

8.1 Synthetic Ammonia

8.1.1 General¹⁻²

Synthetic ammonia (NH_3) refers to ammonia that has been synthesized (Standard Industrial Classification 2873) from natural gas. Natural gas molecules are reduced to carbon and hydrogen. The hydrogen is then purified and reacted with nitrogen to produce ammonia. Approximately 75 percent of the ammonia produced is used as fertilizer, either directly as ammonia or indirectly after synthesis as urea, ammonium nitrate, and monoammonium or diammonium phosphates. The remainder is used as raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products.

Synthetic ammonia plants are located throughout the U. S. and Canada. Synthetic ammonia is produced in 25 states by 60 plants which have an estimated combined annual production capacity of 15.9 million megagrams (Mg) (17.5 million tons) in 1991. Ammonia plants are concentrated in areas with abundant supplies of natural gas. Seventy percent of U. S. capacity is located in Louisiana, Texas, Oklahoma, Iowa, and Nebraska.

8.1.2 Process Description^{1,3-4}

Anhydrous ammonia is synthesized by reacting hydrogen with nitrogen at a molar ratio of 3 to 1, then compressing the gas and cooling it to -33°C (-27°F). Nitrogen is obtained from the air, while hydrogen is obtained from either the catalytic steam reforming of natural gas (methane [CH_4]) or naphtha, or the electrolysis of brine at chlorine plants. In the U. S., about 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas. Figure 8.1-1 shows a general process flow diagram of a typical ammonia plant.

Six process steps are required to produce synthetic ammonia using the catalytic steam reforming method: (1) natural gas desulfurization, (2) catalytic steam reforming, (3) carbon monoxide (CO) shift, (4) carbon dioxide (CO_2) removal, (5) methanation, and (6) ammonia synthesis. The first, third, fourth, and fifth steps remove impurities such as sulfur, CO , CO_2 and water (H_2O) from the feedstock, hydrogen, and synthesis gas streams. In the second step, hydrogen is manufactured and nitrogen (air) is introduced into this 2-stage process. The sixth step produces anhydrous ammonia from the synthetic gas. While all ammonia plants use this basic process, details such as operating pressures, temperatures, and quantities of feedstock vary from plant to plant.

8.1.2.1 Natural Gas Desulfurization -

In this step, the sulfur content (as hydrogen sulfide [H_2S]) in natural gas is reduced to below 280 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) (122 grams per cubic feet) to prevent poisoning of the nickel catalyst in the primary reformer. Desulfurization can be accomplished by using either activated carbon or zinc oxide. Over 95 percent of the ammonia plants in the U. S. use activated carbon fortified with metallic oxide additives for feedstock desulfurization. The remaining plants use a tank filled with zinc oxide for desulfurization. Heavy hydrocarbons can decrease the effectiveness of an activated carbon bed. This carbon bed also has another disadvantage in that it cannot remove carbonyl sulfide. Regeneration of carbon is accomplished by passing superheated steam through the carbon bed. A zinc oxide bed offers several advantages over the activated carbon bed. Steam regeneration to use as energy is not required when using a zinc oxide bed. No air emissions are created by the zinc oxide bed, and

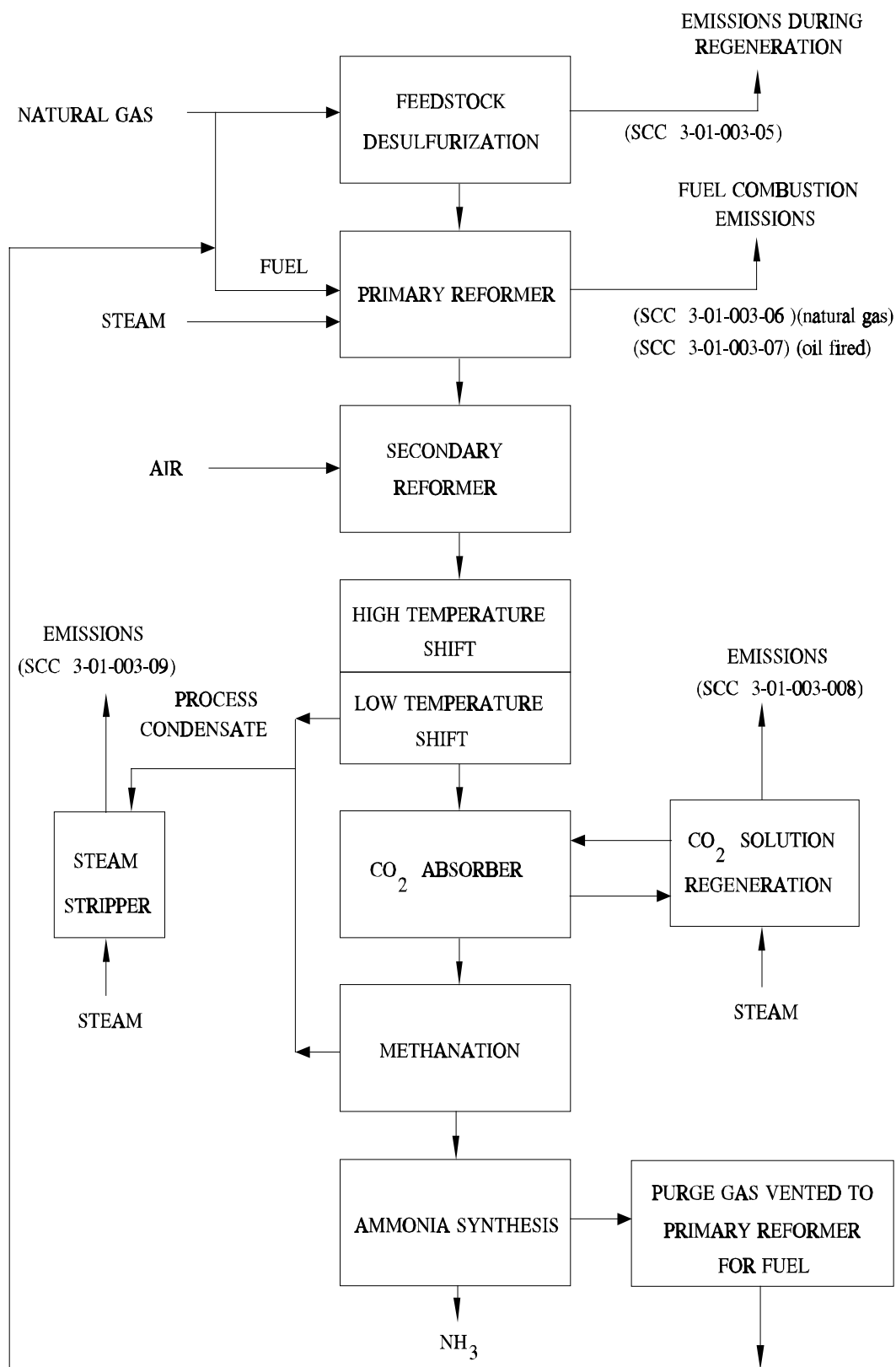


Figure 8.1-1. General flow diagram of a typical ammonia plant.
(Source Classification Codes in parentheses.)

the higher molecular weight hydrocarbons are not removed. Therefore, the heating value of the natural gas is not reduced.

8.1.2.2 Catalytic Steam Reforming -

Natural gas leaving the desulfurization tank is mixed with process steam and preheated to 540°C (1004°F). The mixture of steam and gas enters the primary reformer (natural gas fired primary reformer) and oil fired primary reformer tubes, which are filled with a nickel-based reforming catalyst. Approximately 70 percent of the CH₄ is converted to hydrogen and CO₂. An additional amount of CH₄ is converted to CO. This process gas is then sent to the secondary reformer, where it is mixed with compressed air that has been preheated to about 540°C (1004°F). Sufficient air is added to produce a final synthesis gas having a hydrogen-to-nitrogen mole ratio of 3 to 1. The gas leaving the secondary reformer is then cooled to 360°C (680°F) in a waste heat boiler.

8.1.2.3 Carbon Monoxide Shift -

After cooling, the secondary reformer effluent gas enters a high temperature CO shift converter which is filled with chromium oxide initiator and iron oxide catalyst. The following reaction takes place in the carbon monoxide converter:



The exit gas is then cooled in a heat exchanger. In some plants, the gas is passed through a bed of zinc oxide to remove any residual sulfur contaminants that would poison the low-temperature shift catalyst. In other plants, excess low-temperature shift catalyst is added to ensure that the unit will operate as expected. The low-temperature shift converter is filled with a copper oxide/zinc oxide catalyst. Final shift gas from this converter is cooled from 210 to 110°C (410 to 230°F) and enters the bottom of the carbon dioxide absorption system. Unreacted steam is condensed and separated from the gas in a knockout drum. This condensed steam (process condensate) contains ammonium carbonate ((NH₄)₂CO₃ · H₂O) from the high-temperature shift converter, methanol (CH₃OH) from the low-temperature shift converter, and small amounts of sodium, iron, copper, zinc, aluminum and calcium.

Process condensate is sent to the stripper to remove volatile gases such as ammonia, methanol, and carbon dioxide. Trace metals remaining in the process condensate are removed by the ion exchange unit.

8.1.2.4 Carbon Dioxide Removal -

In this step, CO₂ in the final shift gas is removed. CO₂ removal can be done by using 2 methods: monoethanolamine (C₂H₄NH₂OH) scrubbing and hot potassium scrubbing. Approximately 80 percent of the ammonia plants use monoethanolamine (MEA) to aid in removing CO₂. The CO₂ gas is passed upward through an adsorption tower countercurrent to a 15 to 30 percent solution of MEA in water fortified with effective corrosion inhibitors. After absorbing the CO₂, the amine solution is preheated and regenerated (carbon dioxide regenerator) in a reactivating tower. This reacting tower removes CO₂ by steam stripping and then by heating. The CO₂ gas (98.5 percent CO₂) is either vented to the atmosphere or used for chemical feedstock in other parts of the plant complex. The regenerated MEA is pumped back to the absorber tower after being cooled in a heat exchanger and solution cooler.

8.1.2.5 Methanation -

Residual CO₂ in the synthesis gas is removed by catalytic methanation which is conducted over a nickel catalyst at temperatures of 400 to 600°C (752 to 1112°F) and pressures up to 3,000 kilopascals (kPa) (435 pounds per square inch absolute [psia]) according to the following reactions:



Exit gas from the methanator, which has a 3:1 mole ratio of hydrogen and nitrogen, is then cooled to 38°C (100°F).

8.1.2.6 Ammonia Synthesis -

In the synthesis step, the synthesis gas from the methanator is compressed at pressures ranging from 13,800 to 34,500 kPa (2000 to 5000 psia), mixed with recycled synthesis gas, and cooled to 0°C (32°F). Condensed ammonia is separated from the unconverted synthesis gas in a liquid-vapor separator and sent to a let-down separator. The unconverted synthesis is compressed and preheated to 180°C (356°F) before entering the synthesis converter which contains iron oxide catalyst. Ammonia from the exit gas is condensed and separated, then sent to the let-down separator. A small portion of the overhead gas is purged to prevent the buildup of inert gases such as argon in the circulating gas system.

Ammonia in the let-down separator is flashed to 100 kPa (14.5 psia) at -33°C (-27°F) to remove impurities from the liquid. The flash vapor is condensed in the let-down chiller where anhydrous ammonia is drawn off and stored at low temperature.

8.1.3 Emissions And Controls^{1,3}

Pollutants from the manufacture of synthetic anhydrous ammonia are emitted from 4 process steps: (1) regeneration of the desulfurization bed, (2) heating of the catalytic steam, (3) regeneration of carbon dioxide scrubbing solution, and (4) steam stripping of process condensate.

More than 95 percent of the ammonia plants in the U. S. use activated carbon fortified with metallic oxide additives for feedstock desulfurization. The desulfurization bed must be regenerated about once every 30 days for an average period of 8 to 10 hours. Vented regeneration steam contains sulfur oxides (SO_x) and H₂S, depending on the amount of oxygen in the steam. Regeneration also emits hydrocarbons and CO. The reformer, heated with natural gas or fuel oil, emits combustion products such as oxides of nitrogen, CO, CO₂, SO_x, hydrocarbons, and particulates. Emission factors for the reformer may be estimated using factors presented in the appropriate section in Chapter 1, "External Combustion Source". Table 8.1-1 presents uncontrolled emission factors for a typical ammonia plant.

CO₂ is removed from the synthesis gas by scrubbing with MEA or hot potassium carbonate solution. Regeneration of this CO₂ scrubbing solution with steam produces emission of water, NH₃, CO, CO₂, and MEA.

Cooling the synthesis gas after low temperature shift conversion forms a condensate containing NH₃, CO₂, CH₃OH, and trace metals. Condensate steam strippers are used to remove NH₃ and methanol from the water, and steam from this is vented to the atmosphere, emitting NH₃, CO₂, and CH₃OH.

Some processes have been modified to reduce emissions and to improve utility of raw materials and energy. One such technique is the injection of the overheads into the reformer stack along with the combustion gases to eliminate emissions from the condensate steam stripper.

Table 8.1-1 (Metric And English Units). UNCONTROLLED EMISSION FACTORS FOR A TYPICAL AMMONIA PLANT^a

EMISSION FACTOR RATING: E

Emission Point	CO		SO ₂		Total Organic Compounds		NH ₃		CO ₂	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Desulfurization unit regeneration ^b (SCC 3-01-003-05)	6.9	13.8	0.0288 ^{c,d}	0.0576 ^{c,d}	3.6	7.2	NA	NA	ND	ND
Carbon dioxide regenerator (SCC 3-01-003-008)	1.0 ^e	2.0 ^e	NA	NA	0.52 ^f	1.04	1.0	2.0	1220	2440
Condensate steam stripper (SCC 3-01-003-09)	NA	NA	NA	NA	0.6 ^g	1.2	1.1	2.2	3.4 ^h	6.8 ^h

^a References 1,3. SCC = Source Classification Code. NA = not applicable. ND = no data.^b Intermittent emissions. Desulfurization tank is regenerated for a 10-hour period on average once every 30 days.^c Assumed worst case, that all sulfur entering tank is emitted during regeneration.^d Normalized to a 24-hour emission factor. Total sulfur is 0.0096 kg/Mg (0.019 lb/ton).^e Mostly CO.^f 0.05 kg/Mg (0.1 lb/ton) is monoethanolamine.^g Mostly methanol, which is classified as Non Methane Organic Compound and a hazardous air pollutant.^h ±60%.

References For Section 8.1

1. *Source Category Survey: Ammonia Manufacturing Industry*, EPA-450/3-80-014, U. S. Environmental Protection Agency, Research Triangle Park, NC, August 1980.
2. *North American Fertilizer Capacity Data*, Tennessee Valley Authority, Muscle Shoals, AL, December 1991.
3. G. D. Rawlings and R. B. Reznik, *Source Assessment: Synthetic Ammonia Production*, EPA-600/2-77-107m, U. S. Environmental Protection Agency, Cincinnati, OH, November 1977.
4. *AIRS Facility Subsystem Source Classification Codes And Emission Factor Listing For Criteria Pollutants*, EPA-450/4-90-003, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1990.