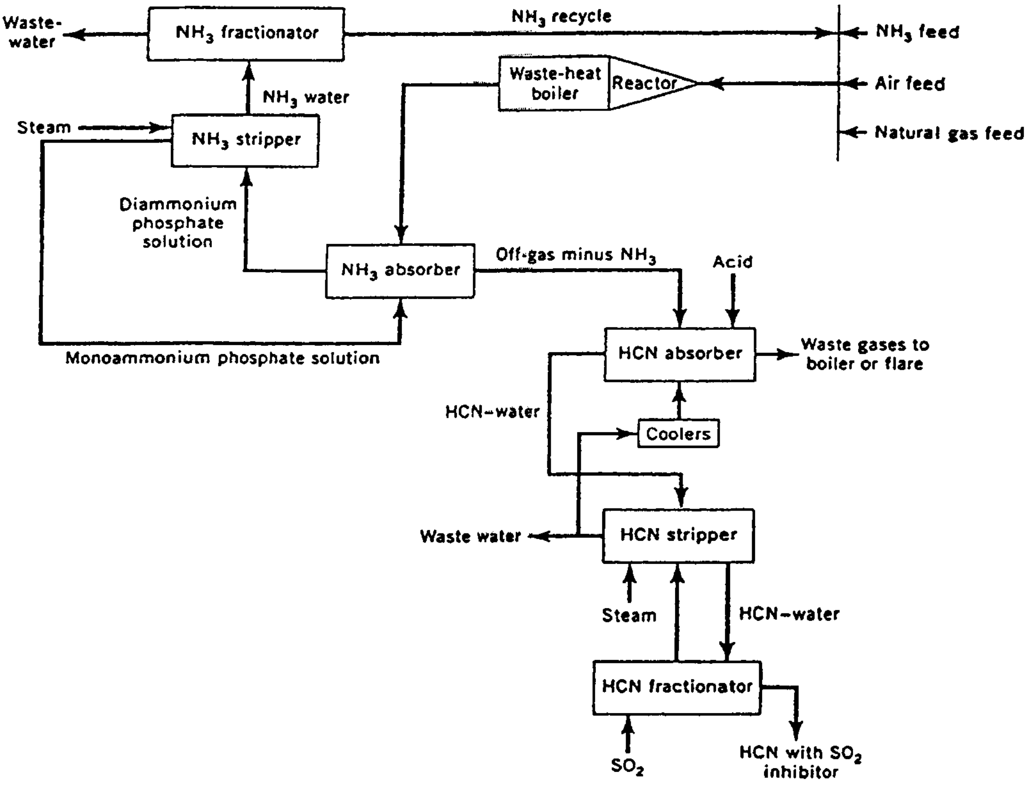


Fig. 22.29. Andrussow HCN process with ammonia recycle.[129] (Copyright by John Wiley & Sons, Inc. and reproduced by permission of copyright owner.)

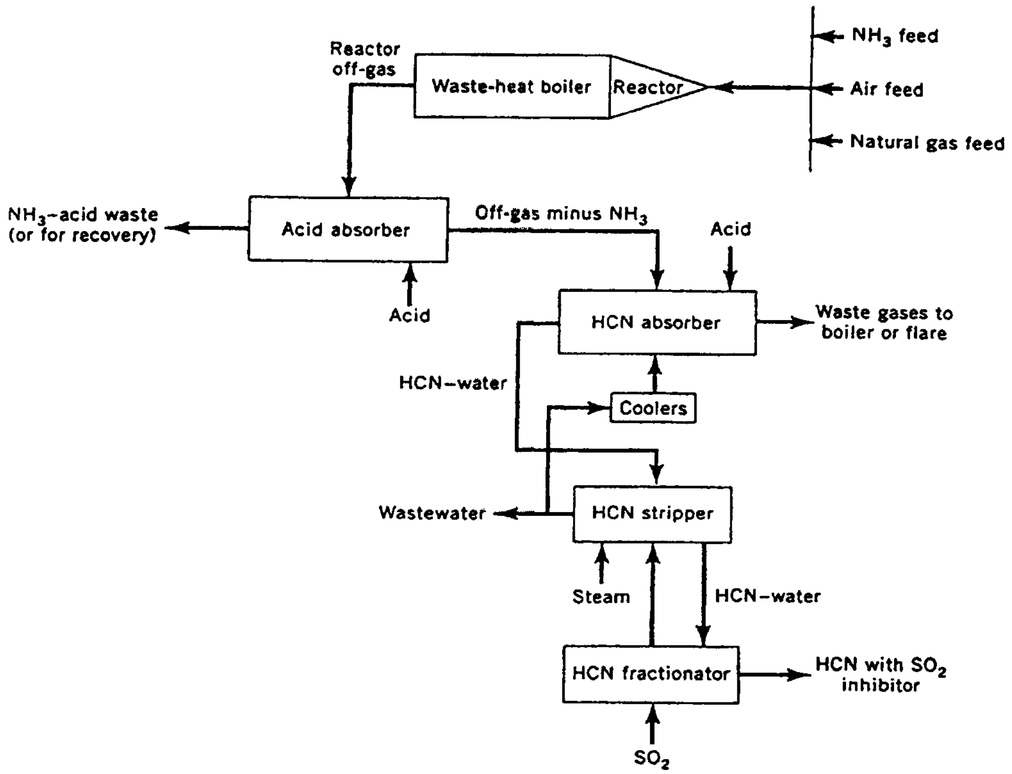


Fig. 22.30. Andrussow HCN process with ammonia removal.[129] (Copyright by John Wiley & Sons, Inc. and reproduced by permission of copyright owner.)

that were made during the mid-1990s. The reaction is:[46]

$$NH_3 + CH_4 \xrightarrow[Pt/Ru]{1300°C} HCN + 3\,H_2 \qquad \Delta H = +\,60 \text{ kcal/mol HCN} \tag{22-74}$$

In a reactor that is similar to a reformer, the reaction occurs in tubes that are heated externally to supply the endothermic heat of reaction.[129] Sintered corundum (α-Al_20_3) tubes with an internal layer of platinum/ruthenium catalyst are normally used. To achieve adequate heat transfer, the tubes may be only 3/4 in. in diameter and 6½ feet long. Selectivities of 90–91 percent for methane and 83–84 percent for ammonia are reached at 1200°C to 1300°C reaction temperatures.

A typical converter is made up of multiple furnaces, each of which contains 8 to 10 reactors. Each reactor contains 10 to 30 tubes with a catalyst lining. Catalyst life is approximately 10,000 hours.[129]

The converter off-gas typically has the following molar composition: HCN = 20 − 23%, NH_3 = 2 − 3%, H_2 = 70 − 72%, N_2 = 0.5 − 1%, and CH_4 = 1 −2.4%.

The unreacted ammonia is removed from the reactor off-gas by scrubbing with sulfuric acid to make ammonium sulfate. Just as with the Andrussow process, ammonia must be removed from the off-gas before HCN can be recovered because the ammonia promotes polymerization of the HCN. After ammonia is removed from the converter off-gases, the remaining gas stream is processed in a way similar to the Andrussow process.[129]

In the BMA process the gas that leaves the HCN absorber has the following molar composition: H_2 = 96%, N_2 & 0_2 = 1.5%, and CH_4 = 2.5%. The vent gas is used either as a chemical feedstock or as fuel gas in the HCN furnaces.

The advantages of the BMA process are high ammonia yields, high natural gas yields, and the useful hydrogen in the vent gas. But the high investment and high maintenance costs for the converter are a disadvantage. The complexity of the reaction system also makes the process less attractive for large-scale production.[129] In 2003 the BMA process was in use at four plants.[131]

Fluohmic Process. The Fluohmic process was developed around 1960 by Shawinigan Chemicals of Canada. This process involves the reaction of ammonia with hydrocarbons (usually propane or butane) in an electrically heated, fluidized bed of coke. The reaction is:

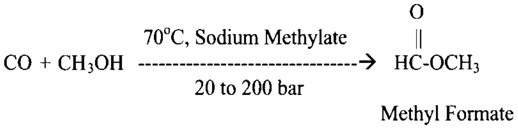
$$3\ NH_3 + C_3H_8 \xrightarrow{1370°C} 3\ HCN + 7\ H_2 \qquad \Delta H = +151\ \text{kcal/mol HCN} \qquad (22\text{-}75)$$

The fluidized bed is heated at 1350°C to 1650°C by passing an electric current between carbon electrodes immersed in the bed. The performance of the reaction system is reported to be:

	Conversion	Yield	
	(Mole %)	(Mole %)	(lb/lb HCN)
C_3H_8	88%	88% to 90%	0.60 to 0.62
NH_3	86%	86% to 90%	0.70 to 0.73

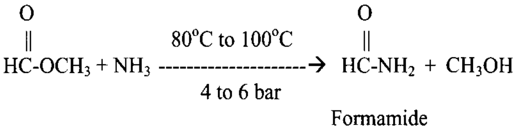
The reactor off-gas typically has the following molar composition: HCN = 25%, NH_3 = 0.25%, H_2 = 72%, and N_2 = 3%. The HCN is separated from the off-gas for refining, and the hydrogen leaves the system as a byproduct together with a small amount of nitrogen and unreacted ammonia. The high electrical consumption (~3 kWh/lb HCN) makes the process attractive only in locations where the cost of electricity is extremely low. In 2003 the Fluohmic process was used in Spain, Australia, and South Africa.

Formamide Process. The formamide process was developed by several companies, but in 2001 it was only used by BASF. The process involves the following steps:[46] (1) methyl formate synthesis, (2) formamide synthesis, and (3) HCN formation/dehydration.



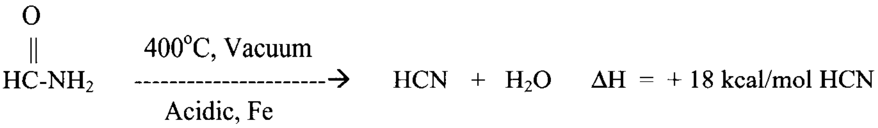
$$CO + CH_3OH \xrightarrow[20\text{ to }200\text{ bar}]{70°C,\ \text{Sodium Methylate}} \underset{\text{Methyl Formate}}{HC(=O)\text{-}OCH_3} \qquad (22\text{-}76)$$

With excess methanol the conversion to methyl formate is 95 percent with nearly 100 percent selectivity.



$$HC(=O)\text{-}OCH_3 + NH_3 \xrightarrow[4\text{ to }6\text{ bar}]{80°C\text{ to }100°C} \underset{\text{Formamide}}{HC(=O)\text{-}NH_2} + CH_3OH \qquad (22\text{-}77)$$

The conversion of ammonia is 60 to 85 percent.



$$HC(=O)\text{-}NH_2 \xrightarrow[\text{Acidic, Fe}]{400°C,\ \text{Vacuum}} HCN + H_2O \qquad \Delta H = +18\ \text{kcal/mol HCN} \qquad (22\text{-}78)$$

The overall performance of the reaction system is:

	Yield	Consumption
	(Mole %)	(lb/lb HCN)
CH_3OH	—	0.20 to 0.30
NH_3	79 to 90	0.70 to 0.80
CO	52 to 94	1.10 to 2.00

The reactor off-gas contains 60 to 70 percent HCN.

BASF has obtained European patent 1,110,913, which describes HCN production from gaseous formamide in a fluidized bed. Elements of the commercialized formamide process are included in a methyl methacrylate process that Mitsubishi Gas Chemical started up in 1997. The formamide is obtained by reacting hydroxyisobutyramide with methyl formate. Therefore the external requirements for HCN are reduced to the replacement of yield losses.[131] The process is described in U.S. patent 6,075,162 and the catalyst is described in European patent 1,086,744.

Methanol Process. HCN is produced when methanol reacts with ammonia and oxygen in the presence of an oxide catalyst that contains iron, antimony, phosphorous, and vanadium. The reaction occurs in the vapor phase in a fluidized bed reactor. The process and the catalyst are described in patents that were issued to Nitto Chemical (now Mitsubishi Rayon) during the late 1990s (European Patent 864,532; Japanese patents 10-167,721, 10-251,012, 11-043,323; U.S. Patent 5,976,482).

In 2003 Mitsubishi Rayon is believed to operate a commercial-scale, methanol-based HCN process and has offered to license the technology to other companies. The technology might provide a low-cost way to convert an acrylonitrile plant to HCN-only production. However methanol is a higher cost source of carbon compared to natural gas so the methanol process probably has a higher operating cost than the Andrussow process.

Acrylonitrile Process. The Standard Oil Company of Ohio (now BP Amoco) commercialized in 1960 a fluidized bed process in which the catalytic oxidation of a mixture of propylene and ammonia produces acrylonitrile (ACRN). Byproducts from this reaction are HCN and acetonitrile. The yields of HCN depend on the process conditions and on the catalyst system.[131] The reactions are:

$$\underset{\text{Propylene}}{CH_2{=}CHCH_3} + NH_3 + \tfrac{3}{2}\,O_2 \rightarrow \underset{\text{Acrylonitrile}}{CH_2{=}CHCN} + 3\,H_2O \qquad (22\text{-}79)$$

$$\underset{\text{Propylene}}{CH_2{=}CHCH_3} + \tfrac{3}{2}\,NH_3 + \tfrac{3}{2}\,O_2 \rightarrow \underset{\text{Acetonitrile}}{\tfrac{3}{2}\,CH_3CN} + 3\,H_2O \qquad (22\text{-}80)$$

$$CH_2{=}CHCH_3 + 3\,NH_3 + 3\,O_2 \rightarrow 3\,HCN + 6\,H_2O \qquad (22\text{-}81)$$

Depending on the type of ACRN process and the operating conditions, about 10 to 24 pounds HCN are obtained per 100 pounds of ACRN.[46] U.S. Patent 5,840,648 describes a catalyst that permits more HCN production.

During the 1990s several patents were issued (European patent 878,464, U.S. patent 5,288,473, and U.S. patent 6,204,407) in relation to the addition of methanol to the feed stream of an ACRN plant to increase HCN production.

BP Sohio and Asahi are developing processes for the ammoxidation of propane to produce ACRN. This process is believed to yield a lower level of HCN than the optimized oxidation of propylene.[131] In 2007 Asahi started up a propane process in Tongsuh, South Korea.

Other HCN Processes. Some alternate HCN processes that have been studied in the 1990s were:

- Production of HCN from Acetonitrile (see Japanese patent 10,167,721),
- Production of HCN by use of a corona (German patent 1,054,982), and
- Production of HCN by use of microwave heating (US patents 5,393,393; 5,470,541; and 5,529,669).

None of these processes is believed to be used in commerical production in 2004.

Production

In 1999 a total of 34 companies were operating 47 HCN production facilites in the United States, Western Europe, and Japan. Capacity in these three regions was about 3.6 billion pounds (1.6 million tonnes). Direct production accounts for 75 percent of total capacity and the balance is co-product from ACRN production. Worldwide capacity is about 1.8 million tonnes.[131]

Between 1994 and 1999 HCN consumption increased about 2.2 percent per year. Consumption is expected to increase at around 2.8 percent per year from 1999 through 2004.[131] In the United States production is expected to grow at a rate of 2.4 percent per year from 1.7 billion pounds in 2003 to 1.87 billion pounds in 2007.[261]

Uses

HCN is usually consumed at its production site, and some consumers without on-site HCN production capability are believed to be developing plans to eliminate HCN shipments. For example, BASF in the United Kingdom produces byproduct HCN in an ACRN plant and ships HCN railcars to Ineos. This HCN is used to produce acetone cyanohydrin (ACH) in a methyl methacrylate plant. To eliminate these shipments, BASF and Ineos plan to (1) install an ACH plant on the BASF plant site and (2) transfer the ACH to Ineos via a 9-km pipeline.[136]

ACRN plants are highly dependent on the actions of the acrylic fiber industry, the major outlet for ACRN. As a result, HCN consumers may have to operate at reduced rates if an adequate supply of HCN is not being produced by the ACRN plant. In the early years of the new century, many consumers of HCN from ACRN plants evaluated options that would give them a more consistent supply of HCN. Some ACRN plants were shut down during this time, and market conditions plus company finances will determine whether any of these plants will be restarted.

Some of the uses of HCN are:

- Adiponitrile (ADN). ADN is made when HCN reacts with butadiene. It is a key ingredient in production of nylon.
- Acetone Cyanohydrin (ACH). ACH is made when HCN reacts with acetone. It is a key ingredient in many methyl methacrylate (MMA) plants. MMA is used to make acrylic sheeting and related products.
- Sodium Cyanide (NaCN). NaCN is made when HCN reacts with sodium hydroxide (NaOH). NaCN is used in precious metals (gold and silver) extraction, metal plating, and some chemical production processes.
- Methionine. Methionine is an essential amino acid that is used in animal feed. The key ingredients are HCN or NaCN, methyl mercaptan, acrolein, and NH_4HCO_3.
- Cyanuric Chloride (CYC). CYC is made when HCN reacts with chlorine and is then rearranged into a ring compound. It is used to make herbicides, pharmaceuticals, and explosives.
- Chelating Agents. Chelating agents are made when HCN reacts with formaldehyde and amines to make aminocarboxylic acids, which are then saponified to produce the acid salts. Their major uses are in soaps, water treating agents, and various cleaning agents.
- Other uses include ferrocyanides (for blue jeans), acrylates, lactic acid, pharmaceuticals, and specialty chemicals.

In 2004 HCN was consumed in the following applications: adiponitrile (for nylon 6/6): 50 percent, acetone cyanohydrin (for methyl methacrylate): 28 percent, methionine: 7 percent, sodium cyanide: 6 percent, cyanuric chloride: 3 percent, chelating agents: 2 percent, and miscellaneous (including nitrilotriacetic acid and salts): 4 percent.[261]

Table 22.32 lists the HCN consumption for different products.

TABLE 22.32 Consumption of Hydrogen Cyanide by Major Region, 1999 (Thousands of Tonnes)

Product	*United States*	*Western Europe*	*Japan*	*Total*
Adiponitrile	340	127	—	467
Acetone cyanohydrin	206	152	50	408
Sodium cyanide	72	55	16	143
Methionine and analogues	37	32	4	73
Cyanuric chloride	20	20	1	41
Chelating agents	18	11	—	29
Other	35	13	13	61
Totals	728	410	84	1,222

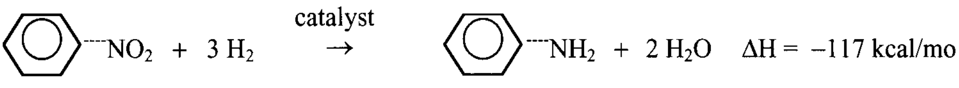
ANILINE

Aniline was first produced in 1826 by the dry distillation of indigo, the oldest known vat dye. Fritsche also obtained aniline from indigo by heating it with potash (K2O). Hofmann obtained aniline by reduction of nitrobenzene in 1843. Aniline is a colorless, oily, flammable liquid that is slightly soluble in cold water and infinitely soluble in alcohol and ether. Its physical properties are summarized in Table 22.33.

Processes

The aniline processes that are currently in use include (1) hydrogenation of nitrobenzene, (2) nitrobenzene reduction with iron filings, and (3) ammonolysis of phenol. Almost 97 percent of the nitrobenzene produced in the United States is converted to aniline between the hydrogenation process and the iron filings process.[137]

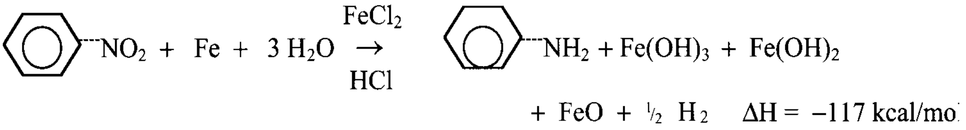
Hydrogenation of Nitrobenzene. The primary aniline production process in the world is the hydrogenation of nitrobenzene. BASF, DuPont, ChemFirst, and Rubicon use this process in the United States. This technology is also used by all Western European aniline producers and all but one Japanese aniline producer.



(22-82)

The catalytic gas-phase hydrogenation processes for nitrobenzene can be carried out using a fixed-bed or a fluidized bed reactor. Details of both processes are given in Reference 46. A typical process diagram is shown in Fig. 22.31.

Nitrobenzene Reduction with Iron Filings. The older Bechamp method for iron oxide pigment production gives aniline as a coproduct and is operated by Bayer in West Virginia. Nitrobenzene is reduced by reaction with iron filings in the presence of a hydrochloric acid catalyst. The iron is oxidized to the ferrous or ferric state and the coproduct aniline is separated. The yield is 90 to 95 percent of theoretical. The reactions are represented as follows.[138]

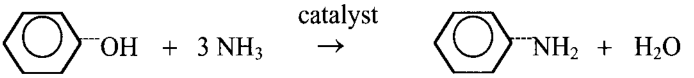


(22-83)

$$2\,Fe(OH)_3 + Fe(OH)_2 \rightarrow Fe_3O_4 + H_2O \qquad (22\text{-}84)$$

This process would have been replaced much earlier by more economical reduction methods if it had not been possible to obtain valuable iron oxide pigments from the iron oxide sludge. However, the increasing demand for aniline has far surpassed the market for iron pigments, so this process is no longer preferred.[46]

Ammonolysis of Phenol. Aniline can also be produced when phenol is subjected to gas-phase ammonolysis at 200 bar and 425°C. This is the Halcon/Scientific Design process. The chemistry is:



(22-85)

The catalysts are $Al_2O_3 \cdot SiO_2$ (possibly as zeolites) and oxide mixtures of Mg, B, Al, and

TABLE 22.33 Physical Properties of Aniline

Property	*Value*
Molecular weight	93.12
Boiling point. °C	
101.3 kPa (760 mm Hg)	184.4
4.4 kPa (33 mm Hg)	92
1.2 kPa (9 mm Hg)	71
Melting point, °C	–6.15
Density, d	
at 20/4°C	1.02173
at 20/20°C	1.022
Viscosity at 20°C, mPa•s (= cP)	4.423–4.435
Dissociation constant, pK	
at 20°C	4.60
at 60°C	8.88
Enthalpy of dissociation, kJ/mol (kcal/mol)	21.7 (5.19)
Heat of combustion, kJ/ mol (kcal/mol)	3389.72 (810.55)
Specific heat, 20–25°C	0.518
Latent heat of vaporization J/g (cal/g)	476.3 (113.9)
Flash point (closed-cup), °C	76
Autoignition Temperature, °C	615
Flammable Limits in Air (% by Volume)	
LEL	1.3
UEL	11.0
Vapor Density (Air= 1)	3.22
Solubility (g in 100 g Water @ 20°C)	3.5
Odor Threshold, ppm	1.1

Ti. These can be combined with additional co-catalysts such as Ce, V, or W. With a large excess of ammonia, the selectivity to aniline is 87 to 90 percent at a phenol conversion of 98 percent. The byproducts are diphenylamine and carbazole. This technology is used at one plant in Ohio and at another plant in Japan. The economics of this process are favorable if low-cost phenol is available, and high-purity aniline is desired. Capital costs are low because benzene nitration is avoided. A typical process sketch along with a material balance is shown in Fig. 22.32.

Uses. MDI (4,4'-methylenebis phenylisocyanate) accounted for almost 85 percent of the worldwide demand for aniline in 2000. MDI is used primarily to make rigid polyurethane foam and polyurethane elastomers. MDI growth is expected to be 6.0 to 8.0 percent per year during the first ten years of the new century as its use continues to increase in the construction industry (the largest user of rigid polyurethane foam) and the auto industry (the largest user of reaction-injection molding plastics).[138,255]

Other aniline uses and the percent of worldwide aniline production that goes into these uses are: rubber-processing chemicals (9%), dyes and pigments (2%), agricultural chemicals (3%), specialty fibers (1%), and miscellaneous, such as explosives, epoxy curing agents, and pharmaceuticals (1%).[138,255]

Production. MDI has been the driving force behind the recovery of the aniline business since 1982 when the industry had a capacity utilization rate of less than 50 percent. By 1996, capacity utilization had approached 95 percent in some regions.[138]

Aniline production is concentrated in the United States, Western Europe, and Japan where aniline capacity is over 1.8 million tonnes per year.[138] Aniline's global production capacity in 1999 was 2.9 million tonnes, and demand in 2000 was estimated to be 2.68 million tonnes per year.[140,256]

Aniline pricing tends to track benzene pricing. In general the aniline price will move 1.2 cents per pound for each 10 cents per gallon movement in benzene price. Between 1995 and 2001, the aniline sales prices varied from US$ 0.35 per pound to US$ 0.40 per pound.[255]

The OSHA Permissible Exposure Limit (PEL) for aniline is 5 ppm for an 8-hour TWA.

OTHER COMPOUNDS

Several other nitrogen compounds are commercially important, including:

- Hexamethylenediamine which is used primarily in the manufacture of nylon.
- Dimethylformamide, a versatile solvent for organic and inorganic compounds and an important reaction medium for ionic and nonionic compounds.

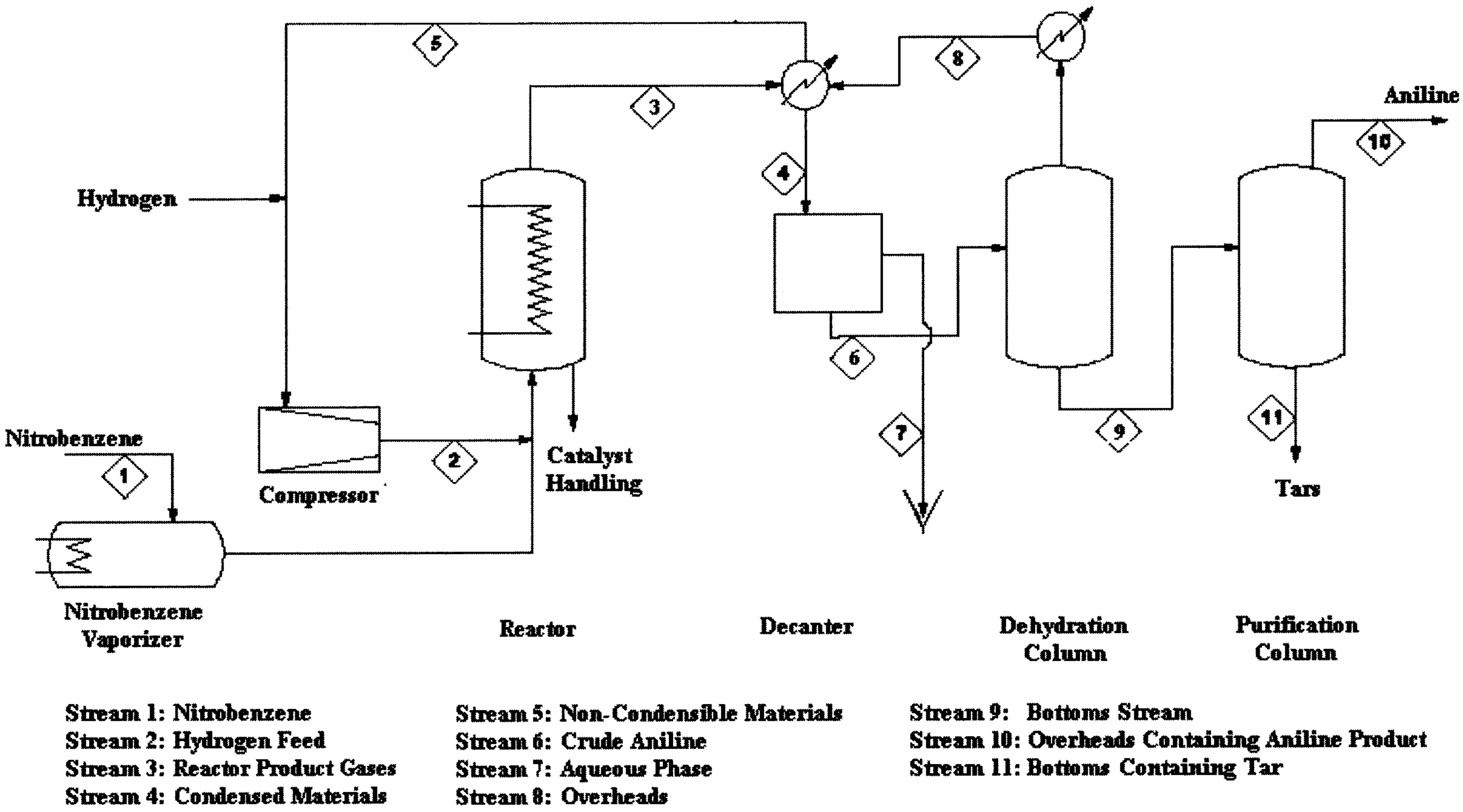
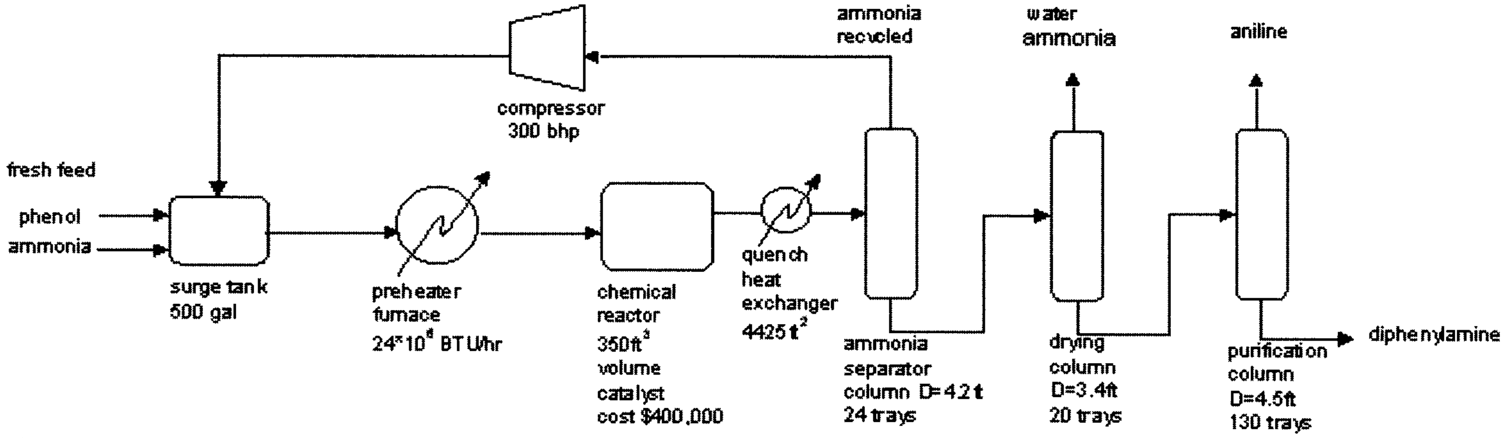


Fig. 22.31. Aniline production process: hydrogenation of nitrobenzene.



Production rate = 100 million pounds per year

Utilities:

Fuel: $24*10^6$ BTU/hr

Steam: 600psig - $10.2*10^6$ BTU/hr 150psig - $10*10^6$ BTU/hr

Cooling water: $9*10^6$ BTU/hr for ΔT=20°F

Electricity to drive the motor for the 300 bhp compressor

Preliminary Material Balance on Process

mass flow rates (lb/hr)	fresh feed	ammonia recycle	reactor feed	reactor product	ammonia separator column overhead	ammonia separator column bottoms	drying column overhead	drying column bottoms	purification column overhead	purification column bottoms
phenol	13,159	0	13,159	13	0	13	0	13	13	0
ammonia	4,199	43,070	47,269	44,900	43,070	1,830	1,830	0	0	0
aniline	0	10	10	12,890	10	12,880	315	12,565	12,565	0
water	0	11	11	2,528	11	2,517	2,505	12	12	0
diphenylamine	0	0	0	118	0	118	0	118	0	118
total	17,358	43,091	60,449	60,449	43,091	17,358	4,650	12,708	12,590	118
	60449				60449		17358		12708	
			preheater	quench exchanger						
temperature (°F)	100	142	118 670	673 110	112	248	141	289	278	491
pressure (psig)	260	260	260 250	240 230	220	220	6	6	5	5

Fig. 22.32. Aniline production process: ammonolysis of phenol.

- Dimethylacetamide, an important industrial solvent for polyacrylonitrile, vinyl resins, cellulose derivatives, styrene polymers, and linear polyesters.
- Isocyanates, important materials in the production of foams, resins, and rubbers.
- Calcium cyanamide, which is used as a fertilizer, herbicide, insecticide, a steel-making additive, and an ore processing material. It can also be used to make thiourea, guanidine, and ferrocyanides.[142]
- Methyl methacrylate, which is used in plastic glass, resins, and paint.[279,280,298]
- Acrylamide, which is used in water treatment chemicals, paper, and resins.[281–283]
- Caprolactam, which is used to make nylon 6.[264–266]
- Acrylonitrile, which is used in many different acrylic fibers.[276,277]

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