AMMONIA

1. Introduction

Ammonia [7664-41-7], NH_3, a colorless alkaline gas, is lighter than air and possesses a unique, penetrating odor. The preparation of ammonium salts dates back to the early Egyptians in the fourth century BC. Ammonia gas was first produced as a pure compound by Priestly in 1774.

In 1840, Justus von Liebig outlined the theoretical principles of plant nutrition and the role of fertilizers as essential plant nutrients. The second half of the century saw increasing use of fertilizers, however nitrogen sources were limited. Ammonium sulfate (a by product of coke ovens), Chilean saltpeter, Peruvian guano, crop rotations and other natural nitrogen sources were the main nitrogen fertilizers during this time.

The first nitric acid production facility based on the Ostwald process of oxidation of ammonia came on stream in 1906 at Gerthe, Germany. At the time, ammonia was still difficult to obtain, so the Ostwald process had to compete with other methods such as acidification of Chilean saltpeter and the electric arc process. During this same time period, the chemistry for production of synthetic ammonia by fixing atmospheric nitrogen was being worked out by Haber. Later in 1913, the first industrial ammonia process using the Haber-Bosch process was installed as a 30 metric ton/day plant at BASF's site in Oppau, Germany. A second ammonia plant went into operation in 1917 Leuna, which produced 350 metric ton/day by the end of World War I. The availability of low cost ammonia secured the long term viability of nitric acid production by oxidation of ammonia.

Both Haber and Bosch won the Nobel Prize for their work on ammonia. The development of the nitrogen fertilizer industry is a prime example of how people have technology to improve living standards. It is estimated that today as much as 40% of human's protein needs are derived indirectly from atmospheric nitrogen fixed by the Haber-Bosch process and its successors (1).

However, technology can also be used to the detriment of humankind. The ammonia and nitric acid technology enabled Germany to produce massive quantities of explosives during World War I even though the country was cut off from their traditional Chilean saltpeter nitrogen source. The Allies acquired the ammonia synthesis technology soon after World War I ended and thereafter began a swift expansion of world production. Today nearly 100×10^6 metric tons of synthetic ammonia and associated nitrogen chemicals are produced each year.

2. Occurrence

Ammonia occurs naturally throughout the universe. For example, ammonia is a minor component of the atmospheres of Jupiter and Saturn. On Earth, natural ammonia deposits contain salts rather than the base form. For example, ammonium chloride, [12125-02-9], NH_4Cl, deposits are found near volcanoes such as Vesuvius in Italy.

Nitrogen, in various forms, is an important element to life. It is a building block for amino and nucleic acids. Bound nitrogen cycles through the biosphere among plants, animals and micro-organisms. The ultimate source of all this nitrogen is the Earth's atmosphere. Atmospheric nitrogen can only be fixed to ammonia by a relatively few number of species of micro-organisms. Some are free living, such as the cyanobacteria; others are symbiotic with certain plants such as legumes.

Many important crops tend to take up nitrogen mainly in the nitrate form. This form of nitrogen is produced by soil organisms from various bound nitrogen sources, or is intentionally applied as a nitrate fertilizer. Unfortunately the nitrate ion is prone to groundwater leaching. Nitrate contamination of groundwater became a significant environmental issue in the 1980s. Improved farm management techniques have been the main tools used to deal with this issue.

Table 1. **Physical Properties of Anhydrous Ammonia**

Property	Value
molecular weight	17.03
boiling point, °C	−33.35
freezing point, °C	−77.7
critical temp, °C	133.0
critical pressure, kPa[a]	11,425
specific heat, J/(kg·K)[b]	
0°C	2097.2
100°C	2226.2
200°C	2105.6
heat of formation of gas, ΔH_f, kJ/mol[b]	
0 K	−39, 222
298 K	−46, 222
solubility in water, wt %	
0°C	42.8
20°C	33.1
40°C	23.4
60°C	14.1
specific gravity	
−40°C	0.690
0°C	0.639
40°C	0.580

[a] To convert kPa to psi, multiply by 0.145.
[b] To convert J to cal, divide by 4.184.

3. Physical Properties

Table 1 lists the important physical properties of ammonia; Table 2 gives the densities at 15°C; Figure 1 is a Mollier diagram giving additional thermodynamic data for ammonia. The flammable limits of ammonia in air are 16 to 25% by volume; in oxygen the range is 15 to 79%. Such mixtures can explode although ammonia–air mixtures are quite difficult to ignite. The ignition temperature is about 650°C.

Ammonia is readily absorbed in water to make ammonia liquor. Figure 2 summarizes the vapor–liquid equilibria of aqueous ammonia solutions and Figure 3 shows the solution vapor pressures. Additional thermodynamic properties may be found in the literature (2,3). Considerable heat is evolved during the solution of ammonia in water: approximately 2180 kJ (520 kcal) of heat is evolved upon the dissolution of 1 kg of ammonia gas.

Table 2. **Density of Aqueous Ammonia at 15°C**

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

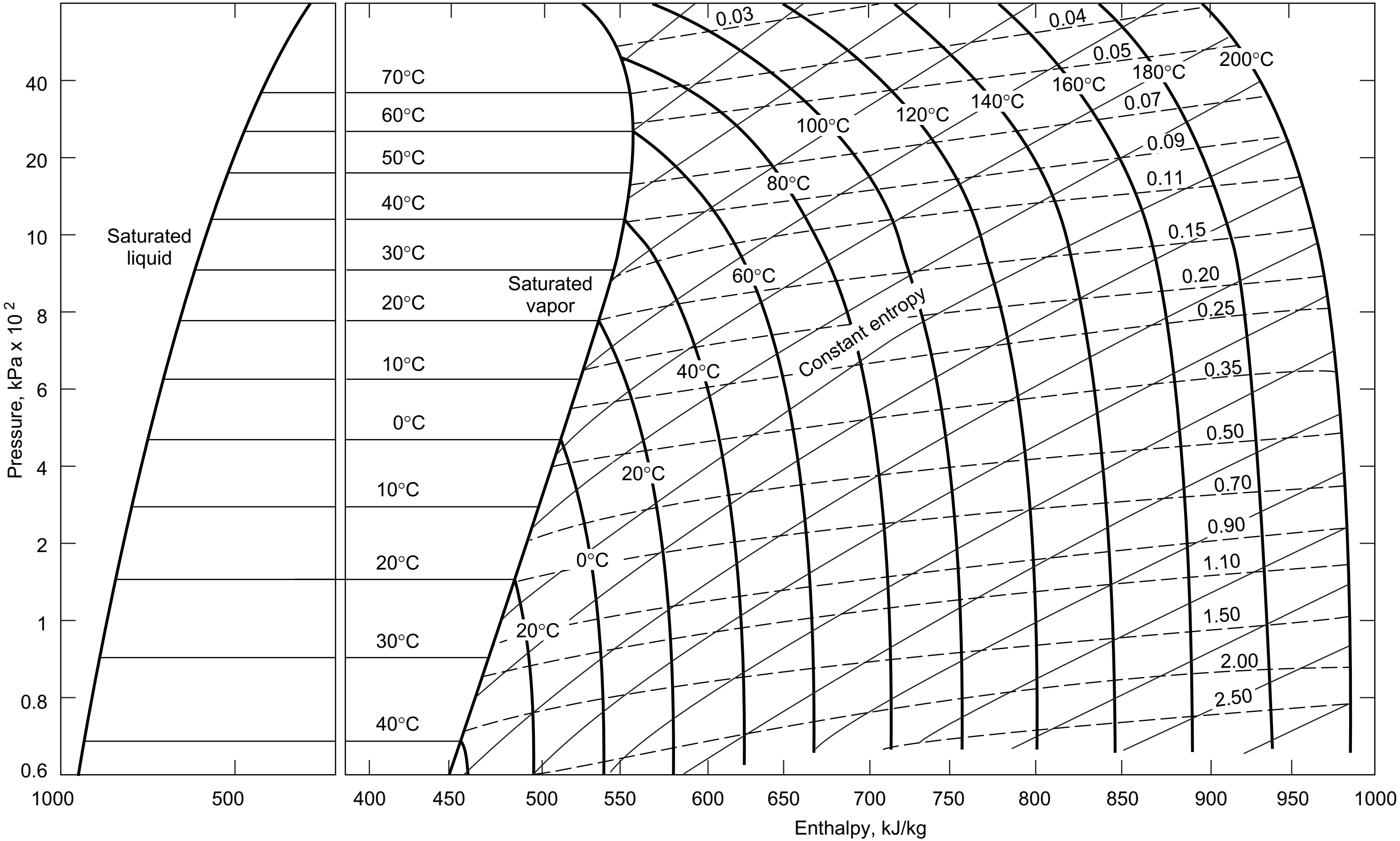

Fig. 1. Mollier diagram for ammonia. Numbers on dashed lines represent specific volume values in m^3/kg. To convert from kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184. Courtesy of Elliot Company.

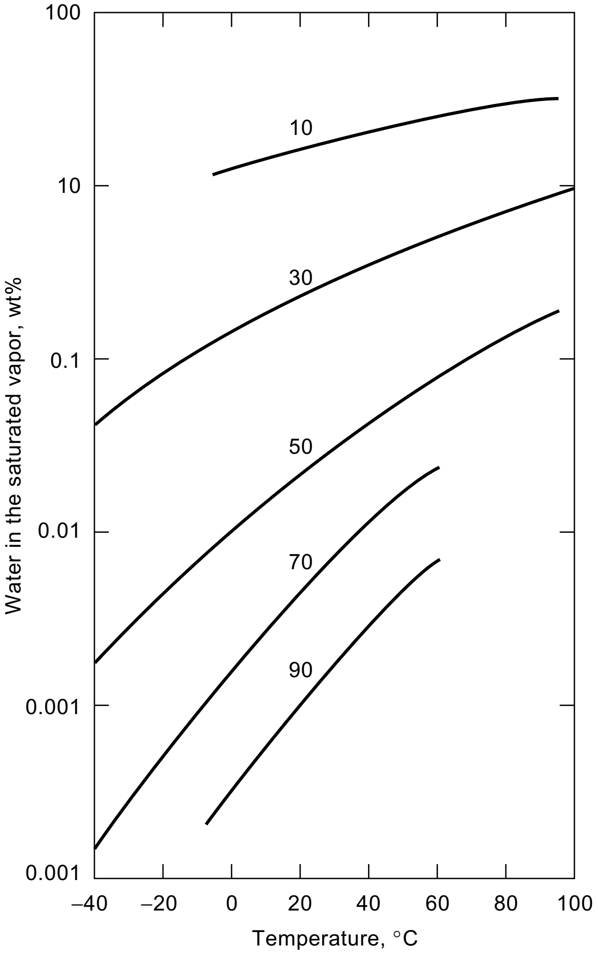

Fig. 2. Vapor–liquid equilibrium of ammonia–water system. Numbers represent the weight percent of ammonia in the liquid (2).

Ammonia is an excellent solvent for salts, and has an exceptional capacity to ionize electrolytes. The alkali metals and alkaline earth metals (except beryllium) are readily soluble in ammonia. Iodine, sulfur, and phosphorus dissolve in ammonia. In the presence of oxygen, copper is readily attacked by ammonia. Potassium, silver, and uranium are only slightly soluble. Both ammonium and beryllium chloride are very soluble, whereas most other metallic chlorides are slightly soluble or insoluble. Bromides are in general more soluble in ammonia than chlorides, and most of the iodides are more or less soluble. Oxides, fluorides, hydroxides, sulfates, sulfites, and carbonates are insoluble. Nitrates (eg, ammonium nitrate) and urea are soluble in both anhydrous and aqueous ammonia making the production of certain types of fertilizer nitrogen solutions possible. Many organic compounds such as amines (qv), nitro compounds, and aromatic sulfonic acids, also dissolve in liquid ammonia. Ammonia is superior to water

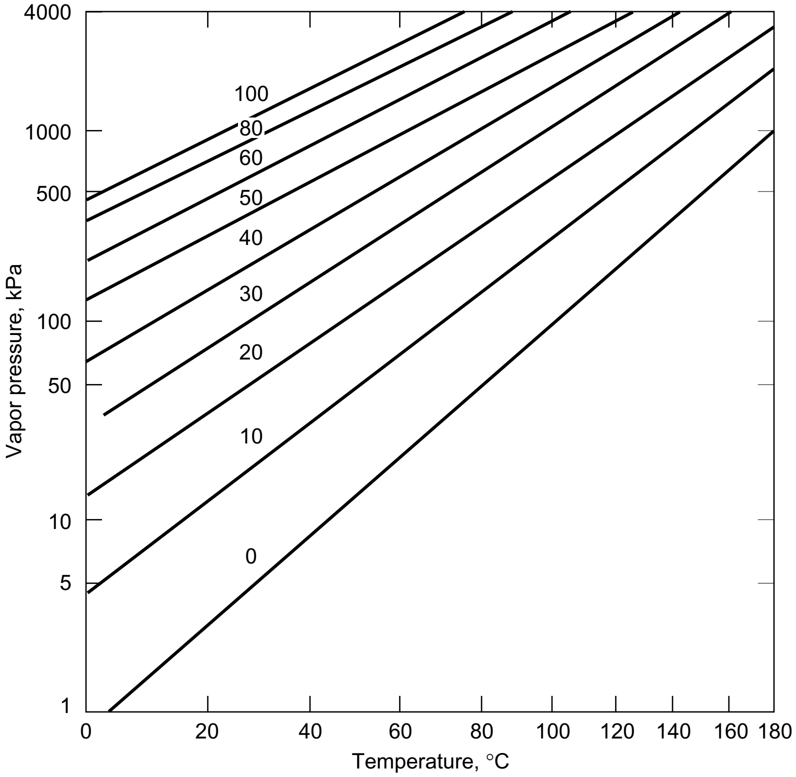

Fig. 3. Vapor pressure of aqueous ammonia solution (2). Numbers represent the weight percent of ammonia in the liquid. To convert kPa to psi, multiply by 0.145.

in solvating organic compounds such as benzene (qv), carbon tetrachloride, and hexane.

4. Chemical Properties

Ammonia is comparatively stable at ordinary temperatures, but decomposes into hydrogen and nitrogen at elevated temperatures. The rate of decomposition is greatly affected by the nature of the surfaces with which the gas comes into contact: glass is very inactive; porcelain and pumice have a distinct accelerating effect; and metals such as iron, nickel, osmium, zinc, and uranium have even more of an effect. At atmospheric pressure, decomposition begins at about 450–500°C, whereas in the presence of catalysts, it begins as low as 300°C and is nearly complete at 500–600°C. At 1000°C, however, a trace of ammonia remains. Ammonia decomposition, a source of high purity hydrogen and nitrogen for use in metals processing, can also be promoted electrically or photochemically.

Ammonia reacts readily with a large variety of substances (see AMMONIUM COMPOUNDS; AMINES BY REDUCTION; AMINES). Oxidation at a high temperature is one of the more important reactions, giving nitrogen and water. Gaseous ammonia is oxidized to water and nitrogen when heated to a relatively high temperature in the presence of oxides of the less positive metals, such as cupric oxide. Powerful oxidizing agents, eg, potassium permanganate, react similarly at ordinary temperatures.

$$2\,NH_3 + 2\,KMnO_4 \longrightarrow 2\,KOH + 2\,MnO_2 + 2\,H_2O + N_2 \qquad (1)$$

The action of chlorine on ammonia can also be regarded as an oxidation reaction.

$$8\,NH_3 + 3\,Cl_2 \longrightarrow N_2 + 6\,NH_4Cl \qquad (2)$$

A major step in the production of nitric acid [7697-37-2] (qv) is the catalytic oxidation of ammonia to nitric acid and water. Very short contact times on a platinum–rhodium catalyst at temperatures above 650°C are required.

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O \qquad (3)$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \qquad (4)$$

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO \qquad (5)$$

The neutralization of acids is of commercial importance. Three principal fertilizers, ammonium nitrate [6484-52-2], NH_4NO_3, ammonium sulfate [7782-20-2], $(NH_4)_2SO_4$, and ammonium phosphate [10361-65-6], $(NH_4)_3PO_4$, are made by reaction of the respective acids with ammonia.

The reaction between ammonia and water is reversible.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (6)$$

The aqueous solubility of ammonia decreases rapidly as temperature increases. The existence of undissociated ammonium hydroxide [1336-21-6], NH_4OH, in aqueous solution is doubtful although there are indications that ammonia exists in water in the form of the hydrates NH_3H_2O and $2\,NH_3{\cdot}H_2O$. The ammonium ion, $NH^+{}_4$, behaves similarly to the alkali metal cations. Ammonia, a comparatively weak base, however, ionizes in water to a much lesser extent than sodium hydroxide. In a molar solution of aqueous ammonia, the concentration of the hydroxyl ion is about two-hundredths that of the hydroxyl ion concentration in a molar sodium hydroxide solution.

Aqueous ammonia also acts as a base precipitating metallic hydroxides from solutions of their salts, and in forming complex ions in the presence of excess ammonia. For example, using copper sulfate solution, cupric hydroxide, which is at first precipitated, redissolves in excess ammonia because of the formation of the complex tetramminecopper(II) ion.

$$CuSO_4 + 2\,NH_3{\cdot}H_2O \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4 \qquad (7)$$

$$Cu(OH)_2 \longrightarrow Cu^{2+} + 2\,OH^- \qquad (8)$$

$$4\,NH_3 + Cu^{2+} \rightleftarrows [Cu(NH_3)_4]^{2+} \qquad (9)$$

Potassium dissolves in liquid ammonia, but the conversion of a small amount of the metallic potassium to the metallic amide takes several days. By applying the same technique using sodium metal, sodium amide [7782-92-5], $NaNH_2$, a white solid, can be formed.

$$2\,Na + 2\,NH_3 \longrightarrow 2\,NaNH_2 + H_2 \tag{10}$$

Heating metallic lithium in a stream of gaseous ammonia gives lithium amide [7782-89-0] $LiNH_2$, which may also be prepared from liquid ammonia and lithium in the presence of platinum black. Amides of the alkali metals can be prepared by double-decomposition reactions in liquid ammonia. For example

$$NaI + KNH_2 \xrightarrow{\text{liq } NH_3} NaNH_2 + KI \tag{11}$$

Heating ammonia with a reactive metal, such as magnesium, gives the nitride.

$$3\,Mg + 2\,NH_3 \longrightarrow Mg_3N_2 + 3\,H_2 \tag{12}$$

Magnesium reacts slowly at lower temperatures to give the amide, as do all active metals; this reaction is catalyzed by transition metal ions. Aluminum nitride [24304-00-5], AlN, barium nitride [12047-79-9], Ba_3N_2, calcium nitride [12013-82-0], Ca_3N_2, strontium nitride [12033-82-8], Sr_3N_2, and titanium nitride [25583-20-4], TiN, may be formed by heating the corresponding amides.

Halogens react with ammonia. Chlorine orbromine liberate nitrogen from excess ammonia and give the corresponding ammonium salt. Substitution probably takes place first. The resulting trihalide combines loosely with another molecule of ammonia, to give $NCl_3 \cdot NH_3$ for example. These ammoniates are very unstable and decompose in the presence of excess ammonia to give the ammonium salt and nitrogen.

$$NCl_3{\cdot}NH_3 + 3\,NH_3 \longrightarrow N_2 + 3\,NH_4Cl \tag{13}$$

The iodine compound is more stable and separates as so-called nitrogen triiodide monoammoniate [14014-86-9], $NI_3 \cdot NH_3$, an insoluble brownish-black solid, which decomposes when exposed to light in the presence of ammonia. In reactions of the halogens with the respective ammonium salts, however, the action is different. Chlorine replaces hydrogen and nitrogen chloride [10025-85-1], NCl_3, separates as oily, yellow droplets capable of spontaneous explosive decomposition.

$$NH_4Cl + 3\,Cl_2 \longrightarrow NCl_3 + 4\,HCl \tag{14}$$

The hydrogen of the ammonium salt is not replaced by bromine and iodine. These elements combine with the salt to form perhalides.

$$NH_4Br + Br_2 \longrightarrow NH_4Br_3 \tag{15}$$

A number of perhalides are known, and one of the most stable is ammonium tetrachloroiodide [19702-43-3], NH_4ICl_4. Ammonia reacts with chlorine in dilute solution to give chloramines, a reaction important in water purification (see CHLORAMINES AND BROMAMINES). Depending upon the pH of the water, either monochloramine [10599-90-3], NH_2Cl, ordichloramine [3400-09-7], $NHCl_2$, is formed. In the dilutions encountered in waterworks practice, monochloramine is nearly always found, except in the case of very acidic water (see BLEACHING AGENTS; WATER).

Ammonia reacts with phosphorus vapor at red heat to give nitrogen and phosphine.

$$2\,NH_3 + 2\,P \longrightarrow 2\,PH_3 + N_2 \tag{16}$$

Sulfur vapor and ammonia react to give ammonium sulfide and nitrogen; sulfur and liquid anhydrous ammonia react to produce nitrogen sulfide [28950-34-7], N_4S_4.

$$10\,S + 4\,NH_3 \longrightarrow 6\,H_2S + N_4S_4 \tag{17}$$

Ammonia and carbon at red heat giveammonium cyanide [12211-52-8], NH_4CN.

Ammonia forms a great variety of addition or coordination compounds (qv), also called ammoniates, in analogy with hydrates. Thus $CaCl_2{\cdot}6NH_3$ and $CuSO_4{\cdot}4NH_3$ are comparable to $CaCl_2{\cdot}6H_2O$ and $CuSO_4{\cdot}4H_2O$, respectively, and, when regarded as coordination compounds, are called ammines and written as complexes, eg, $[Cu(NH_3)_4]SO_4$. The solubility in water of such compounds is often quite different from the solubility of the parent salts. For example, silver chloride, AgCl, is almost insoluble in water, whereas $[Ag(NH_3)_2]Cl$ is readily soluble. Thus silver chloride dissolves in aqueous ammonia. Similar reactions take place with other water insoluble silver and copper salts. Many ammines can be obtained in a crystalline form, particularly those of cobalt, chromium, andplatinum.

Of major industrial importance is the reaction of ammonia and carbon dioxide giving ammonium carbamate [1111-78-0], $CH_6N_2O_2$.

$$2\,NH_3 + CO_2 \longrightarrow NH_2CO_2NH_4 \tag{18}$$

which then decomposes to urea (qv) and water

$$NH_2CO_2NH_4 \longrightarrow NH_2CONH_2 + H_2O \tag{19}$$

This is an example of an ammonolytic reaction in which a chemical bond is broken by the addition of ammonia. It is analogous to the hydrolysis reactions of water. An impressive number of inorganic and organic compounds undergo ammonolysis.

5. Source and Supplies

Ammonia is a world class commodity. It is manufactured in over 80 countries. Global ammonia production capacities are given in Table 3. China and the former USSR are currently the largest producers. Table 4 lists U.S. ammonia production capacities by company.

Table 3. **Estimated 1998 Global Ammonia Capacity By Region**[a]

Region	Capacity, 1000 t/yr	Share, %
United States	18,465	15
China	27,082	22
former USSR	20,927	17
South Asia	14,772	12
Western Europe	11,079	9
Near East	8,617	7
Central Europe	7,386	6
Indonesia and Japan	4,924	4
Mexico and Caribbean	3,693	3
other	6,155	5
Total	*123,100*	*100*

[a] Ref. 1.

Table 4. **Table 1999 U.S. Ammonia Producers and Capacities**[a]

Type	Company	Locations	Capacity, 1000 t/yr
Exisiting:	Agrium US	Borger, TX	430
	Air Products	Pace, FL	90
	Allied Signal	Hopewell, VA	535
	Avondale Ammonia	Waggaman, LA	400
	Borden	Geismar, LA	370
	CF Industries	Donaldson, LA	2,455
	Chevron	El Segundo, CA; Richmond, CA	35
	Coastal	Cheyenne, WY; Freeport, TX; St. Helens, OR	1,105
	Dakota Gasification	Beulah, ND	330
	DuPont	Beaumont, TX	430
	Farmland Industries	Beatrice, NE; Dodge City, KS; Enid, OK; Ft. Dodge IA; Lawrence, KS; Pollock, LA	2,230
	Green Valley	Creston, IA	50
	IMC	Faustina, LA	510
	Koch Nitrogen	Sterlington, LA	1,100
	LaRoche	Cherokee, AL	155
	Mississippi Chemical	Yazoo City, MS	645
	PCs	Augusta, GA; Geismar, LA; Lima, OH; Memphis, TN	2,500
	Royster-Clark	East Dubuque, IL	275
	J.R. Simplot	Pocatello, ID	110
	Terra	Blytheville, AR; Sergeant Bluff, IA; Verdigris, OK; Woodward, OK	2,060
	Triad Nitrogen	Donaldson, LA	925
	Ultramar Diamond Shamrock	Dumas, TX	135
	Unocal	Finely, WA; Kenai, AK	1,335
	Wil-Gro	Pryor, OK	255
		Total exisiting	*18,465*
Announced:	Farmland Industries	Coffeyville, KS	600
	Terra	Beaumont, TX	280
		Total announced	880

[a] Ref. 4

The current global situation is one of overcapacity and weak prices. The past few years have seen several U.S. plant closures and temporary shutdowns. Many of the plants in the United States were built in the 1960s and 1970s. Although U.S. natural gas prices are high compared to natural gas prices in remote regions, U.S. plants are often able to compete with imports on a cash basis since the original plant investment has been fully depreciated. Many U.S. plants have been modernized to upgrade technology and to expand production beyond their original nameplate capacity. However, low cost imports and soft demand for nitrogen fertilizers are expected to plague the U.S. ammonia industry.

In order to compete with existing facilities, new complexes must use modern technologies and have access to low cost feedstock. Usually new plants are built at world scale capacities to enjoy economies of scale. The trend of the past 10–20 years has been that new ammonia plants are built primarily in regions such as Trinidad, the Middle East, North Africa, etc, where large quantities of low cost natural gas are available. Countries in these areas often view a nitrogen fertilizer plant as a way to monetize remote natural gas which otherwise would have little value due to the lack of natural gas infrastructure and local markets.

6. Manufacture

The ammonia synthesis reaction is deceptively simple: nitrogen is combined with hydrogen in a 1:3 stoichiometric ratio to give ammonia with no by-products. The difficulty lies in how to obtain the hydrogen needed for the reaction. As shown in Figure 4, the hydrogen production method is the main source of distinction between the various ammonia production routes. In fact, the majority of the equipment in a typical ammonia plant is devoted to hydrogen production rather than ammonia synthesis. Most of the improvements in technology over the past 90 years have concerned the hydrogen production step.

The bulk of world ammonia production is based on steam reforming. Any hydrocarbon feed that can be completely vaporized can be used. Natural gas and naphtha are common. The bulk of existing and nearly all new steam reforming facilities use natural gas for feedstock. Economics and availability influence the decision on feedstock and production technology. The recent trend towards using ammonia and other synthesis gas products to monetize remote natural gas suggests that steam reforming of natural gas will maintain its dominant position in the foreseeable future.

The exact technology used within a facility depends upon the age of the plant, economics, and the overall fit of the ammonia facility within the entire nitrogen or syngas complex. A standard steam methane reforming plant with conventional gas purification is described in some detail. Other technology routes based on partial oxidation, water electrolysis plus predictions on future technologies are also briefly discussed.

6.1. Steam Reforming With Conventional Gas Purification. Today's prevailing plant design is the single-train plant in which all of the large equipment and machinery are single units. This gives lower capital costs but

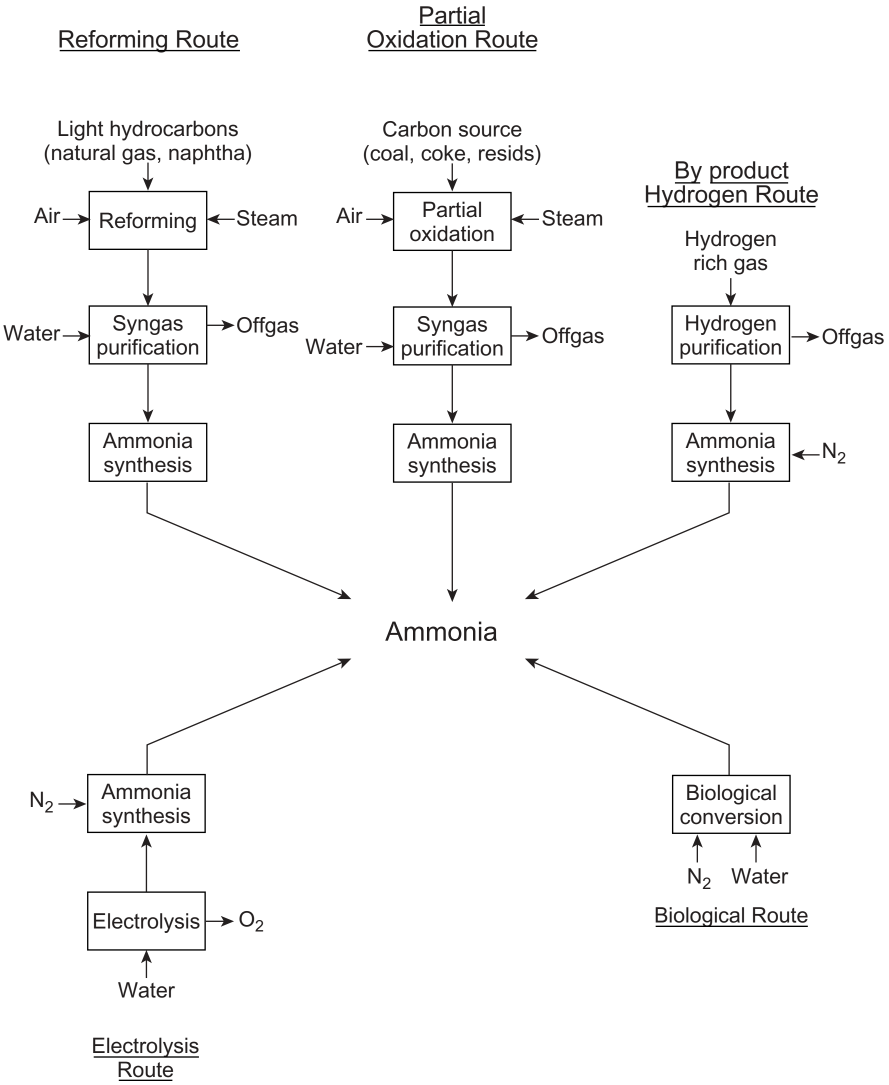

Fig. 4. Ammonia production routes.

reduces the ability to operate the plant at reduced rates during failures of major pieces of equipment. However, attention to equipment reliability issues and preventative maintenance has resulted in on-line factors greater than 95%. Reference 5 reports on the causes of unscheduled downtime for four large ammonia plants.

Figure 5 is a flow diagram for a steam reforming plant. The main steps are (1) feed preparation where the natural gas is compressed to reforming pressures and desulfurized to protect downstream catalysts, (2) reforming where the natural gas is mixed with steam and air to produce a crude syngas mixture, (3) Syngas clean-up where a purified stream of nitrogen and hydrogen is produced in the

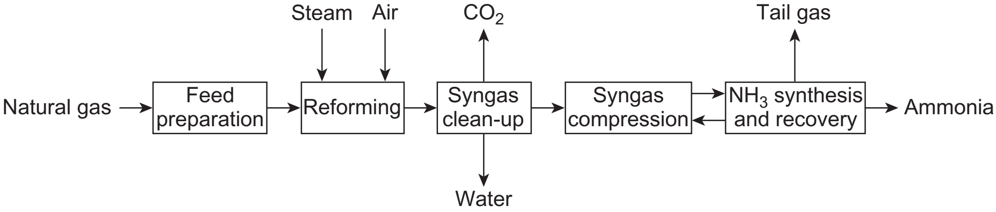

Fig. 5. Block flow diagram for ammonia production by steam reforming of methane.

correct stoichiometric ratio, (4) Syngas compression followed by (5) ammonia synthesis and recovery.

Figure 6 is a flow sheet for a Kellogg high capacity single-train ammonia plant using conventional technologies. Although these diagrams represent only one of many possible flow sheet variations, Figures 5 and 6 are used to illustrate a typical ammonia plant. Common variations are also discussed.

Feed Preparation. Steam reforming of methane is usually conducted at ca 3–4 MPa (30–40 atm). This pressure is a compromise leading to a minimum capital and/or operating cost for the overall process while satisfying mechanical constraints of the process equipment.

Usually downstream ammonia synthesis occurs at a much higher pressure than what is allowed by the mechanical limits of the steam reforming furnace, so the natural gas is compressed to reforming pressures. A second compression step occurs later in the flow sheet where the purified nitrogen and hydrogen mixture produced from the reforming operation is further compressed to ammonia synthesis pressure.

Conceptually, this two-step compression sequence is not very satisfactory since it leads to higher costs than a single compression step would require. However, current mechanical constraints and ammonia synthesis reaction kinetics force this compromise solution. Compression costs are roughly related to the number of moles processed. The advent of high pressure reforming in the 1960s lead to a significant decline in ammonia production cost since much of the compression was shifted upstream of the reformer where there are fewer moles of gas to process. Much work has been done to lower the ammonia synthesis pressure using higher activity catalysts. The long term goal is to eliminate completely the need for the intermediate syngas compressors and provide all of the process compression upstream of the reformer.

The feed gas compressor may or may not be needed depending upon plant location. The feed compressor is not needed if a high pressure gas transmission line supplies the plant. Much attention has been paid to all of the compressors in ammonia plants (natural gas feed, process air, syngas, and refrigeration) since they strongly influence plant reliability, capital and operating costs, and plant capacity.

Sweet natural gas typically contains 1–5 ppm of sulfur. About half of the sulfur is in the form of H_2S. This is just the residual sulfur left in the gas after sweetening at the gas plant. The other half of the sulfur is organic sulfur from odorants added to help locate pipeline leaks. The odorants may not be

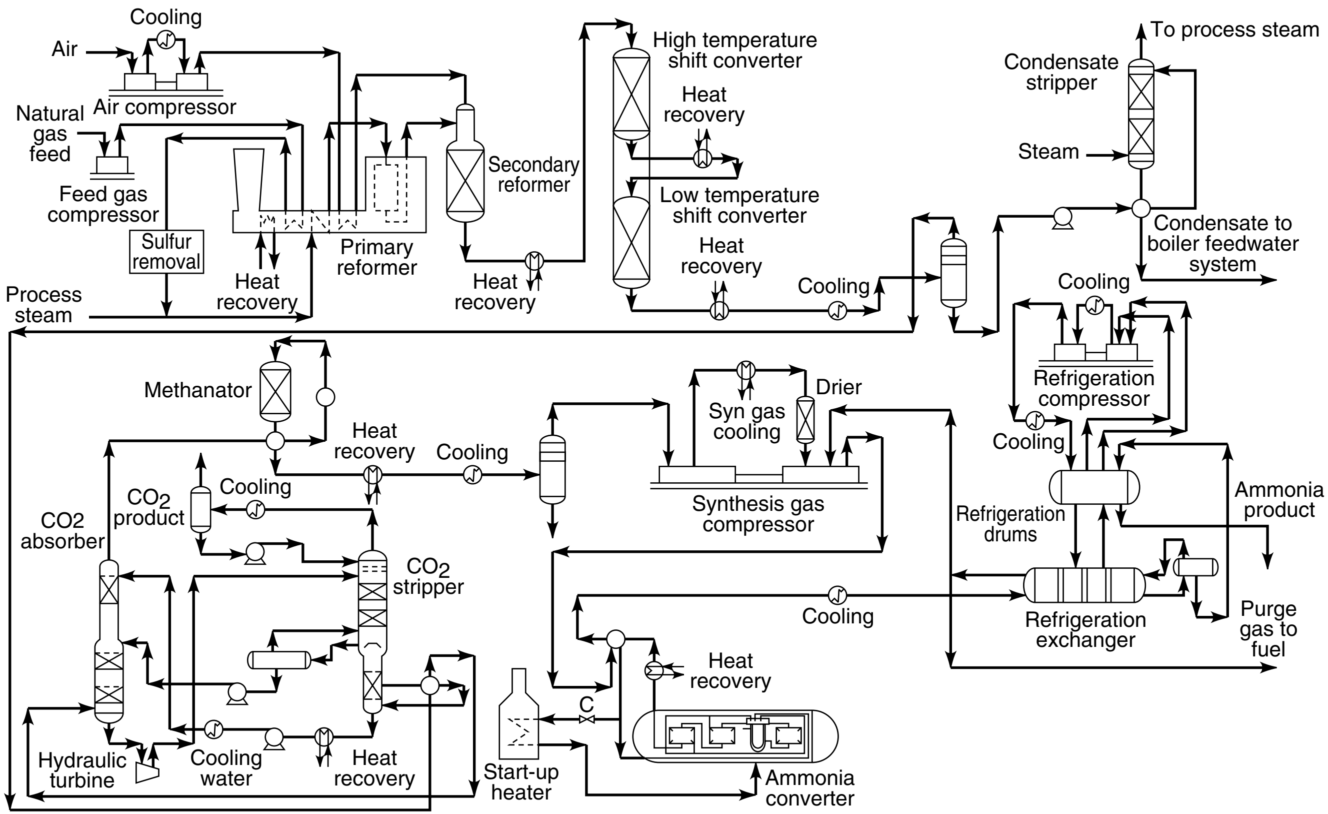

Fig. 6. Flow sheet for a Kellogg high capacity single-train ammonia plant.

present in the gas if the ammonia plant is located in a remote region close to the natural gas source.

The catalysts used in the downstream reactors are very sensitive to sulfur poisoning. Conventional steam reformers are designed for 2–3 years of operation between catalyst changeout. This translates into a total sulfur specification of less than 1 ppm. Even lower levels (ca 0.1 ppm) are required when low temperature shift catalysts are used. Most conventional plants meet these stringent requirements by pretreatment of the feed using a combination of hydrogenation to convert organic sulfur into H_2S followed by absorption of H_2S onto zinc oxide.

In the hydrogenation step, a small slipstream of product hydrogen is recycled back into the feed and the combined feed and recycle hydrogen is passed over a cobaltmolybdenum catalyst. For a mercaptan (or thiol), the reaction is

$$\mathrm{RCH_2SH + H_2 \longrightarrow H_2S + RCH_3} \tag{20}$$

Typically this reaction is done at 350–400°C . The H_2S is then absorbed on a bed of zinc oxide:

$$\mathrm{ZnO + H_2S \longrightarrow ZnS + H_2O} \tag{21}$$

The zinc oxide beds are typically not regenerated but are replaced with new absorbent once exhausted.

Fixed bed desulfurization is impractical if the natural gas contains large amounts of sulfur. In this case, bulk sulfur removal and recovery in an acid gas absorption stripping system, followed by fixed bed residual clean up is usually employed.

Chlorides may be found in natural gas, particularly associated with offshore reservoirs. Modified alumina catalysts have been developed to irreversibly absorb these poisons from the feed gas. Some natural gases have also been found to contain mercury, which is a reformer catalyst poison when present in sufficiently large amounts. Activated carbon beds impregnated with sulfur have been found to be effective in removing this metal.

Reforming. The steam reforming reactions for the alkanes present in natural gas are shown in equations 22–24, ΔH° values are at 25°C in kJ/kgmol; ΔS° values are at 25°C in kJ/K kgmol

$$\mathrm{CH_4 + 2\,H_2O \leftrightarrow CO + 3\,H_2} \quad \Delta H^\circ,\ 206,172;\ \Delta S^\circ,\ 214.6 \tag{22}$$

$$\mathrm{CH_3\,CH_3 + 2\,H_2O \leftrightarrow 2\,CO + 5\,H_2} \quad \Delta H^\circ,\ 347,338;\ \Delta S^\circ,\ 441.4 \tag{23}$$

$$\mathrm{CH_3\,CH_2\,CH_3 + 3\,H_2O \leftrightarrow 3\,CO + 7\,H_2} \quad \Delta H^\circ,\ 497,797;\ \Delta S^\circ,\ 671.3 \tag{24}$$

As indicated these are reversible equilibrium type reactions. The reforming reaction is highly endothermic, as shown by the large positive values of ΔH°. Conventional primary steam reformers operate in the gas phase at high temperature (750–850°C) and medium pressures (3–4 MPa). Temperatures and pressures are dictated by chemistry, mechanical limitations and the design philosophy used for compression within the overall process train.

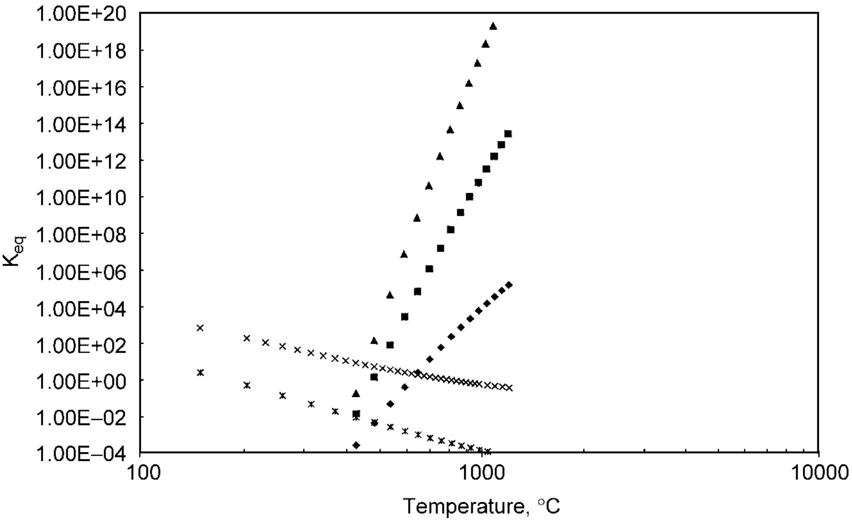

Fig. 7. Effects of temperature on equilibrium constants ◆ methane reforming; ■ ethane reforming; ▲ propane reforming; × shift; ⁎ ammonia synthesis.

Temperature has a strong effect on the position of equilibrium for the reforming reactions. The equilibrium constant at any temperature can be approximated by:

$$\ln\left(K_{eq}\right) = \ln\left(\frac{[CO]^n [H_2]^{(2n+1)}}{[C_n\, H_{(2n+2)}][H_2O]^n}\right) = -\frac{\Delta H^\circ - T\Delta S^\circ}{RT}$$

where K_{eq} is the equilibrium constant, the terms in bracket represent concentrations, n is the number of carbon atoms in the hydrocarbon feed, and R is the gas constant. Figure 7 shows that higher temperatures lead to larger equilibrium constants. This means that higher temperatures favor hydrogen production. The figure also shows that at a given temperature, the equilibrium constant is larger as the molecular weight of the hydrocarbon feed increases. In fact, at conditions typically used for conventional primary steam reformers, about 95% of the methane is converted while nearly 100% conversions are obtained for the ethane and higher hydrocarbons in the feed. The values in Figure 7 deviate slightly from the above approximation since corrections were made to account for the effects of temperature on ΔH° and ΔS°.

The effect of pressure can be qualitatively examined using LeChatelier's principle. The left hand side of the reforming reactions contain fewer moles than the right, so a lower system pressure would favor hydrogen production. Operating pressures, however, are usually set by the compression philosophy rather than being based on the process chemistry. Compression costs can be significant and these are related to the number of moles processed. The hydrogen product contains more moles than the feed, so the compression philosophy is usually to operate the reforming section at as high a pressure as allowed by mechanical limitations of the primary reformer. This minimizes the cost associated with the downstream synthesis gas compressor and leads to lower overall costs.

The steam to carbon ratio (S/C ratio) of the reformer feed can also be manipulated. This ratio is defined as the number of moles of steam divided by the number of moles of carbon atoms in the feed. High S/C ratios favor hydrogen production but at the expense of larger equipment and higher utility costs. Low S/C ratios encourage carbon soot formation reactions. Conventional steam reformers are designed for S/C between 2 to 6, with 3 being a typical value.

Decades of R&D have gone into improving reforming catalysts. Commercial reforming catalysts typically contain nickel oxide (15–25 wt%) on a carrier such as α-alumina. Sometimes promoters such as uranium oxide or chromium oxide are also used. The nickel oxide must be reduced to metallic nickel prior to start-up since the catalyst is active only in this form. This requirement also explains why reforming catalyst are sensitive to sulfur poisoning since metallic nickel can react with sulfur compounds to form nickel sulfide. In addition to catalyzing the reforming reaction, commercial catalysts also catalyze the water-gas shift reaction described later, although the conditions required by the reforming reactions are such that the equilibrium for the shift reaction is to the left of its normal position in conventional shift reactors.

Conventional steam reformers use a fired heater to supply high temperature heat to drive the reforming reactions. The heat needed to drive the reforming reactions to a high degree of conversion must be supplied at a high temperature. Usually this is done by passing the feed gas through tubes in the radiant section of the furnace. The tubes are packed with catalyst to improve the reaction rate. The fuel to the reforming furnace is usually natural gas and process tail gases, although other fuel sources could be used. After leaving the radiant section of the furnace, the combustion gases still contain a large amount of available heat energy that can be recovered by producing high pressure steam. This high pressure steam can either be exported to other units in the facilities, used directly for process gas compression with steam driven turbines, or used for electricity production in a Rankine or similar cycle.

Prereforming (not shown in Fig. 6) is another potential use for the heat available in the convection section of the furnace. In this scheme, the natural gas and steam mixture is preheated in the convection section of the reforming furnace and then past through an external adiabatic bed of reforming catalyst. The temperatures in prereforming are not high enough to drive the reforming reactions to high conversion, thus the effluent from a prereformer is usually further heated in the furnace convection section and then routed to the radiant section for primary reforming. The main advantage of prereforming is that all of the ethane and higher hydrocarbons in the feed will be reformed prior to reaching the primary reformer. This results in more even operation of the reformer furnace in the face of feed composition changes. Prereforming also allows for lower S/C ratios since coking is less likely to occur. Prereforming uses a portion of the available heat in the convection section to drive the reforming reaction. Whether it is more cost effective to use the convection section heat for prereforming or for steam/electricity production depends on the specific economic details for the plant.

The product gases from the primary reforming step contain about 5–8% unreacted methane. The gases are usually sent to a secondary reformer to complete the reforming reactions. A secondary reformer consists of a burner in a refractory lined vessel and another reforming catalyst bed. In primary reforming, the high temperature energy absorbed by the reaction is supplied indirectly by a fired heater that uses natural gas, fuel oil, or tail gases as the fuel. In secondary reforming, a portion of the feed is combusted in an oxygen starved environment. Burner exit temperatures are on the order of 1200°C. The hot gases are then passed over reforming catalysts and the temperature drops to ca 1000°C due to the endothermic heat of reaction. At this temperature, the methane content of the syngas has been reduced to ca 0.2–0.3%. The heat released during combustion is used to drive the reforming reactions. From a chemistry point of view, primary and secondary reforming are closely related with the main difference being the source of high temperature heat used to the drive the reforming reaction.

The combustion reactions for natural gas components are hown in equations 25–29. The ΔH° values are at 25°C in kJ/kgmol ard the ΔS° values at 25°C are in kJ/(K kgmol)

$$CH_4 + 3/2\,O_2 \leftrightarrow CO + 2\,H_2O \quad \Delta H^\circ,\ -519{,}306\,\Delta S^\circ,\ 81.3 \tag{25}$$

$$CH_3\,CH_3 + 5/2\,O_2 \leftrightarrow 2\,CO + 3\,H_2O \quad \Delta H^\circ,\ -861{,}792\,\Delta S^\circ,\ 219.3 \tag{26}$$

$$CH_3\,CH_2\,CH_3 + 7/2\,O_2 \leftrightarrow 3\,CO + 4\,H_2O \quad \Delta H^\circ,\ -1{,}194{,}985\,\Delta S^\circ,\ 360.4 \tag{27}$$

$$CO + 1/2\,O_2 \leftrightarrow CO_2 \quad \Delta H^\circ,\ -282{,}995\,\Delta S^\circ,\ -86.4 \tag{28}$$

$$H_2 + 1/2\,O_2 \leftrightarrow H_2O \quad \Delta H^\circ,\ -241{,}826\,\Delta S^\circ,\ -44.4 \tag{29}$$

Reactions 25–29 produce carbon monoxide, reaction 27 completes the oxidation to carbon dioxide, and reaction 29 is for the oxidation of hydrogen. The thermodynamic functions are evaluated for gaseous water. These reactions are irreversible and strongly exothermic as indicated by the large negative values for ΔH°.

The oxygen used in the partial oxidation route can be supplied from compressed air, or from enriched oxygen steams obtained from membrane units, vacuum swing adsorption units or cryogenic air separation plants. The source of the oxygen used depends upon economics, process constrains, and specifications on hydrogen product purity. Frequently compressed air is used with the amount used being set by the nitrogen stoichiometry for ammonia synthesis.

It is possible to eliminate completely the primary reforming step and do all of the reforming in a special secondary reformer design called an autothermal reformer. The energy balance usually requires than either an oxygen enriched air source is needed or nitrogen in excess of that needed for ammonia synthesis has to be removed in the downstream syngas clean-up step.

Syngas Clean-up. The reformer effluent gas contains the desired hydrogen and nitrogen plus bulk impurities such as carbon monoxide, carbon dioxide, water, residual methane and trace impurities such as argon and helium. The bulk impurities have to be removed prior to ammonia synthesis. Oxygen containing compounds are serious catalyst poisons for the ammonia synthesis catalyst. A 10 ppm total is a typical maximum specification allowed for all oxygen containing compounds in the ammonia synthesis reactor feed. In addition, the economics for removal of trace inerts from the synthesis gas are sometimes justified since this reduces and potentially eliminates the need to purge the ammonia synthesis gas loop.

As shown in Figure 6, most conventional ammonia plants use the following combination of steps for syngas clean-up: high temperature and low temperature shift conversion to convert the bulk of the carbon monoxide into carbon dioxide, bulk water removal by cooling of the shifted gas followed by knockout of the water condensate, bulk carbon dioxide removal using an absorber–stripper system, methanation to convert residual carbon oxides back to essentially inert methane gas followed by desiccant drying to remove trace water.

The shift reactors are adiabatic packed bed reactors used to convert carbon monoxide into carbon dioxide and additional hydrogen. The stoichiometry and thermodynamics of the water-gas shift reaction (eq. 30) are ΔH° at 25°C, $\mathrm{kJ/kgmol} = -41,169$; ΔS° at 25°C, $\mathrm{kJ/(K\,kgmol)} = -42.0$.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (30)$$

Like the reforming reactions, the water-gas shift reaction is a reversible equilibrium type reaction. The reaction is exothermic, as indicated by the negative value of ΔH°.

Figure 7 shows the effect of temperature on the equilibrium constant. Lower temperatures shift the reaction to the right. Reforming catalyst will also catalyze the shift reaction, however the position of equilibrium favors the left hand components at the temperatures commonly encountered in reforming. Industrial shift catalysts do not catalyze reforming reactions. Pressure does not influence the thermodynamics of the shift reaction since the number of moles is the same on both sides of the equation. Pressure does, however, affect the kinetics of the shift reaction, with higher pressures leading to faster kinetic rates.

The shift reaction can occur without the presence of a catalyst. Depending upon pressure, temperatures in excess of 900°C will permit the shift reaction to proceed without a catalyst. The high temperatures encountered in partial oxidation and experimental plasma reactors are high enough that the uncatalyzed shift reaction has to be considered.

Decades of R&D have also gone into improving shift catalyst. In clean gas services, the high temperature shift (HT shift) catalysts are typically a chromium promoted iron oxide. The catalyst is supplied in a oxidized state and must be reduced *in-situ* prior to start-up. Like reforming catalysts, iron-based shift catalysts are poisoned by sulfur compounds. Dirty shift catalysts based on cobalt–molybdenum are used in raw gas processes containing elevated sulfur levels. These catalysts actually require sulfur in the feed to maintain their activity. High temperature shift reactions are carried out between 300–530°C. This range is set by the catalyst activity and the desired conversion. Typically, carbon monoxide content is ca 3 vol% after high temperature shift conversion. The reaction is commonly carried out in a packed-bed reactor. Since the reaction is exothermic, temperature rises on the order of 70°C are common. When large amounts of carbon monoxide are to be converted, the bed is broken-up into two or more vessels and intercoolers are used to limit the temperature rise and stay within the operating temperature range for the catalyst.

Low temperature shift (LT shift) catalysts are typically copper–zinc oxide catalysts supported on alumina. The catalyst is active in the temperature range of 200–270°C. The lower temperature results in a lowering of the carbon monoxide effluent to ca 0.2–0.3 vol%. LT shift catalysts are extremely sensitive to sulfur poisoning and feed specifications on sulfur content are lowered to <0.1 ppm sulfur when LT shift catalysts are used. Depending upon the catalyst, a small amount of methanol side product is also formed (6).

After shift, the syngas is cooled with a combination of process cross-exchange and ejection of excess heat to the atmosphere using either an air fin cooler, a cooling water cooled exchanger, or a combination of the two. Cooling the gas to near ambient temperature causes water to condense, which is easily removed from the system using a knockout drum. Steam reforming of methane is a net overall consumer of water. The condensate from the knockout drum is steam stripped to remove dissolved gases and then it is usually recycled back into the boiler feedwater system to reduce the total amount of make-up water required for the unit.

The effluent gases from the shift converters contain about 17–19 vol% (dry basis) carbon dioxide. The levels of carbon dioxide are reduced to the 100–2000 ppm range by bulk CO2 removal. The mechanisms of CO2 removal systems can be classified as reaction, combination reaction-physical, and physical absorption systems. The processes generally have an absorber–stripper configuration. Table 5 compares the main features of various CO2 removal systems.

In many ammonia plants the carbon dioxide by product has value. It can be used as a feed for urea manufacture if a urea unit is part of the nitrogen complex. Carbon dioxide can also be used to adjust the C:H ratio in a methanol or other syngas plant if they are present as part of the industrial complex. Some ammonia plants further process the carbon dioxide to make it suitable for the carbonated beverage industry. Others sell byproduct CO2 for use in enhanced oil recovery.

Methanation is the simplest method for lowering the residual carbon monoxide and carbon dioxide content down to the levels needed to prevent ammonia synthesis catalyst poisoning. Methanation is simply the reverse of the steam reforming and shift reactions (eq. 31 and eq. 32): ΔH° at 25°C, in kJ/kg mol; ΔS° at 25°C, in kJ/(K kgmol)

$$CO + 3\,H_2 \;\leftrightarrow\; CH_4 + H_2O \quad \Delta H^\circ,\ -206,172;\ \Delta S^\circ,\ -214.6 \tag{31}$$

$$CO_2 + H_2 \;\leftrightarrow\; CO + H_2O \quad \Delta H^\circ,\ +41,169;\ \Delta S^\circ,\ +42.0 \tag{32}$$

Normal operating temperatures and pressures are 250–350°C and 3 MPa. Most methanation catalysts contain nickel supported on alumina, kaolin, or calcium aluminate cement. Sulfur, arsenic and carryover liquids from the CO_2 removal systems are catalyst poisons.

Methanation of carbon monoxide is highly exothermic. Temperatures exceeding the safe limits of operation can quickly be reached in out-of-control

Table 5. **Acid Gas Treating Processes**[a]

Process	Solvent	Solution circulation	Acid gas content in treated gas, ppm
	Reaction systems		
MEA[b]	20% monoethanolamine	medium	<50
promoted MEA	25–35% monoethanolamine plus Amine Guard	medium	<50
DGA[c]	60% diglycolamine	medium	<100
MDEA[d]	40% methyldiethanolamine plus additives	medium	<50
Vetrocoke	K_2CO_3 plus As_2O_3–glycine	high	500–1000
Carsol	K_2CO_3 plus additives	high	500–1000
Catacarb	25–30% K_2CO_3 plus additives	high	500–1000
Benfield	25–30% K_2CO_3 plus diethanolamine and additives	high	500–1000
Flexsorb HP	K_2CO_3 amine promoted	high	500–1000
Lurgi	25–30%K_2CO_3 plus additives	high	500–1000
Alkazid	potassium salt of 2-(or 3-) methylaminopropionic acid	[e]	[e]
	Combination reaction-physical systems		
Sulfinol	sulfone and 1.1′-imminobis-2-propanol	medium	<100
TEA-MEA[f]	triethanolamine and monoethanolamine	high (TEA) low (MEA)	<50
MDEA–sulfinol–H_2O		medium	<50
	Physical absorption systems		
Purisol (NMP)	*N*-methyl-2-pyrrolidinone	medium	<50
Rectisol	methanol	medium	<10
Fluor Solvent	propylene carbonate	[g]	[g]
Selexol	dimethyl ether of polyethyleneglycol	[g]	[g]

[a] Ref. 7.
[b] MEA is monoethanolamine.
[c] DGA is diglycolamine.
[d] MDEA is methyldiethanolamine.
[e] Dependent on service.
[f] TEA–MEA is triethanolanine–monoethanolamine.
[g] Dependent on pressure.

situations. Control systems for methanation reactions are carefully designed to a prevent runaway reaction which could potentially damage the catalyst or the pressure vessel used for the reaction.

Methanation results in a slight loss of hydrogen. However, the low cost and simple operation make it the most common method for removal of carbon oxides. More sophisticated cryogenic systems have also been used to remove carbon oxides. These systems have the additional advantage of reducing inerts, resulting in better ammonia yields by either reducing or eliminating the purge from the ammonia synthesis loop. Cryogenic systems have also been used to eliminate surplus nitrogen. Adding the capability to remove surplus nitrogen allows larger amounts of air to be injected in the secondary or autothermal reformer step. This in turn, lowers or eliminates the cost of the primary reformer.

Trace water removal using molecular sieve desiccant dryers is the last purification step commonly used in commercial processes. Often, as shown in Figure 6, the dryers are located on an interstage stream of the syngas compressor. This location minimizes the size of the dryer. Final syngas water levels below 1 ppm are achieved.

The overall sequence of steps used for syngas clean-up is rather complicated. The front end of an ammonia plant is basically the same as a hydrogen plant with the exception of the secondary reforming step. Hydrogen is widely used in petroleum refining for upgrading fuels. Hydrogen production facilities installed in the refining industry after the mid-1980s have a much simplified gas clean-up method based on high temperature shift, cooling and knockout of bulk water followed hydrogen purification using pressure swing adsorption (PSA). The pressure swing adsorption unit produces two streams. One is an extremely high purity hydrogen product stream that is at a pressure only slightly lower than the feed pressure. The other stream, called PSA tail gas, is a mix of carbon oxides, water, methane and hydrogen. This tail gas stream is at a pressure only slightly higher than ambient. It is usually fed to the burners of the reforming furnace, where it provides up to 90% of the heat needed for the furnace. The remaining furnace duty is supplied by a trim of natural gas to improve controllability of the furnace. In any case, the pressure swing adsorption unit replaces many of the processing steps used in the syngas clean-up method described for conventional ammonia plants.

Figure 8 is a process flow sheet for an ammonia plant that uses pressure swing adsorption for syngas clean-up. Despite the fact that the PSA unit greatly simplifies the process flow sheet, PSA based units have not been widely used in recently constructed ammonia plants. One reason for this is that the carbon dioxide by-product of the conventional clean-up process has value for urea synthesis and other markets as discussed previously. The carbon dioxide by-product in the PSA route is at low pressure and is mixed with many other chemical species. If there is no market or internal use for CO_2 then the PSA-based clean-up route would be preferred. This would be the case for a stand alone ammonia plant. However, in general, ammonia units are part of a larger nitrogen fertilizer/syngas product complex and thus the CO_2 by-product has value. Strong proponents of the PSA-based syngas clean-up route argue that purified CO_2 can be recovered from the PSA tail gas, however this clearly adds complexity and reduces the overall benefits of the PSA-based method.

Synthesis Gas Compression. Modern ammonia plants with capacities greater than 600 metric ton/day exclusively use centrifugal compressors for syngas compression. Usually more than one stage of compression is used with interstage cooling. The last compression stage also boosts the ammonia synthesis loop recycle gas to overcome pressure drop in the synthesis loop.

Typically, the syngas compressors are driven by steam turbines. The high pressure steam supplied to the turbine is generated by heat recovery in the reformer furnace convection section and elsewhere in the flow sheet. Integration of support utilities, mainly steam and electricity, into the ammonia production process is a significant part of the design and operation of ammonia facilities.

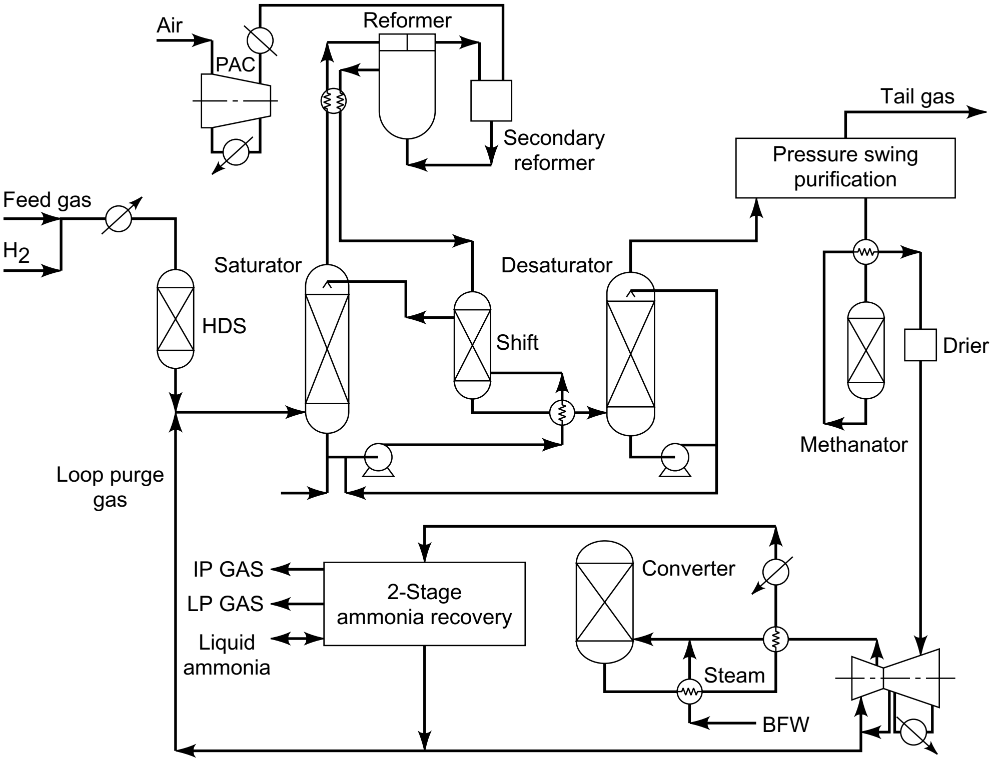

Fig. 8. ICI-LCA process flow sheet; PAC, purified air compressor; HDS, hydrodesulfurization; IP, intermediate pressure; LP, liquefied petroleum; BFW, boiler feed water.

Ammonia Synthesis and Recovery. The stoichiometry and thermodynamics of the ammonia synthesis reaction (eq. 33) are ΔH° at 25°C, kJ/kgmol $= -46,110$; ΔS° at 25°C, kJ/(K kgmol) $= -99.381$.

$$1/2\,N_2 + 3/2\,H_2 \leftrightarrow NH_3 \tag{33}$$

The thermodynamic values were taken from reference (8). The ammonia synthesis reaction is a reversible equilibrium type reaction. The reaction is exothermic, as indicated by the negative value of ΔH°.

Most commercial catalysts are just improved versions of the original iron catalyst used in the original Haber-Bosch process. Metallic iron, produced from magnetite, Fe_3O_4, is promoted with alkali in the form of potash and various metals such as aluminum, calcium, and magnesium. Recent commercial efforts have focused on fundamentally different catalysts. For example, Kellogg's Advanced Ammonia Process (KAAP) uses a promoted ruthenium catalyst with a high surface area graphite support. The catalyst has improved activity at high ammonia concentration with excellent low pressure and low temperature performance (9–11).

Ammonia synthesis typically occurs in the range of 350–550 °C. Figure 7 shows the effect of temperature on the equilibrium constant. Lower temperatures shift the reaction to the right. However, kinetics limit the lowest useful temperature to ca 350 °C. A quench converter is a common reactor configuration. A quench converter contains a series of adiabatic beds which are used to produce ammonia from syngas. Cold feed is injected between the beds to cool the reaction products, resulting in a saw-tooth temperature profile across the entire reactor. Typical per pass conversions are only ca 25–35%.

Pressure affects synthesis reactor performance. Following LeChatelier's principle, higher pressures improve equilibrium conversion. Higher pressures also improves kinetics. A wide range of pressures have been used in commercial processes, ranging from 8 to 40 MPa with most recent plants operating in the range of 15–25 MPa.

Pressure also affects the details of ammonia recovery. Ammonia is recovered by cooling the ammonia synthesis effluent to cause the ammonia product to condense into a liquid. The residual gas is then recycled back to the synthesis gas compressor where it compressed and then used to produce more ammonia product. Older plants using high ammonia synthesis loop pressures were able to use air fin coolers or cooling water to condense the product ammonia in the recovery step. However, today most plants need refrigeration systems to recover ammonia because of the lower synthesis pressures commonly used. Mechanical refrigeration using ammonia as the working fluid is most common. Absorption refrigeration systems using a water-ammonia mixture have also been used. These have the advantage of being able to use low temperature waste heat from the process (12,13).

The synthesis gas used for ammonia synthesis typically contains inerts such as methane from the methanation step, argon from the air used for secondary reforming and helium from the natural gas. These inerts have some solubility in the liquid ammonia product, but usually the solubility is too low to prevent build-up in the synthesis loop. In this case, the inerts are removed by taking a small gas purge from the ammonia synthesis loop. The purge rate can have an impact on the overall process economics. Often recovery of hydrogen from the purge stream using cryogenics, pressure swing adsorption or membrane processes is economically justified. The recovered hydrogen is recycled for additional ammonia production while the offgas containing the inerts are incinerated in the primary reforming furnace.

6.2. Other Production Routes. Partial oxidation of heavy feedstocks such as petroleum resids, petroleum coke, and coal is responsible for most of the non steam reformer based production of hydrogen used in ammonia synthesis. Partial oxidation routes are able to handle a wide variety of feedstocks. Solids handling equipment and the need to deal with soot by-products increase the complexity and capital costs for these routes. Ammonia synthesis is unique in syngas processes since air-blown rather than oxygen-blown units can be used for partial oxidation. Nitrogen associated with the oxygen in air is needed in the downstream ammonia synthesis step. Nitrogen is considered as an undesirable impurity in processes for most other synthesis gas products (eg, methanol). The requirement for large amounts of high purity oxygen has been the major hurdle preventing wider use of partial oxidation in syngas technologies. Recent advancements in air separation technologies based upon membranes and vacuum swing adsorption have resulted in renewed interest in industrial scale partial oxidation technologies for all synthesis gas products.

By-product hydrogen is generated in units that were designed for other purposes but happen to produce hydrogen as a by-product. Examples include many petroleum refining operations such as catalytic reforming, catalytic crackers, thermal crackers, and cokers. Other major by-product sources are: offgas from ethylene crackers, offgas from industrial electrolysis processes such as those used for caustic/chlorine manufacture, and tail gases from other synthesis gas processes such methanol production.

A very small portion of on-purpose hydrogen production comes from electrolysis. The electrolysis route is not currently used for ammonia production. For hydrogen, it is currently only competitive for small scale production and/or for high purity hydrogen applications such as hydrogen for use in semiconductor processing.

The electrolysis route fits well with the vision of using either hydrogen or ammonia as an energy carrier. In this view, renewable-based electricity generated is generated from hydroelectric, solar, geothermal, ocean thermal, or other sources. The electricity is used to split water, the hydrogen is stored and/or transported, and then electricity is regenerated from the hydrogen using a fuel cell. Temporary conversion of the hydrogen to ammonia followed by back-conversion to hydrogen is envisioned as one way to simplify storage and transport. In either case, the hydrogen or the ammonia is merely being used as an energy carrier rather than as an ultimate source of energy.

At the time of this writing, the hydrogen economy is still in the future. Production costs and lack of infrastructure remain as significant hurdles. Continued availability of low cost nonrenewable hydrocarbons and their associated existing and largely depreciated infrastructures will slow commercialization progress in this area.

Biological processes based on genetic engineering have the potential to eliminate the synthetic nitrogen fertilizer industry completely. The genes responsible for nitrogen fixation could potentially be isolated from symbiotic soil organisms and then transferred and expressed in non-leguminous crops. Alternatively, nitrogen fixation could be transferred and expressed in a wider range of natural soil bacteria. At this point in time, these are rather futuristic scenarios.

7. Storage and Shipment

Although much ammonia serves as feedstock for other processes, the largest single use in the United States is as a direct application fertilizer without further processing. This direct application consumption is mostly in the farm belt and ammonia produced in the Gulf Coast or other locations is shipped to terminal facilities and then distributed by retail outlets to the farmer.

Anhydrous ammonia is ordinarily stored in refrigerated tanks at the plant site and major distribution points. Atmospheric pressure and at temperature of ca -33°C are typical conditions. Very large quantities have to be stored since the fertilizer market is seasonal. Cylindrical tank of large (27,000–50,000 t) capacities, either of single-walled or doubled-walled construction, have been installed in primary market areas (14). Double integrity tanks have been designed with secondary containment for added safety (15).

Evaporating ammonia must be vented. The vented gas is reliquefied for recycle or absorbed in water to make aqua ammonia. Refrigerated storage tanks are insulated using great care to minimize heat loss and access of air and moisture to the insulation or metal surface. In double-wall tanks, the annular space is usually filled with perlite and the external surface of the outer tank is painted for corrosion protection.

Relatively small quantities of anhydrous ammonia are stored in spherical vessels at pressures above 275 kPa gauge (40 psig) and ambient temperature. Not more than 19 m^3 (50,000 U.S. gal) of ammonia should be stored in an unrefrigerated tank (16). Storage tanks must not be filled to more than 56% of the water weight capacity of the container at 15 °C (17). There is a tendency to design foundations for the weight of the tank filled with water to hydrostatically test the tank completely. Tanks should be built of steel and designed for a minimum working pressure of 1724 kPa gauge (250 psig).

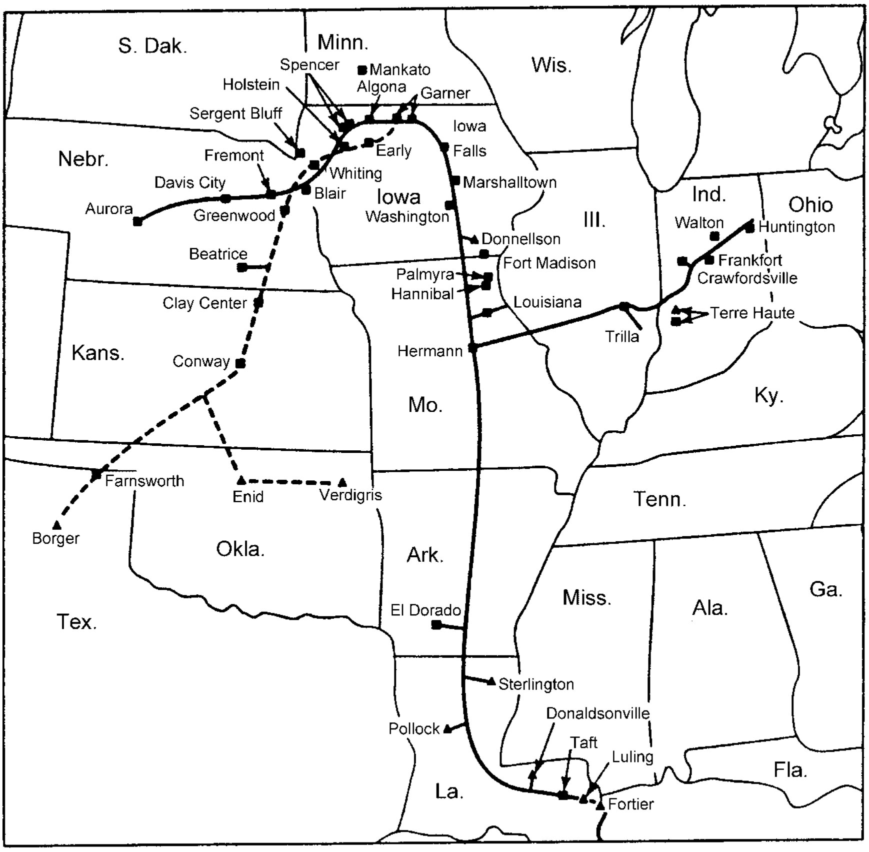

Fig. 9. Pipeline systems of transport for anhydrous ammonia within the United States where ▲ represnts an ammonia plant location; ■, storage terminals; (—), Gulf Central pipeline; and (—), MAPCO pipeline.

Ammonia is usually transported for long distances by barge, pipeline, rail, and for short distances, by truck. Factors that govern the type of carrier used in anhydrous ammonia transportation systems are distance, location of plant site in relation to consuming area, availability of transportation equipment, and relative cost of available carriers. Typical costs of pipeline, barge, and rail modes for long distance transport are \$0.0153, \$0.0161 and \$0.0215 per ton per kilometer, respectively, for distances of about 1600 km (18). Short truck transportation costs are much higher. Costs are typically \$0.0365/(t/km) for distances on the order of 160 km. Ammonia in the world trading markets costs on the order of \$35/t to ship between the United States and Western Europe.

The primary ammonia pipelines in the United States are the Mid-America Pipeline Company (MAPCO) and Gulf Central (see Fig. 9) (see FERTILIZERS). The MAPCO pipeline (20) contains 1763 kilometers of 101 mm, 152 mm, and 203 mm pipe have a pumping capacity of 3885 metric tons per day and supporting terminal storage facilities. Peak delivery from the system is 4,216 metric tons per day. The Gulf Central system (21) contains 3220 km of 152 mm, 203 mm, and 254 mm pipe and has a pumping capacity of 2545 metric tons per day and supporting terminal storage facilities. The Tampa Bay Pipeline network services several ammonia plants along a 133 km route in Florida.

The other major ammonia pipeline is in the former Soviet Union. A 2400-km mainline extends from Togliatti on the Volga River to the Port of Odessa on the Black Sea. A 2200-km branch line extends from Gorlovka in the Ukraine to Panioutino. Mainline operating pressure is 8.15 MPa (1182 psi) and branch line operating pressure is 9.7 MPa (1406 psi) (22).

Export oriented ammonia producing countries utilize huge ocean going tankers that contain up to 50,000 t for distribution of ammonia. Co-shipment in refrigerated LNG tankers in usually done. Capacities for trucks and rail cars are normally 100–150 m^3. Barges can usually accommodate from 400–2000 t.

8. Economic Aspects

Examination of typical ammonia production economics explains the recent trend in new plant location. Table 6 provides a breakdown of the estimated manufacturing cost of ammonia in a 1000 metric ton per day reduced energy natural gas reforming plant built in early 1990 on the U.S. Gulf Coast. As can be seen from this analysis, the natural gas feedstock accounts for nearly 70% of cash operating costs. Natural gas feedstock and capital charges amount to over 93% of production costs.

Over the past decade inflation rates have been quite low. Natural gas prices have been more of a function of geography rather than time. A natural gas delivered price of \$1.90/GJ (\$2.00/MMBTU), on lower heating value (LHV) basis, was reported for February 1990 in the United States (24). In the energy-rich countries of the Near East, in the former USSR, Trinidad, and in North Africa, natural gas prices are on the order of \$0.47/GJ (\$0.5/MMBTU); however construction cost at these locations tends to be higher than on the U.S. Gulf Coast. Cost of transporting ammonia from these more remote locations to current agricultural centers also has to be taken into account; however, the rationale for siting of new nitrogen complexes near remote gas sources is clear.

Table 6. **Estimated Ammonia Manufacturing Cost**[a]

Factor	Unit rate/t	$US/units	Cost, $/t
Variable costs			
natural gas (feed-fuel), GJ[b]	28.45	1.90	54.06
boiler feed water make-up, m^3	1.1	0.25	0.28
cooling water circulation, m^3 (Δ temperature = 10°C)	210	0.01	2.10
catalyst cost			1.7
Fixed costs[c]			
labor, personnel shift ($10/h)	6	10	1.44
supervision, 100% of labor			1.44
interest on working capital, %	10		1.30
indirect charges, %[d]	16		44.06
Total production cost			*106.38*
pretax return on investment (ROI), %	20		55.07
ammonia cost (FOB plant)			161.45
cash cost of production[e]			78.84

[a] Reduced energy ammonia process utilizing natural gas feed at a U.S. Gulf Coast location. Daily production of 1,000 t, yearly production of 345,000 t, and total investment of $99,500,000 (U.S. $95 million in fixed investment and $4.5 million in working capital).

[b] To convert GJ to Gcal, divide by 4.184.

[c] Fixed investment includes cooling tower, boiler feedwater treatment, raw water ammonia storage as minimum off-sites requirement.

[d] Indirect charges are 16% of fixed investment per ton per year: 10% depreciation; 1.5%, insurance; 3%, maintenance (labor, materials); 1.5%, general sales and marketing.

[e] Cash cost excludes 10% depreciation allowance and 20% pretax ROI.

Whereas manufacturing costs are strongly influenced by energy prices and capital investment, ammonia selling prices are determined by supply and demand. The profitability of an ammonia plant is determined by the margin between cost of production and ammonia price. In February 1990, the FOB price of ammonia on the U.S. Gulf Coast was $107 per short ton (24). Therefore a Gulf Coast producer with a reduced energy unit would have a $28 margin at the assumed natural gas price. However, most plants on the U.S. Gulf Coast were built in the late 1960s and early 1970s. Energy consumption for plants of this era is about 34.85 GJ/t (30 MMBtu/short ton) vs. 28.45 GJ/t (24.5 MMBtu/short ton) for the modern reduced energy designs, thus cash margins for older plants that did not modernize their technology were only $16/ton.

Most ammonia production is processed or used in the countries where it is produced. World trade of ammonia accounts for only 11% of world production; however, this statistic does not take into account ammonia present in derivatives such as urea. The major net exporters of ammonia in 1997 were Russia and the Ukraine accounting for 43% of world exports, Trinidad for 22% and the Middle East for 13%. The major net importers were the United States (43%) and Western Europe (26%) (1).

9. Grades and Specifications

Anhydrous and aqua ammonia are manufactured in various grades depending on use. Specifications are given in Table 7 and 8, respectively.

Table 7. **Anhydrous Ammonia Specifications**[a]

Material content	Commercial or fertilizer grade	Refrigeration grade	Metallurgical grade
ammonia, min wt %	99.5	99.98	99.99
water, max ppm by wt	5000	150	33
oil, max ppm by wt	5	3	2
noncondensable gases, max mL/g		0.2	10

[a] Ref. 25.

Table 8. **Aqua Ammonia Specifications**[a]

Grade	Ammonia, wt %
United States Pharmacopeia	
stronger ammonia water	28–30
ammonia test solution	9.5–10.5
normal (1 *N*) aqua ammonia	1.7
chemically pure	28
technical, Bé°[b]	
26	29.4
16	10.3
18	14
20	17.75

[a] Ref. 26, 27.

[b] Bé° = degree Baumé; specific gravity = 145/(145 − Bé°).

10. Analytical Methods

Anhydrous ammonia is normally analyzed for moisture, oil and residue. The ammonia is first evaporated from the sample and the residue tested (28). In most instances, the amount of oil and sediment in the samples are insignificant and the entire residue is assumed to be water. For more accurate moisture determinations, the ammonia can be dissociated into nitrogen and hydrogen and the dewpoint of the dissociated gas obtained. This procedure works well where the concentration of water is in the ppm range. Where the amount of water is in the range of a few hundredths of a percent, acetic acid and methanol can be added to the residue and a Karl Fischer titration performed to an electrometrically detected end point (29–32).

11. Environmental Concerns

Ammonia production by steam reforming of natural gas is a relatively clean operation and presents no unique environmental problems. NO_x, emissions from the flue gas of the primary reformer can be suitably treated by a combination of conventional control techniques including low NO_x burners, selective catalytic reduction and flue gas scrubbing.

Ammonia production using heavy feedstocks raises additional environmental issues. Particulate emissions from solids handling of the feeds must be controlled. The soot, ash and slag produced from these routes must also be disposed of in an environmentally acceptable manner. These feeds are also more likely to create liquid and gases by-products such as tars, phenols, sulfur, cyanides, etc, which must be handled properly.

12. Health and Safety Factors

The American Institute of Chemical Engineers sponsors a yearly symposium on plant safety for ammonia and related facilities. The published papers from these symposia are a rich source of information on the design and operations of safe facilities. Fire is the most frequent cause of safety incidents in ammonia production. In a recently published survey based on 89 ammonia plants operating in 25 countries, the average ammonia plant had one fire every 14.2 months over the three year survey period of 1994–1996 (33). The most common fuel sources were flanges leaking hydrogen rich gases and oil leaks associated with compressor and pump lubricating–sealing systems. The good news is that safety programs seem to be working since the percentage of plants reporting no fires has steadily increased over time. Survey results from 1994–1996 had 41% of plants reporting no fires compared to 30% for the period 1982–1985, 23% for the period 1977–1981 and 7% for the period 1973–1976.

The National Fire Protection Association (NFPA) ratings for anhydrous ammonia (34) are Health = 3, Fire = 1 and Reactivity = 0. Ammonia is a strong local irritant that also has a corrosive effect on the eyes and the membranes of the pulmonary system. Vapor concentrations of 10,000 ppm are mildly irritating to the skin, whereas 30,000 ppm may cause burns. The physiological effects from inhalation are described in Table 9. Prolonged, intentional exposure to high levels of ammonia is unlikely because its characteristic odor can be detect at levels as 1–5 ppm (35).

OSHA standards specify the threshold limit value (TLV) 8-h exposure to ammonia as 50 ppm (35 mg/m^3). However, the ACGIH recommends a TLV of 25 ppm (36). Respiratory protection should be provided for workers exposed to ammonia. Protective clothing such as rubber aprons, boots, gloves and goggles should be worn when handling ammonia.

Table 9. **Physiological Effects of Ammonia**[a]

Concentration, ppm	Effects
20–50	perceptible odor
40–100	eye and respiratory system irritation
400–700	severe eye and respiratory irritation; potential for permanent damage
1,700	convulsive coughing and bronchial spasms; half four exposure potentially fatal
5,000–10,000	death from suffocation

[a] Ref. 27.

Table 10. **1998 U.S. Ammonia Demand by Category**[a]

Category	Demand, 1000 t/yr	Share, %
fertilizers		
direct application	3,600	20
nitrogen derivatives	10,800	60
chemical Intermediates	3,420	19
Other	180	1
Total	*18,000*	*100*

[a] Ref. 4.

The flammable limits of ammonia in air are 16 to 25% by volume at atmospheric pressure; in oxygen the range is 15 to 79%. Ignition temperature is ca 650°C. Although ignition is difficult, it is not impossible as proved by an explosion resulting from a leak in an indoor ammonia refrigeration system (37). Ammonia does not produce unstable or hazardous decomposition products. However, contact with calcium, gold, mercury, silver or chlorates may result in explosive compounds.

13. Uses

Table 10 shows the break down of uses for ammonia in the United States. Nonfertilizer use accounts for about 20% of consumption. Globally, the chemical markets for ammonia are smaller, only accounting for about 15% of consumption. The vast majority of ammonia is used for nitrogen fertilizers. Three principal fertilizers, ammonium nitrate [6484-52-2], NH_4NO_3, ammonia sulfate [7782-20-2], $(NH_4)SO_4$, and ammonium phosphate [10361-65-6], $(NH_4)_3PO_4$, are made by reaction of the respective acids with ammonia. Table 11 gives a current global breakdown of nitrogen fertilizer products by type.

The catalytic oxidation of ammonia in the presence of methane is commercially used for the production of hydrogen cyanide.

Acrylonitrile, [107-13-1], $CH_2{=}CHC{\equiv}N$, is produced in commercial quantities almost exclusively by the ammoxidation of propylene.

Table 11. **World Nitrogen Fertilizer Consumption**[a]

Fertilizer	Amount, 1000 t/yr	Share, %
ammonium sulfate	2,610	3.2
urea	37,570	46.4
ammonium nitrate	7,100	8.8
calcium arnmoniun nitrate	3,580	4.4
direct ammonia application	4,180	5.2
nitrogen solutions	3,990	4.9
MAP/DAP & other NP compounds	6,220	7.7
NK/NPK compounds	6,510	8.0
others	9,190	11.4
Total	*80,950*	*100*

[a] Ref. 1.

Urea, formed from the reaction of ammonia with carbon dioxide, has enjoyed a long term steady rise in market share to point where today it is the most common nitrogen fertilizer. This increase in market share for urea has been at the expense of ammonium nitrate, ammonium sulfate and direct application of ammonia.

Caprolactam [105-60-2] is made from ammonia and cyclohexanone. Caprolactam is the monomer for nylon 6. By-product ammonium sulfate from this route is a major source of this fertilizer ingredient. Ammonia is also used in the production of pyridines, amines and amides.

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