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SOURCE ASSESSMENT:
SYNTHETIC AMMONIA PRODUCTION

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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SOURCE ASSESSMENT: SYNTHETIC AMMONIA PRODUCTION

by

G. D. Rawlings and R. B. Reznik

Monsanto Research Corporation
1515 Nicholas Road
Dayton, Ohio 45407

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EPA Task Officer: Ronald A. Venezia

Office of Energy, Minerals, and Industry
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

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PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility to develop control technology for a large number (>500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to make that decision for the air emissions from synthetic ammonia production.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of synthetic ammonia production, Dr. Ronald A. Venezia served as EPA Task Leader.

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ABBREVIATIONS AND SYMBOLS

AAQS --ambient air quality standard

e --natural logarithm base (=2.72)

F --hazard factor

h --stack height

Q --mass emission rate

S --source severity

t_o --instantaneous averaging time

t --averaging time

TLV --threshold limit value

u --national average wind speed

x --downwind dispersion distance from a source of emissions

χ --downwind ground level concentration at reference coordinate with emission height of h

$\bar{\chi}$ --time-averaged ground level concentration of an emission species

χ_{max} --instantaneous maximum ground level concentration

$\bar{\chi}_{max}$ --time-averaged maximum ground level concentration

π --3.14

SECTION 1

INTRODUCTION

In 1976, 90 synthetic ammonia plants located in 30 states produced 15.2 x 10^6 metric tons[a] of synthetic anhydrous ammonia, making it the fourth largest chemical manufactured in the U.S. Texas and Louisiana together accounted for almost half of the national production. Most of the ammonia was used as a direct application fertilizer and in the manufacture of other fertilizer products such as urea, ammonium nitrate, and ammonium phosphates. A small amount of ammonia was used to produce nonfertilizer materials.

Ammonia production involves not only the reaction of nitrogen and hydrogen to form ammonia, but also the formation and purification of the hydrogen needed in the synthesis. Catalytic steam reforming of natural gas to produce hydrogen is the only manufacturing process studied in this report because 98% of the ammonia in the U.S. is produced by this method at 84 of the 90 plants. The remaining six plants purchase hydrogen feedstock from plants that produce hydrogen and chlorine by electrolysis of sodium chloride.

This report discusses air emissions released during the manufacture of synthetic anhydrous ammonia. Emission points within the manufacturing process are identified, types and quantities of emission species are delineated, and characteristics of emissions are discussed. The total mass of each emission species is calculated. State and national emissions of criteria pollutants [particulates, nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), and hydrocarbons] from ammonia plants are compared to total state and national emissions from all stationary sources. Time-averaged maximum ground level concentrations of emissions from a typical ammonia plant are compared to the corresponding ambient air quality standards. Effects of present and emerging control technology are also discussed.

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[a] 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented at the end of this report.

SECTION 2

SUMMARY

This report summarizes the assessment of air emissions released during the production of synthetic anhydrous ammonia, Standard Industrial Classification No. 2873131. It encompasses the reforming of the feedstock to produce hydrogen, synthesis gas purification, and ammonia synthesis. Catalytic steam reforming of natural gas is the only process covered in this report because 98% of the ammonia in the U.S. is produced by that method.

In 1976, 15.2 x 10^6 metric tons of synthetic anhydrous ammonia were produced in the U.S. Approximately 80% of this ammonia was used as a direct application fertilizer and in the production of other fertilizer products such as urea, ammonium nitrate, and ammonium phosphates. The remaining ammonia was used to manufacture nonfertilizer materials such as ammonium nitrate for explosives, urea for animal feeds and resins, nitric acid, acrylonitrile, and amines.

Synthetic ammonia was produced in 30 states by 90 plants which have a combined annual production capacity of 16.8 x 10^6 metric tons. Ammonia plants are concentrated in areas with abundant supplies of natural gas, such as along the Texas and Louisiana coast, in California, and in the Central Plains states. Texas and Louisiana accounted for 45% of national production in 1974.

An average ammonia plant has a capacity of 180 x 10^3 metric tons/yr, has a daily production rate of 480 metric tons/day, and is located in a county having a population density of 117 persons/km^2.

In the United States 98% of the synthetic production of anhydrous ammonia begins with the catalytic steam reforming of natural gas. Natural gas is first desulfurized and then sent to the primary reformer where methane is reformed into carbon monoxide and hydrogen. This process gas is sent to the secondary reformer where it is mixed with enough compressed air to give a hydrogen-to-nitrogen mole ratio of 3:1. A carbon monoxide shift reactor, a carbon dioxide removal system, and a methanation reactor are then used to remove all traces of carbon monoxide, carbon dioxide, and methane from the synthesis gas. Synthesis gas is compressed and cooled to -33°C for anhydrous ammonia production.

Condensate generated by the carbon monoxide shift reactor, the carbon dioxide removal system, and the methanation reactor is steam-stripped to remove ammonia and methanol impurities. Steam and stripped impurities are vented directly to the atmosphere. Purge gas from the synthesis loop containing hydrogen, argon, methane, and nitrogen impurities is vented to the primary reformer for use as fuel in the radiant heat section.

Air emissions from an ammonia plant result from regeneration of the desulfurization tank, from combustion occurring in the radiant heat section of the primary reformer, from regeneration of the carbon dioxide scrubbing solution, and from steam stripping of process condensate. Emission species and emission factors associated with these emission sources are shown in Table 1. On the average, emissions from the regeneration of the desulfurization tank are released for 10 hours but only once every 30 days. Emissions from the three other sources are continuous while the plant is on stream. The industry does not employ controls on these emission points because no state or federal standards are exceeded.

TABLE 1. EMISSION CHARACTERISTICS FROM AVERAGE AMMONIA PLANT PRODUCING 480 METRIC TONS/DAY

Emission point	Emission species	Emission factor, g/kg	Source severity	Affected population, persons
Desulfurization tank[a]	Total sulfur	0.0096[b,c]	0.05[d]	0[e]
	CO	6.9	0.30	0
	Hydrocarbons	3.6	32.4	130
Primary reformer				
Burning natural gas	NO_x	2.7 ± 23%	4.1	357
	SO_x	0.0024	<0.01	0
	CO	0.068	<0.01	0
	Particulates	0.072	0.03	0
	Hydrocarbons	0.012	0.01	0
Burning fuel oil	NO_x	2.7	4.1	357
	SO_x	1.3	0.44	0
	CO	0.12	<0.01	0
	Particulates	0.45	0.21	0
	Hydrocarbons	0.15	0.16	0
Carbon dioxide regenerator	Ammonia	1.0	2.2	197
	CO	1.0	<0.01	0
	Carbon dioxide	1,220	0.25	0
	Hydrocarbons	0.47	0.54	0
	Monoethanolamine	0.05	0.33	0
Condensate stripper	Ammonia	1.1 ± 4%	3.2	237
	Carbon dioxide	3.4 ± 60%	<0.01	0
	Methanol	0.6 ± 2%	0.12	0

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[a] Intermittent source of emissions; desulfurization tank is regenerated on the average once every 30 days for a 10-hr period.

[b] Worst case condition assuming all sulfur entering the tank is emitted during regeneration.

[c] Normalized to a 24-hr emission factor.

[d] Based on all sulfur being emitted as sulfur dioxide; if hydrogen sulfide is released, severity is 0.21 and affected population is 0.

[e] Zero affected population indicates that $\overline{\chi}/F$ is always less than 1.0.

In order to measure potential environmental effects from ammonia plant emissions, the source severity, S, has been defined as the ratio of the time-averaged maximum ground level pollutant concentration ($\overline{\chi}_{max}$) to a hazard factor, F. For criteria pollutants, F is equal to the primary ambient air quality standard. For noncriteria emission species, it equals a reduced threshold limit value (TLV®). Values of S are shown in Table 1. The highest continuous source severities result from nitrogen oxide emissions from the primary reformer (4.1), and ammonia emissions from the regeneration of the carbon dioxide scrubbing solution (2.2) and from the condensate steam stripper (3.2).

The affected population is defined as the number of persons living in the area around an ammonia plant where the ratio of the time-averaged ground level concentration ($\overline{\chi}$) to the hazard factor is greater than 1.0. The affected populations for the emission sources from ammonia plants where this ratio exceeds 1.0 are shown in Table 1. These values are based on the average county population density for 90 ammonia plants of 117 persons/km^2.

The mass of criteria pollutants emitted from ammonia plants by states was computed by multiplying the appropriate emission factor by the amount of ammonia produced in each state. The range in the mass of emissions for the 30 states which produce ammonia are shown in Table 2. Total national emissions are also reported. On a state and national basis, the mass of criteria pollutants emitted from ammonia plants was compared to total state and national emissions from all stationary sources. Only emissions of criteria pollutants can be compared because a comprehensive data base is only available for these materials. Percent contributions of ammonia plant emissions to these burdens are given in Table 2.

TABLE 2. SUMMARY OF MASS OF EMISSIONS OF CRITERIA POLLUTANTS FROM AMMONIA PLANTS

Emission species	Mass of emissions, metric tons/yr		Contribution to total state or national emission burden, %	
	State	National	State	National
Particulate	6 to 441	2,051	<0.1	0.01
NO_x	113 to 8,810	40,954	<0.1 to 6.3	0.44
SO_x	9 to 716	3,325	<0.1 to 0.24	0.01
CO	40 to 3,144	14,616	<0.1 to 7.0	0.02
Hydrocarbons[a]	46 to 3,562	16,557	<0.1 to 1.4	0.10

[a] Includes monoethanolamine and methanol.

The trend in the ammonia industry is toward large capacity, >1,000 metric tons/day plants. With the construction of new plants and demand for ammonia, annual production should increase by 4% to 8% through 1980. Industry emissions should also increase at this rate since no new emission controls are planned.

SECTION 3

SOURCE DESCRIPTION

GENERAL DESCRIPTION

The Bureau of the Census, U.S. Department of Commerce reported that 15.2 x 10^6 metric tons of synthetic anhydrous ammonia were produced in the U.S. in 1976, with approximately 88% produced for fertilizer use (1-14). Ammonia is used as a direct application fertilizer and also as feedstock in the production of other nitrogen fertilizers such as urea, ammonium nitrate, and ammonium phosphates. Remaining ammonia is used to produce such nonfertilizer materials as ammonium nitrate for explosives, urea for animal feeds and resins, nitric acid, acrylonitrile, and amines (15). It is believed that a portion (∿10%) of the ammonia

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(1) Current Industrial Reports, Inorganic Chemicals 1976. Publication No. M28A(76)-14, U.S. Department of Commerce, Washington, D.C., August 1977. 30 pp.

(2) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products June 1977. Publication No. M28B(77)-6, U.S. Department of Commerce, Washington, D.C., August 1977. 7 pp.

(3) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products May 1977. Publication No. M28B(77)-5, U.S. Department of Commerce, Washington, D.C., July 1977. 7 pp.

(4) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products April 1977. Publication No. M28B(77)-4, U.S. Department of Commerce, Washington, D.C., June 1977. 7 pp.

(5) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products March 1977. Publication No. M28B(77)-3, U.S. Department of Commerce, Washington, D.C., May 1977. 6 pp.

(6) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products February 1977. Publication No. M28B(77)-2, U.S. Department of Commerce, Washington, D.C., April 1977. 6 pp.

(continued)

reported as produced for fertilizer use is actually consumed in compounds such as urea and ammonium nitrate that are destined for nonfertilzier end use. This occurs because the major use for both urea and ammonium nitrate is as fertilzier. Consequently, only ∿80% of ammonia produced is believed to be consumed in fertilizers.

Locations of the 90 synthetic ammonia plants in the U.S. are shown in Figure 1 (16). A description of each plant is given in

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(7) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products January 1977. Publication No. M28B(76)-12, U.S. Department of Commerce, Washington, D.C., February 1977. 6 pp.

(9) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products November 1976. Publication No. M28B(76)-11, U.S. Department of Commerce, Washington, D.C., January 1977. 6 pp.

(10) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products October 1976. Publication No. M28B(76)-10, U.S. Department of Commerce, Washington, D.C., December 1976. 6 pp.

(11) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products September 1976. Publication No. M28B(76)-9, U.S. Department of Commerce, Washington, D.C., December 1976. 6 pp.

(12) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products August 1976. Publication No. M28B(76)-8, U.S. Department of Commerce, Washington, D.C., September 1976. 6 pp.

(13) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products July 1976. Publication No. M28B(76)-7, U.S. Department of Commerce, Washington, D.C., September 1976. 6 pp.

(14) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products June 1976. Publication No. M28B(76)-6, U.S. Department of Commerce, Washington, D.C., August 1976. 6 pp.

(15) Carbone, W. E., and O. F. Fissore. Ammonia. In: Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 2. John Wiley & Sons, Inc., New York, New York, 1963. pp. 258-312.

(16) Hargett, N. World Fertilizer Capacity - Computer Printout. Tennessee Valley Authority, Muscle Shoals, Alabama, 1976. 7 pp.

Appendix A. These plants have a combined annual production capacity of approximately 16.8 x 10^6 metric tons.

Figure 1. Location of synthetic ammonia plants in the United States (16).

Anhydrous ammonia is synthesized by reacting hydrogen with nitrogen at a molar ratio of 3:1, then compressing the gas and cooling it to -33°C. Nitrogen is obtained from the air, but hydrogen must be produced from a feedstock by one of the following processes: 1) catalytic steam reforming of natural gas (methane) or naphtha, 2) partial oxidation of heavier hydrocarbons (petroleum oil or distillates), 3) maximum cryogenic recovery from petroleum refinery gases or other cracking operations, 4) gasification of coal or coke, or 5) brine electrolysis cells at chlorine plants.

It is estimated that 75% to 80% of world ammonia production utilizes hydrogen produced from catalytic steam reforming operations, with approximately 60% to 65% of this production based on natural gas feedstock (17). In the U.S., 84 of the 90 ammonia plants use the catalytic steam reforming process and natural gas feedstock for producing hydrogen. The other six plants, representing less than 2% of the ammonia production, obtain their feedstock hydrogen from electrolysis cells in chlorine-caustic soda plants. Only those plants that use catalytic steam reforming of natural gas were studied in detail in this assessment.

PROCESS DESCRIPTION

Six process steps are required to produce synthetic ammonia by the catalytic steam reforming method:

1. natural gas desulfurization
2. catalytic steam reforming
3. carbon monoxide shift
4. carbon dioxide removal
5. methanation
6. ammonia synthesis

The first, third, fourth, and fifth steps are designed to remove impurities such as sulfur, CO, CO_2, and water from the feedstock, hydrogen, and synthesis gas streams. In the second step, hydrogen is manufactured and nitrogen is introduced into the process. The sixth step produces anhydrous ammonia from the synthesis gas. While all ammonia plants use this basic process, process details such as pressures, temperatures, and quantities of feedstock, vary from plant to plant.)

The volume of natural gas required depends on its heating value and varies from 35 to 47 GJ/metric ton of ammonia produced, with an average value of approximately 37 GJ/metric ton (18). For natural gas with a heating value of 39 MJ/m^3, approximately 900 m^3 to 1,200 m^3 are required per metric ton of ammonia produced.

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(17) Buividas, L. J., J. A. Finneran, and O. J. Quartulli. Alternate Ammonia Feedstocks. In: Ammonia Plant Safety, Vol. 17, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1975. pp. 4-18.

(18) Strelzoff, S. Partial Oxidation for Syngas and Fuel. Hydrocarbon Processing, 53(12):79-87, 1974.

An average of 65% to 75% of the natural gas is used as chemical feedstock, while 25% to 35% is used as fuel for the radiant heat section of the primary reformer and for steam production (17, 19). Approximately 40% of the plants have had to use No. 2 fuel oil to heat the primary reformer because of natural gas curtailments in the winter.

A general process flow diagram of a typical synthetic ammonia plant using the catalytic steam reforming process is shown in Figure 2. The six process steps are described in detail in the following sections.

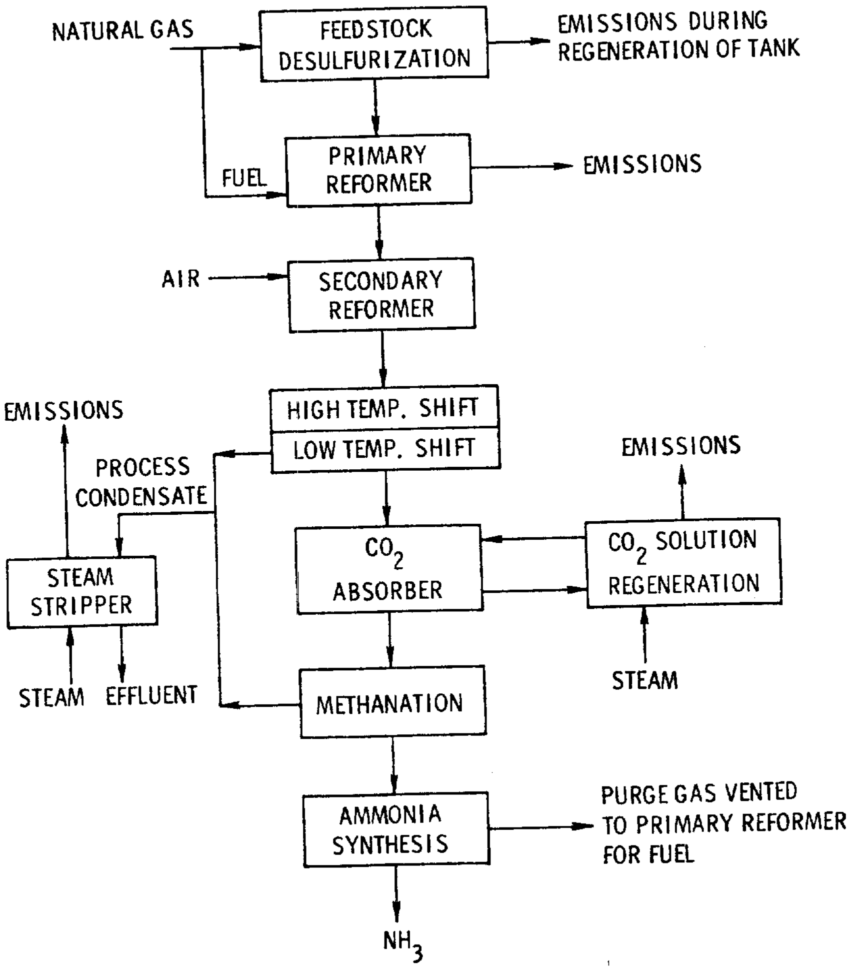

Figure 2. General process flow diagram of a typical ammonia plant.

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(19) Finneran, J. A., L. J. Buividas, and N. Walen. Advanced Ammonia Technology. Hydrocarbon Processing, 51(4):127-130, 1972.

Natural Gas Desulfurization

Sulfur content of natural gas feedstock must be reduced to as low a level as is economically possible to prevent poisoning the nickel catalyst in the primary reformer. Sulfur is present as hydrogen sulfide, 70%; mercaptans, 10%; monosulfides (such as dimethylsulfide, CH_3-S-CH_3) 12%; and disulfides (such as dimethyldisulfide, CH_3-S-S-CH_3) 8% (20). Total sulfur concentration in pipeline grade natural gas ranges from 229 $\mu g/m^3$ to 915 $\mu g/m^3$, with an average value of 450 $\mu g/m^3$. This concentration must be reduced to <280 $\mu g/m^3$.

Over 95% of the ammonia plants use a regenerable activated carbon fortified with a metallic additive, such as copper, for feedstock desulfurization. Remaining plants use a zinc oxide bed which is replaced. Ammonia plants using activated carbon for desulfurization employ a dual-tank system so that one tank is always on-stream while the other is being regenerated. The tank design factor is 200,000 m^3 of natural gas per cubic meter of carbon (21). Tank sizes depend on the process flow rate and the length of time the unit remains on stream. Pressures in the tank range from 3.4 MPa to 4.1 MPa at temperatures of 38°C to 425°C, depending on the particular plant design (22).

Sulfur compounds such as hydrogen sulfide are removed from the feedstock by reaction with the metallic oxide in the carbon to form a metallic sulfide. A typical reaction is:

$$CuO + H_2S \longrightarrow CuS + H_2O \quad (1)$$

The activated carbon tank is used until the elemental sulfur buildup reaches 13 to 25 weight percent of the carbon. When the concentration in the exit gas reaches about 0.2 ppm, the feedstock flow is diverted to a second carbon tank, while the first is regenerated. Regeneration is accomplished by passing superheated steam (230°C to 290°C) through the bed at a rate of about 900 kg/hr. The carbon bed is then heated to 230°C for

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(20) Personal communication with Dayton Power and Light Company, Dayton, Ohio, July 1976.

(21) Green, R. V. Synthetic Nitrogen Products. In: Riegel's Handbook of Industrial Chemistry, Seventh Edition. J. A. Kent, ed. Van Nostrand Reinhold Company, New York, New York, 1974. pp. 75-122.

(22) Haney, G., and K. Wright. Media for Removing Sulfur from Natural Gas. In: Ammonia Plant Safety, Vol. 12, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1970. pp. 50-54.

8 to 10 hours. During this period, additional air or oxygen may be added with the steam to increase the oxygen concentration to ∿5,000 ppm (23, 24). Free oxygen reacts with the metal sulfide to form a metal oxide and elemental sulfur, for example:

$$2\ CuS + O_2 \rightarrow 2CuO + 2S \qquad (2)$$

Elemental sulfur is trapped in the pores of the carbon bed. Calgon Corporation, a major manufacturer of activated carbon units, reports that all of the elemental sulfur remains on the carbon surface, and is not removed by the regeneration steam (25, 26). However, because the vapor pressure of sulfur[a] at 230°C to 290°C is 0.8 kPa to 6.0 kPa, some sulfur must be lost by vaporization.

Activated carbon will also adsorb hydrocarbons. C_1-C_4 hydrocarbons are weakly adsorbed, while C_5-C_7 hydrocarbons are more strongly adsorbed. Shorter chain hydrocarbons are gradually replaced by longer chain compounds during the desulfurization cycle. Hydrocarbon loading can be as much as 5% to 10% of the weight of the carbon in the bed (23, 25). During regeneration, portions of the C_1-C_4 and C_5-C_7 compounds are desorbed and vented with the steam. A hydrocarbon analysis of typical pipeline grade natural gas is shown in Table 3.

Catalytic Steam Reforming

Natural gas leaves the desulfurization tank containing less than 0.2 ppm sulfur. Sweetened natural gas is mixed with process

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[a] Vapor pressures of sulfur at 230°C and 290°C were obtained by interpolation of data given in Reference 27.

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(23) Personal communication with P. D. Langston, Calgon Corporation, Pittsburgh, Pennsylvania, 5 September 1975.

(24) Personal communication with F. R. Bossi, Calgon Corporation, Pittsburgh, Pennsylvania, 29 September 1975.

(25) Personal communication with W. Lovett, Calgon Corporation, Pittsburgh, Pennsylvania, 29 September 1975.

(26) Air Purification with Granular Activated Carbon, Brochure 23-55, Calgon Corporation, Pittsburgh, Pennsylvania. 1975. p. 24.

(27) Liley, P. E., and W. R. Gambill. Physical and Chemical Data. In: Chemical Engineers' Handbook, Fifth Edition, Section 3, R. H. Perry and C. H. Chilton, eds. McGraw-Hill Book Company, New York, New York, 1973. p. 48.

TABLE 3. HYDROCARBON ANALYSIS OF TYPICAL PIPELINE GRADE NATURAL GAS (20)

Compound	Concentration, mole %
Methane	95.398
Ethane	2.666
Propane	0.143
iso-Butane	0.030
n-Butane	0.029
iso-Pentane	0.012
n-Pentane	0.008
Hexane	0.015
Nitrogen	0.323
Carbon dioxide	1.376

steam and preheated to ~540°C in the second coil in the waste heat removal section of the primary reformer, Figure 3. The steam-to-gas ratio normally ranges from 3.5 to 4.0 moles steam per mole carbon. A lower ratio could be used, but the higher ratio improves conversion and helps supply the steam needed in the carbon monoxide conversion step. Moreover, an excess of steam in the reformer prevents carbon formation on the catalyst.

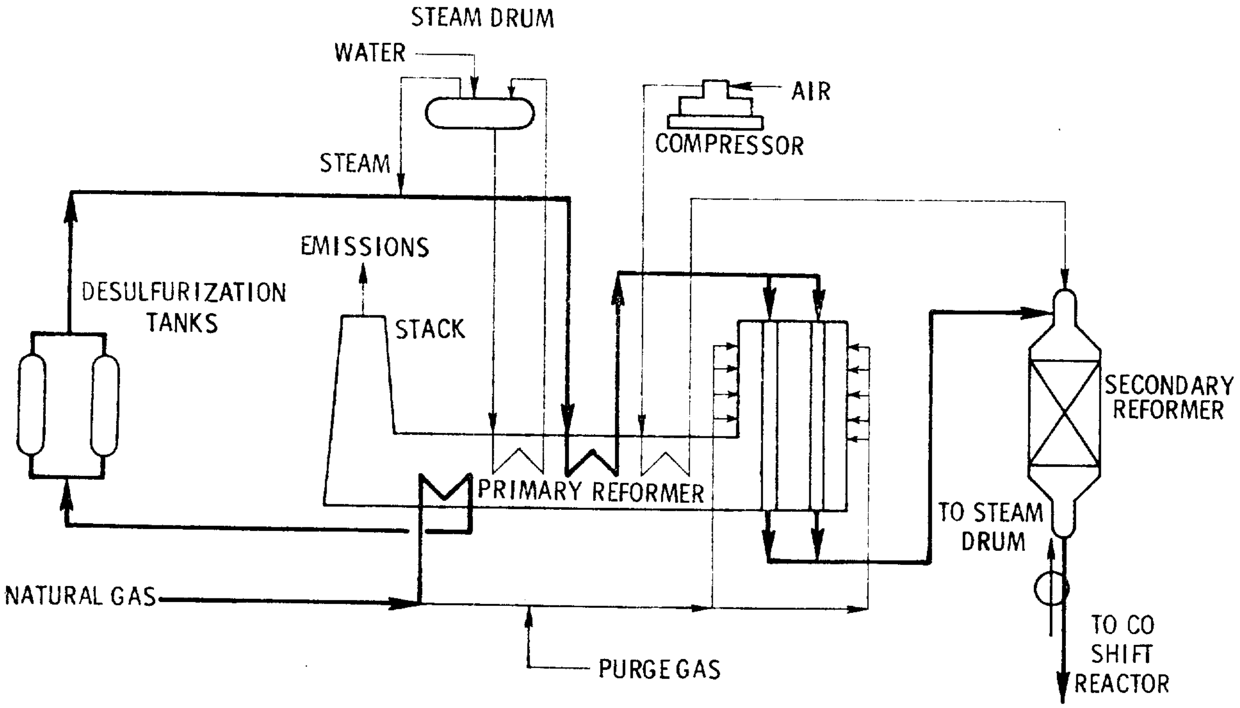

Figure 3. Synthesis gas formation.

A mixture of steam and gas enters the vertically supported primary reformer tubes, which are filled with a nickel-based reforming catalyst. The endothermic reforming reaction (Equation 2) requires heat input of 227 kJ/mole:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (3)$$

Radiant heat for the reforming reaction is supplied by firing natural gas and purge gas (from the synthesis loop) on the outside of the reformer tubes. Approximately 70% of the methane is converted to hydrogen and carbon monoxide in the primary reformer. Reformed gas contains about 8% methane (dry basis). Gas exits the primary reformer tubes at ∿730°C to ∿820°C. Flue gas leaves the radiant section at ∿960°C. Excess heat in the flue gas is removed by waste heat coils and preheaters. Flue gas leaves the reformer stack at 230°C.

Process gas is sent to the secondary reformer, where it is mixed with air that has been compressed in a centrifugal compressor to ∿3.4 MPa and preheated to about 540°C in heat exchangers in the primary reformer. Sufficient air is added to produce a final synthesis gas having a hydrogen-to-nitrogen mole ratio of 3:1. Heat necessary for completion of the reforming reactions is supplied by combustion of the two gases as they mix in the top of the secondary reformer. Reaction gases pass over a bed of nickel-based reforming catalyst similar to that used in the primary reformer. Gas temperature at the exit of the secondary reformer is 950°C to 1,000°C which is reduced to ∿360°C in a waste heat boiler. Sufficient heat is recovered to produce from 50% to 100% of the 10.3 MPa steam required in the plant.

Carbon Monoxide Shift

After cooling, the secondary reformer effluent gas (12.0% carbon monoxide and 8.4% carbon dioxide on a dry basis) enters a high temperature (330°C to 550°C) CO shift converter, shown in Figure 4, which is filled with a chromium oxide promoted - iron oxide shift catalyst. Conversion of carbon monoxide to carbon dioxide and hydrogen is necessary for economical use of the raw synthesis gases. The following reaction takes place in the carbon monoxide shift converter:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (4)$$

Heat from the exothermic reaction (41 kJ/mole of CO) is used to produce steam. The temperature of the exit gas from the converter is ∿425°C.

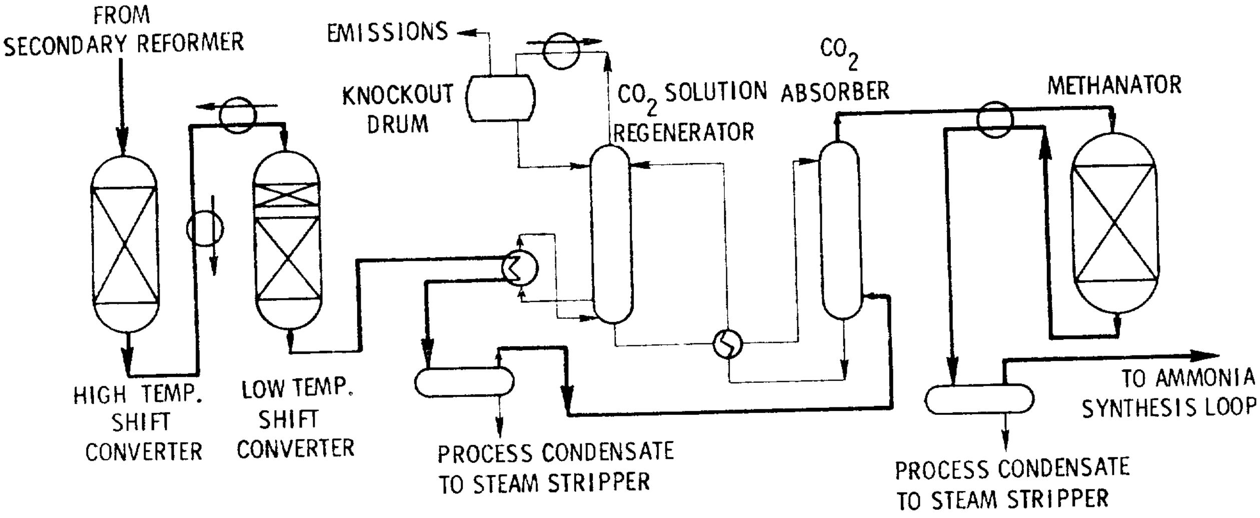

Figure 4. Synthesis gas purification.

Shift gas is cooled to ∿200°C in a heat exchanger. In some plants (∿85%), the gas is then 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 insure that the unit will operate through its expected lifetime (28).

The low temperature shift converter is filled with a copper oxide/zinc oxide catalyst which is highly active between 200°C and 260°C. Final shift gas (0.3% CO on a dry basis) is cooled from ∿210°C to ∿110°C, and enters the bottom of the carbon dioxide absorption system. Unreacted steam is condensed and separated from the gas in a knockout drum.

A 544-metric ton/day ammonia plant produces 7.89×10^{-3} m^3/s of condensed steam (process condensate). A 900-metric ton/day plant produces 1.39×10^{-2} m^3/s of condensate. This water contains

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(28) Personal communication with J. C. Barber, Tennessee Valley Authority, Muscle Shoals, Alabama, June 1976.

approximately 600 ppm to 1,200 ppm ammonia, 200 ppm to 1,000 ppm methanol, and 200 ppm to 2,800 ppm carbon dioxide (29-32).

Ammonia in the process condensate is formed in the high temperature shift converter. It is present as ammonium bicarbonate because the condensate is saturated with carbon dioxide. Methanol is formed in the low temperature shift converter. Condensate also contains small amounts (<1 ppm) of sodium, iron, copper, zinc, calcium, and aluminum, which enter the process stream through contact with catalyst, internal refractory, vessel walls, and piping (29, 33).

Process condensate is sent to a stripper to remove volatile gases such as ammonia, methanol, and carbon dioxide. The concentration of ammonia in the effluent is reduced to 20 ppm, the methanol to 20 ppm, and the carbon dioxide to 40 ppm with 96 kg to 240 kg of steam per cubic meter of condensate (29). Ion exchange units or molecular sieves are then used to further purify the condensate if it is to be recycled to the boilers. Steam and volatile gases are vented to the atmosphere. Trace metals remaining in the process condensate are removed by the ion exchange unit.

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(29) Quartulli, O. J. Stop Wastes: Reuse Process Condensate. Hydrocarbon Processing, 54(10):94-99, 1975.

(30) Romero, C. J., F. Yocum, J. H. Mayes, and D. A. Brown. Treatment of Ammonia Plant Process Condensate Effluent. EPA-600/2-77-200, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1977. 85 pp.

(31) Spangler, H. D. Repurification of Process Condensate. In; Ammonia Plant Safety, Vol. 17, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1975. pp. 85-86.

(32) Quartulli, O. J. Review of Methods for Handling Ammonia Plant Process Condensate. Presented at the Fertilizer Institute Manufacturing Environmental Seminar, New Orleans, Louisiana, January 14-16, 1976. 20 pp.

(33) Finneran, J. A., and P. H. Whelchel. Recovery and Reuse of Aqueous Effluent from a Modern Ammonia Plant. In: Ammonia Plant Safety, Vol. 13, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1971. pp. 29-32.

Carbon Dioxide Removal

The final shift gas contains CO_2 which must be removed. (About 1.22 metric tons (34) of carbon dioxide are produced per metric ton of ammonia.) Removal of carbon dioxide depends on its acid-gas character; it tends to form carbonic acid in water:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{5}$$

Carbonic acid can be absorbed by solutions of amines, for example:

$$2NH_2CH_2CH_2OH + H_2CO_3 \longrightarrow (NH_2CH_2CH_2)_2CO_3 + 2H_2O \tag{6}$$

or by solutions of alkaline salts, such as:

$$K_2CO_3 + H_2CO_3 \longrightarrow 2KHCO_3 \tag{7}$$

to form carbonates. These carbonates decompose into CO_2 and the amine or salt on heating, regenerating the absorption solution (Figure 4). Carbon dioxide scrubbing systems used in the U.S. today employ either monoethanolamine or hot potassium carbonate as the scrubbing medium (21, 34).

Monoethanolamine Scrubbing--

The classical method for removing carbon dioxide, used by 80% of the ammonia plants, is absorption in monoethanolamine (MEA). Gas containing carbon dioxide is passed upward through an absorption tower countercurrent to a 15% to 30% solution of MEA in water fortified with effective corrosion inhibitors (21). The amine solution, after absorbing the carbon dioxide, is first preheated, then regenerated in a reactivating tower. Carbon dioxide is removed from the solution first by steam stripping and then by heating. Two kilograms of steam per kilogram of carbon dioxide are used for regeneration (35). Carbon dioxide gas (98.5% CO_2) is then vented to the atmosphere or used for chemical feedstock in other parts of the plant complex. After being cooled in a heat exchanger and solution cooler, regenerated MEA is pumped back to the absorber tower. This process permits carbon dioxide removal at atmospheric pressure.

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(34) Strelzoff, S. Choosing the Optimum CO_2-Removal System. Chemical Engineering, 82(19):115-120, 1975.

(35) Hahn, A. V. The Petrochemical Industry - Market and Economics. McGraw-Hill Book Company, New York, New York, 1970. pp. 19-38.

Hot Potassium Carbonate Scrubbing--
A comparatively new process for carbon dioxide removal uses hot potassium carbonate (K_2CO_3) as a scrubbing medium and is based on the reaction:

$$K_2CO_3 + CO_2 + H_2O \longrightarrow 2KHCO_3 \qquad (8)$$

The scrubbing system is "hot" because the gas enters at 120°C. Normally, the solution from the regenerator is not cooled before it returns to the absorber. In this system, the cost of heat exchangers can be eliminated and the solubility of hydrogen and nitrogen is decreased.

Because the capacity of hot carbonate solutions (25% to 30%) for absorbing carbon dioxide is between that of water and MEA solutions, carbon dioxide is removed in two stages operating at different pressures. Higher pressure is required for cleanup, whereas removal of the bulk of the carbon dioxide at lower pressure reduces compression costs. Converted synthesis gas at about 120°C and 1.5 MPa enters the bottom of the absorber and passes up through the packing, countercurrent to a 40% carbonate solution. This stage reduces the carbon dioxide to about 3%.

In the top section of the absorber, a 40% carbonate solution at about 90°C and 5.2 MPa to 5.5 MPa scrubs the residual carbon dioxide from the gas and reduces the carbon dioxide content to $<1\%$. As the solution absorbs carbon dioxide, some carbonate becomes bicarbonate. Spent solution from the absorbers is reactivated in a two-stage regenerator. The rich carbonate solution flashes as it enters the regenerator, producing carbon dioxide and water vapor. This vapor is condensed and approximately 80% is returned to the regenerator. The carbon dioxide has a purity of at least 98.5% and is either vented to the atmosphere or used in urea manufacture.

Flashed carbonate solution is stripped further by reboiler-generated steam. The solution leaving the top section of this regenerator contains $<1\%$ CO_2 and is used as the absorbent in the lower portion (low-pressure section) of the absorber tower. A leaner carbonate solution is available at the bottom of the regenerator section, and it is used as the absorbent in the top (higher pressure) section of the absorber, after being cooled to $\sim$90°C.

Similar potassium carbonate systems have been developed: the Fluor solvent process which employs propylene carbonate, the

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(36) Haase, D. J. New Solvent Cuts Costs of Carbon Monoxide Recovery. Chemical Engineering, 82(16):52-54, 1975.

Giammarco-Vetrocoke hot carbonate process which employs solution activators such as arsenic trioxide, and the Catacarb process which activates hot carbonate with an organic additive (21, 34, 36).

Methanation

In commercial practice, all carbon dioxide absorption methods leave a small amount of carbon dioxide (usually <1.0%) in the synthesis gas which must be removed because it is a poison to most ammonia synthesis catalysts. Residual CO_2 is removed by catalytic methanation (Figure 4) which is conducted over a nickel catalyst (nickel oxide on alumina) at temperatures of 400°C to 600°C and pressures up to 3 MPa according to the following reactions:

$$CO + 3H_2 \longrightarrow Ch_4 + H_2O \tag{9}$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \tag{10}$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \tag{11}$$

The methanation reaction (Equation 11) is the reverse of catalytic steam reforming of methane. Methane formation is favored by the use of lower temperatures and the removal of excess water.

Exit gas from the methanator which contains <20 ppm total carbon oxides is cooled to 38°C. Condensate is removed from the synthesis gas in a process condensate drum. Final synthesis gas at 38°C and ∿2.5 MPa has a 3:1 mole ratio of hydrogen to nitrogen and contains less than one percent methane and argon.

Ammonia Synthesis

Many variations of the original Haber process are used commercially. Most important of these are the modified Haber-Bosch, Claude, Casale, Fauser, and Mont Cenis processes. Fundamentally, these processes are the same: nitrogen is fixed with hydrogen as ammonia in the presence of a catalyst. They vary, however, in the arrangement and construction of equipment, the composition of catalysts, and the temperature and pressure used.

The first step in the synthesis process is to compress the synthesis gas from the methanator (Figure 5). Within the last 15 years, the application of centrifugal compressors to handle synthesis gas at pressures ranging from 13.8 MPa to 68.9 MPa has revolutionized the ammonia industry (21, 37). Centrifugal

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(37) Looking at Ammonia Technology. Chemical and Process Engineering, 51(10):5, 1970.

compressors require a minimum gas volume at the entrance of any given stage which can be met only at high capacities and low synthesis loop pressures. These units have several advantages over reciprocal compressors: 1) they are cheaper; 2) they require less frequent and cheaper maintenance; 3) they require no lubrication and thus eliminate oil entrainment into the synthesis loop, which can foul the catalyst and contaminate the product; and 4) they can be turbine driven by the steam generated in the high-pressure steam reforming unit that precedes the synthesis loop, and still supply exhaust steam at a level sufficient to regenerate the carbon dioxide absorption solution. Thus, centrifugal compressors involve lower investments and maintenance costs (36, 38). However, plants using centrifugal compressors consume more natural gas for producing the steam to drive the compressors, than do plants equipped with reciprocating compressors (38).

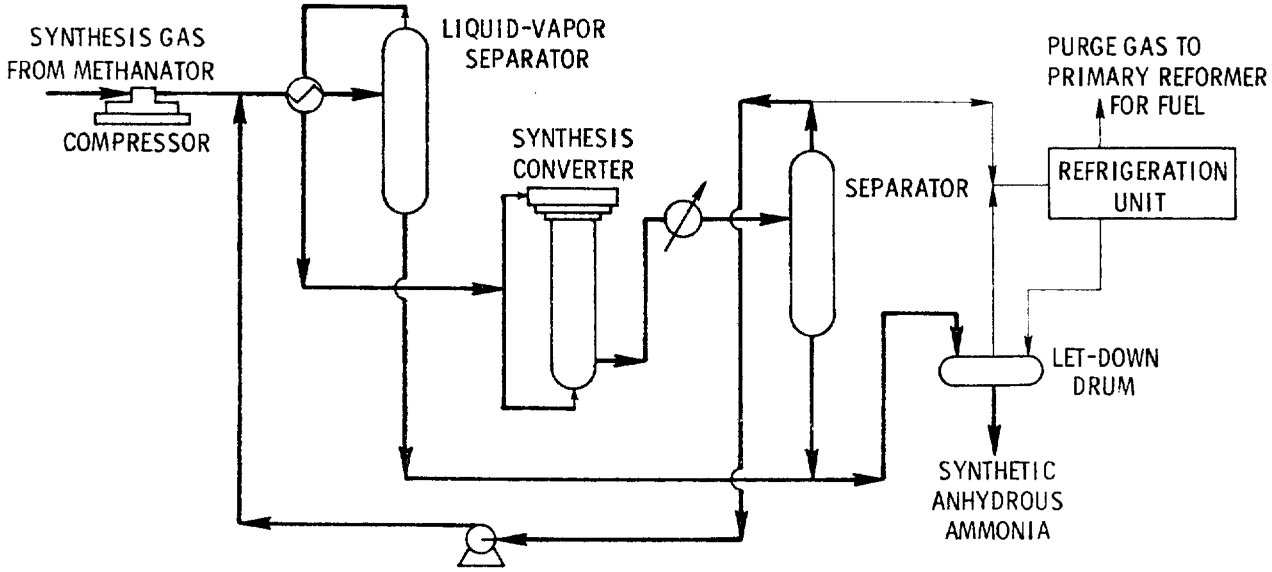

Figure 5. Ammonia synthesis loop.

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(38) Scheel, L. F. Refrigeration: Centrifugal or Recip? Hydrocarbon Processing, 48(3):123-129, 1969.

Centrifugal compressors are driven by high-pressure, high temperature steam which is generated in the plant by recovering heat from the secondary reformer process gas and the primary reformer flue gases. Fresh synthesis gas from the methanator is compressed to 13.8 MPa to 34.5 MPa and is mixed with recycled synthesis gas and is cooled to 0°C.

Condensed ammonia is separated from the unconverted synthesis gas in a liquid-vapor separator and sent to a let-down separator. Unconverted gas is compressed and preheated to ∿180°C before entering the synthesis converter. This gas contains about 13% inerts and 3.7% ammonia with a hydrogen-to-nitrogen mole ratio of 3:1.

Synthesis gas enters the converter and is radially dispersed through the triply promoted iron oxide (Fe_3O_4) synthesis catalyst. Exit gas from the converter contains ∿15% ammonia and ∿14% inerts and is cooled from ∿370°C to ∿38°C. Ammonia which condenses is separated in a primary separator. A small portion of the overhead gas is taken as a purge to prevent the buildup of inerts such as argon in the circulating gas system (21). Purge gas is cooled to -23°C to minimize the loss of ammonia and used as fuel in the primary reformer (Table 4) (39). A recently developed cryogenic unit recovers the hydrogen in the purge gases from the synthesis loop (40). Sufficient hydrogen can be recovered by this process to produce an additional 5% to 6% ammonia from the feedstock.

TABLE 4. TYPICAL PURGE GAS ANALYSIS (39)

Component	Mole %
Hydrogen	60
Nitrogen	20
Argon	3.5
Methane	16.5
TOTAL	100.0

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(39) Haslam, A. A., and W. H. Isalski. Hydrogen from Ammonia Plant Purge Gas. In: Ammonia Plant Safety, Vol. 17, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1975. pp. 80-84.

(40) Ammonia Plants Seek Routes to Better Gas Mileage. Chemical Week, 116(8):29, 1975.

Liquid ammonia from the primary, secondary, and purge separators collects in the let-down separator where the ammonia is flashed to 0.1 MPa at -33°C to remove impurities such as argon from the liquid. The flash vapor is condensed in the let-down chiller where anhydrous ammonia is drawn off and stored in a low temperature (-28°C) atmospheric storage tank or piped to other locations within the plant.

SECTION 4

EMISSIONS

EMISSION CHARACTERISTICS

At a typical synthetic ammonia plant, four process steps are responsible for air emissions: 1) regeneration of desulfurization tanks, 2) primary reforming, 3) regeneration of carbon dioxide scrubbing solution, and 4) steam stripping of process condensate.

In addition to emissions from process vents and stacks, potential fugitive emission sources include leaking seals from ammonia compressors and pumps, ammonia storage tank vents, pressure relief valves, and ammonia spillages. The following sections characterize the emission species associated with each emission point.

Desulfurization

More than 95% of the ammonia plants in the U.S. use activated carbon fortified with metallic oxide additives for feedstock desulfurization (25, 41). Each plant is equipped with a dual-tank system so that one tank is always on stream while the other is being regenerated. Regeneration of this activated carbon desulfurization tank may cause emissions of sulfur oxides (SO_x) and Hydrogen sulfide (H_2S), depending on the amount of oxygen in the regeneration steam. Regeneration also results in hydrocarbon and carbon monoxide (CO) emissions.

The remaining 5% of the ammonia plants use a tank filled with zinc oxide for feedstock desulfurization. This tank is not an emission source because it is replaced instead of regenerated at the plant site.

The desulfurization tank is regenerated once every 30 days by passing steam through the bed for an average of 8 hr to 10 hr. Metallic sulfide is converted to metallic oxide and elemental sulfur. Calgon Corporation reported that the sulfur remains on the carbon surface and is not vented to the atmosphere with the regeneration steam (23-25). However, sulfur has an

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(41) Personal communication with N. Walen, The M. W. Kellogg Company, Houston, Texas, 9 September 1975.

appreciable vapor pressure[a] at the regeneration temperatures (0.8 kPa at 230°C to 6.0 kPa at 290°C), and some sulfur must be lost by vaporization. In addition, sulfur may react to form H_2S or SO_2. Because source data are not available, a worst-case emission factor for sulfur emissions has been calculated in order to estimate potential environmental effects.

On this basis all sulfur that is adsorbed on the carbon bed is assumed to be vented to the atmosphere during regeneration. The quantity of sulfur in the carbon bed can be determined from the sulfur concentration in the feedstock, the feedstock process rate, the size of the carbon bed, and the age of the carbon tank. Total sulfur concentrations of pipeline grade natural gas range from 229 $\mu g/m^3$ to 915 $\mu g/m^3$ and average 450 $\mu g/m^3$ (18, 19, 41). The carbon bed reduces the sulfur concentration of the exiting process gas below 280 $\mu g/m^3$.

Ammonia plants consume 35 GJ to 47 GJ of natural gas per metric ton of ammonia produced, with an average value of 37 GJ/metric ton (18, 21). About 75% of this natural gas (26 GJ to 35 GJ) is desulfurized and used for feedstock, while 25% (8.7 GJ to 11.6 GJ) is used as fuel for the radiant heat section of the primary reformers. For natural gas with a heating value of 39 MJ/m^3, the quantity of feedstock natural gas used to produce one metric ton of ammonia ranges from 700 m^3 to 900 m^3, with an average value of 710 m^3.

Desulfurization tank size varies considerably among ammonia plants and depends on the sulfur concentration of the feedstock, the production rate, and the desired length of time between regenerations. Consequently, the tanks at one plant may need regeneration only once a year, while those at another plant require regeneration every 5 days. On the average, desulfurization tanks are regenerated every 30 days. For design considerations, 1 m^3 of metal-impregnated activated carbon will remove all of the sulfur species in 2×10^5 m^3 of natural gas (21).

An average ammonia plant produces 480 metric tons/day (see Section 4, page 36). Therefore, on the average this plant desulfurizes 3.41×10^5 m^3/day of natural gas and, for a feedstock containing 450 $\mu g/m^3$ of sulfur, collects 153 g/day of sulfur in the desulfurization tank. For a 30-day regeneration schedule, the tank must hold 51 m^3 of carbon and collect a total of 4.6 kg of sulfur.

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[a] Sulfur vapor pressures were obtained by interpulation of data given in Reference 27.

Therefore, a maximum of 4.6 kg of sulfur will be emitted to the atmosphere during the 10-hr regeneration period which occurs once every 30 days. This results in an emission rate of 0.128 g/s over the 10-hr period or 0.053 g/s normalized over a 24-hr period. For an average ammonia plant producing 480 metric tons of ammonia per day, the corresponding emission factors are 23 mg/kg of ammonia produced over a 10-hr period and 9.6 mg/kg of ammonia produced over a 24-hr period. If all of this sulfur is emitted in the form of SO_2 or H_2S, the corresponding 24-hr emission factors are 0.019 g/kg or 0.010 g/kg, respectively.

The carbon bed also collects quantities of longer chain hydrocarbons which are present in the feedstock. Upon regeneration of the carbon bed with steam, hydrocarbons and carbon monoxide are emitted. Based on one set of source test measurements in the public files at the Texas Air Control Board, the emission factors for total hydrocarbons (measured as methane[a]) and for carbon monoxide are 3.6 g/kg and 6.9 g/kg of ammonia produced, respectively.

Vent heights for the desulfurization tank range throughout the industry from 6 m to 12 m, with an average height of 10 m.

Primary Reformer

Natural gas and purge gases are fired at 1,000°C to 1,200°C using 10% to 20% excess air in the radiant heat section of the primary reformer (19, 39). Hot combustion gases are cooled by a series of four to six waste heat boilers and heat exchangers before they are vented via a stack to the atmosphere. Final stack gas temperatures are ∿230°C.

Emission species from this source consist of natural gas or fuel oil combustion products (NO_x, CO, SO_x, hydrocarbons, and particulates). Natural gas is currently the primary fuel, but natural gas shortages have forced about 50% of the ammonia plants to use No. 2 fuel oil to fire the primary reformer during the winter months (approximately 4 months).

Data collected from the literature (30), from public files at the Texas Air Control Board, and from the Louisiana Air Control Commission on emissions from the primary reformer were used to establish emission factors as shown in Table 5. All four plants were 900 metric ton/day units. Emission factors from plants A and B were established from a material balance and engineering estimates. Emission factors at plant C were the result of sampling the primary reformer stack gases. Except where noted, all emission factors are based on natural gas fuel.

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[a] The test method for hydrocarbons reports total hydrocarbons in terms of methane equivalents; individual species are not determined.

TABLE 5. PLANT DATA FOR EMISSIONS FROM PRIMARY REFORMER

Plant	Type of data	Emission species	Emission factor, g/kg
A[a]	Material balance	NO_x	4.38
B[b]	Material balance	NO_x	5.95
		Particulate	0.15
		SO_x	0.005
		CO	0.003
C[d]	Stack test	NO_x	2.03
		Hydrocarbons	0.10
		CO	0.14
		Particulate[c]	0.51
		SO_2[c,d]	0.49
D[e]	Stack test	NO_x	2.71
		NO_x	4.04
		NO_x	2.83
		NO_x	4.23
		NO_x	2.76
		NO_x	1.99
		NO_x	2.57
		NO_x	2.72
		Average	2.98

Stack Tests
2.03
2.71
4.04
2.83
4.23
2.76
1.99
2.57
2.72
Avg 2.77

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[a] Public files at Texas Air Control Board, Austin, Texas, 1976.

[b] Public files at Louisiana Air Control Commission, New Orleans, Louisiana, 1976.

[c] Material balance estimates for burning fuel oil in reformer.

[d] Assuming all sulfur in fuel oil is converted to sulfur dioxide.

[e] Eight stack tests collected over a nine-month period from a plant representative of industry (30).

Emission factors from plant D come from recent stack test data at a 900 metric ton/day ammonia plant (30). These numbers were generated in a study designed to evaluate the effect of adding the overhead gases from a condensate steam stripper to the primary reformer stack gases. Measurements reported in Table 5 were collected when no overhead gases were added.

Emission factors for criteria pollutants from the primary reformer, shown in Table 6, were determined by averaging the appropriate values in Table 5. The uncertainty value associated with the NO_x emission factor was calculated from the Student "t" test at a 95% confidence limit.

TABLE 6. AVERAGE EMISSION FACTORS FOR EMISSIONS FROM PRIMARY REFORMER BASED ON PLANT DATA

Emission species	Emission factor, g/kg	
	Natural gas	Fuel oil
NO_x	2.87 ~~2.7~~ ± 23%[a]	N.A.[b]
CO	0.07	N.A.
SO_x	0.005	0.49
Hydrocarbons	0.1	N.A.
Particulate	0.15	0.51

[a] Average based on test measurements only.

[b] Not available.

In order to supplement the data in Table 6, emission factors were also calculated from data (42) on the combustion of natural gas and fuel oil (see Table 7). Because emissions from the primary reformer result from the combustion of fuels used to heat process gas in the reformer, these calculated values are believed to be a good estimate of the actual emission factors. The emissions data in Reference 42 are reported in terms of fuel consumed and must be converted to the proper units for comparison with Table 6. The conversion was based on energy requirements of 8.7 GJ to 11.6 GJ for every metric ton of ammonia production; i.e., 200 m^3 to 300 m^3 of natural gas with a heating value of 39 MJ/m^3 are burned in the primary reformer per metric ton of ammonia produced (18, 21). The corresponding combustion rate for distillate fuel oil with a heating value of 39 GJ/m^3 is 0.2 m^3 to 0.3 m^3 of fuel oil per metric ton of ammonia. The combustion rate for each fuel type was then multiplied by the appropriate emission factors (42) to arrive at the calculated emission factors in Table 7.

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(42) Compilation of Air Pollutant Emission Factors, Second Edition. Publication No. AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1973. pp. 1.3-1 to 1.3-4 and 1.4-1 to 1.4-3.

TABLE 7. EMISSION FACTORS FOR PRIMARY REFORMER BASED ON COMBUSTION DATA FOR NATURAL GAS AND DISTILLATE FUEL OIL

Emission species	Reported emission factor (42), mg/m^3 of fuel	Calculated emission factor for primary reformer, g/kg of product
Natural gas		
Particulate	290	0.058 to 0.087
SO_x	9.6[a]	0.0019 to 0.0029
NO_x	1,920 to 3,700	0.384 to 0.576
CO	270	0.054 to 0.081
Hydrocarbons (as CH_4)	48	0.0096 to 0.0144
Distillate fuel oil		
Particulate	1.8	0.36 to 0.54
Sulfur dioxide	17 S[b]	1.02 to 1.53[c]
Sulfur trioxide	0.25 S[b]	0.015 to 0.022[c]
NO_x	4.8 to 9.6	0.96 to 2.88
CO	0.5	0.10 to 0.15
Hydrocarbons	0.35	0.070 to 0.105
Aldehydes	0.25	0.050 to 0.075

[a] For natural gas containing 460 μg/m^3 of sulfur.

[b] S is the percent sulfur in the fuel oil.

[c] Based on fuel oil containing 0.3% sulfur.

A general comparison of Tables 5, 6, and 7 indicates that emission factors based on stack test measurements are higher than the corresponding calculated values in Table 7 (i.e., for NO_x, CO, and hydrocarbons), and that emissions from the combustion of fuel oil are higher than those for natural gas. The following specific observations and conclusions can be made:

- Measured and calculated NO_x emission factors demonstrate that combustion conditions in the primary reformer are more severe than those in a typical industrial boiler. Because nitrogen oxides are formed by the combination of atmospheric nitrogen and oxygen at elevated temperatures, more are produced as the temperature, residence time, or excess oxygen increases.
- As a result, the actual emissions from the combustion of fuel oil are expected to be higher than those given in Table 7. However, they will not be higher by a factor of five to seven, as in the case of natural gas, because fuel oil combustion normally produces higher flame temperatures than natural gas.

- Sulfur oxide emissions result from the oxidation of sulfur in the fuel. Consequently, emission factors can be calculated from a material balance once the fuel sulfur content is known.
- The greatest effect in changing from natural gas to fuel oil will be the increase in SO_x emissions. These may increase by a factor of 100 to 1,000 or more, depending on the percent sulfur in the fuel.
- Conditions that favor an increase in NO_x emissions also favor a decrease in CO and hydrocarbon emissions. In this respect the test results from Plant C in Table 5 are surprising. Emission factors for NO_x, CO, and hydrocarbons are greater than those in Table 7. One possible explanation is higher flame temperatures along with some regions of poor fuel/air mixing. Another possibility is error in the test measurements. Under good combustion conditions (i.e., adequate fuel/air mixing to ensure complete combustion) CO and hydrocarbon emission factors are expected to be equal or lower than those shown in Table 7.

A summary of primary reformer emissions takes these factors into consideration and is presented in Table 8.

TABLE 8. SUMMARY OF PRIMARY REFORMER EMISSIONS

Emission species	Emission factor, g/kg
Natural gas	
Particulate	0.072
SO_x	0.0024
NO_x	2.7 ± 23%
CO	0.068
Hydrocarbons	0.012
Fuel oil	
Particulate	0.45
SO_x	1.3
NO_x	2.7
CO	0.12
Hydrocarbons	0.15

The following are conclusions regarding emissions from the primary reformer:

NO_x - For natural gas combustion the average emission factor is 2.7 g/kg, based on actual test measurements. This same value is taken as an estimate for combustion with fuel oil. Table 7 indicates that NO_x levels may be higher when fuel oil is burned in the primary reformer, but no test data are available to determine the actual amount. The increase shown in Table 7 is from two to seven times the NO_x emissions for natural gas.

SO_x - None of the data are from source tests. Average values taken from the material balance calculations reported in Table 7 are 2.4 mg/kg for natural gas, and 1.3 g/kg for fuel oil.

Particulate - Average material balance data from Table 7 are 72 mg/kg for natural gas and 0.45 g/kg for fuel oil.

Particulate - Average material balance data from Table 7 are 72 mg/kg for natural gas and 0.45 g/kg for fuel oil.

CO and hydrocarbons - Emission factors for combustion with fuel oil as taken from Table 7 are 0.12 g/kg for CO and 0.15 g/kg for hydrocarbons (including aldehydes). It is difficult to arrive at final CO and hydrocarbon emission factors for natural gas combustion without knowing more about the test measurements at Plant C. Because natural gas is burned in the primary reformer with 25% excess air, and because NO_x data indicate severe combustion conditions are present, it is believed the data from Plant C are higher than the average primary reformer. Therefore average emission factors obtained from Table 7 are 68 mg/kg for CO and 12 mg/kg for hydrocarbons.

Primary reformer stacks vary in height from 10 m to 70 m. Average stack height and standard deviation for the stack heights at 16 ammonia plants is 28.6 m ± 14.9 m.[a] Stack gas temperatures range from 150°C to 370°C with an average value and standard deviation for 16 samples of 226°C ± 58°C.

Regeneration of the Carbon Dioxide Scrubbing Solution

Carbon dioxide is removed from the process gas by absorption in an amine solution or a carbonate solution. Approximately 80% of the ammonia plants use a MEA scrubbing solution and the remainder use a hot potassium carbonate solution. As the solution becomes saturated with carbon dioxide, it must be regenerated resulting in air emissions.

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[a] Obtained from public data on file at Texas Air Control Board and Louisiana Air Control Commission.

Carbon dioxide is separated from the scrubbing solution by steam stripping and then by heating. Stripped gas containing at least 98.5% carbon dioxide is either vented to the atmosphere or used as chemical feedstock for a urea plant. Approximately 30% of the ammonia plants employing the MEA system pipe the carbon dioxide gas to a urea plant. In addition to carbon dioxide, vented gas contains smaller quantities of water, methane, ammonia, carbon monoxide, and MEA.

Approximately 20% of the ammonia plants use hot potassium carbonate solutions to scrub carbon dioxide from process gas. Saturated solution is regenerated by flashing. Overhead vapors contain carbon dioxide and water which is condensed from the vapor and recycled to the regenerator. Carbon dioxide is either vented to the atmosphere or used as a feedstock for producing urea. Approximately 50% of the ammonia plants with hot potassium carbonate systems sell the carbon dioxide gas as chemical feedstock. In addition to the carbon dioxide which is vented to the atmosphere, the gas contains smaller quantities of water, methane, ammonia, and carbon monoxide.

Gas vented from the regenerator contains a minimum of 98.5% carbon dioxide and 1.0% water. Local air pollution control authorities have not required ammonia plants to sample this source. Source test data on these emissions are unavailable. Worst-case emission factors can be determined from material balances and unit design calculations.

Data collected from public information files at the Texas Air Control Board and the Louisiana Air Control Commission in June 1976 concerning emissions from this source are shown in Table 9. Emissions data from plants A, C, D, E, F, and G were obtained from material balances and engineering estimates. Data from plant B are based on unit design calculations.

During regeneration of the CO_2 scrubbing solution, 1.22 metric tons of CO_2 are released per metric ton of ammonia produced (34). Emission factors developed from data in Table 9 and shown in Table 10 were calculated by averaging the appropriate values. Corresponding values from both types of system for total hydrocarbons, ammonia, and CO were averaged together because data for establishing separate emission factors for both types of plants were unavailable, and no definite trend in emission factors was discernible.

Data from 10 plants indicate that the stack height on the carbon dioxide solution regenerator ranges from 10 m to 65 m, with an average value and standard deviation of 27.9 m ± 15.5 m. Stack gas temperature ranges from 37°C to 146°C, with an average value and standard deviation of 64°C ± 14°C.

TABLE 9. DATA FROM MATERIAL BALANCES AND DESIGN CALCULATIONS USED TO ESTABLISH EMISSION FACTORS

Plant	Emission species	Emission factor kg/hr	Emission factor g/kg
With hot potassium carbonate system			
A	Hydrocarbons	25.4	0.65
B[a]	NH_3	37.2	1.0
	Hydrocarbons	< 6.4	<0.1
	CO	<25	<0.2
With monoethanolamine system			
C	Monoethanolamine	0.59	0.015
D	Hydrocarbons	6.9	0.26
	Monoethanolamine	6.8	0.15
E	CO	11.8	1.0
F	Hydrocarbons	5.0	0.85
	Monoethanolamine	0.23	0.02
G	Monoethanolamine	0.14	0.005

[a] Based on unit design calculations for 1,360-metric ton/day plant.

TABLE 10. EMISSION FACTORS FOR EMISSIONS FROM REGENERATION OF THE CARBON DIOXIDE SCRUBBING SOLUTION

Emission species	Emission factor, g/kg
Hydrocarbons	0.47
Ammonia	1.0
Monoethanolamine[a]	0.05
Carbon dioxide	1,220
CO	1.0

[a] Only for plants with monoethanolamine absorption system.

Condensate Stripper

Process condensate forms upon cooling the synthesis gas after low temperature shift conversion. This water contains quantities of ammonia, methanol, carbon dioxide, and trace metals. In the past, ammonia plants discharged the water which contains a high nutrient value that might cause eutrophication in the receiving stream. The EPA has set effluent standards which require industry to reduce ammonia discharges in effluent to <50 kg/day (30). Ammonia plants now use process condensate steam strippers to remove ammonia from water. Instead of discharging ammonia to the water, plants now discharge it to the atmosphere. The steam stripping process results in air emissions of ammonia and methanol. Trace metals are discharged with the stripper bottoms which are discharged from the plant to a receiving stream or recycled to the boilers.

Table 11 shows the range in concentrations and average values for the contaminants in the process condensate from a plant that reforms natural gas and uses a high- and low-temperature shift converter (29-32).

TABLE 11. CONTAMINANTS IN PROCESS CONDENSATE (29-32)

Component	Concentration, ppm	
	Range	Average
Ammonia	600 to 1,200	1,000
Carbon dioxide	200 to 2,800	1,500
Methanol	200 to 1,000	500
Total trace metals	0.4 to 0.8	0.7

Process condensate also contains trace amounts of metals such as iron, copper, sodium, zinc, calcium, and aluminum. These can originate either from carryover or from the leaching operations in the various catalytic services: desulfurization, reforming, and shift conversion (29, 33).

Theoretical reaction equations indicate that amines and lower molecular weight alcohols might also be present in the condensate, but several tests for these species by industry representatives proved negative (30, 43).

A 544-metric ton/day unit produces 7.89×10^{-3} m^3/s of process condensate, a 900-metric ton/day unit produces 1.39×10^{-2} m^3/s, and a 1,360-metric ton/day unit produces up to 2.20×10^{-2} m^3/s (29, 32). The quantity of low-pressure, low-temperature (100°C to 115°C) steam used to strip the impurities from the condensate ranges from 96 kg/m^3 to 240 kg/m^3 of condensate treated, with an average value of 144 kg/m^3 (29, 41).

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(43) Personal communication with J. H. Mayes, Gulf South Research Institute, Baton Rouge, Louisiana, 1976.

For conventional stripping operations where an atmospheric vented steam stripper is used, ammonia concentration in the condensate can be reduced to ∿20 ppm to 50 ppm, methanol to ∿10 ppm to 50 ppm, and carbon dioxide to 40 ppm. (29, 31, 32, 43).

The only available data concerning emissions from the condensate steam stripper are reported in a recent study by Gulf South Research Institute where different techniques were evaluated for handling steam stripper overheads at a typical ammonia plant (30). Complete material balances were calculated around a 10 m tall steam stripper at a 900-metric ton/day ammonia plant generating 1.26×10^{-2} m^3/s of process condensate.

The condensate stripper system is shown in Figure 6, and the mass balance resulting from 65 measurements is shown in Table 12.

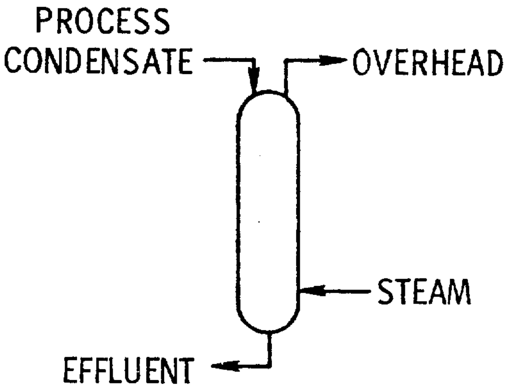

Figure 6. Process condensate steam stripper.

TABLE 12. MASS BALANCE AROUND CONDENSATE STEAM STRIPPER-RESULT OF 65 TEST MEASUREMENTS (30)[a]

Stream	Stream flow rates, kg/hr	Mass flow rate, kg/hr Ammonia	Methanol	Carbon dioxide
Process condensate	80,500	39.2	21.1	127
Steam	7,980	0	0	0
Effluent	81,200	0.57	0.28	0
Overhead	8,680	41.2	22.7	127

[a] Mass entering stripper does not exactly equal mass exiting since these values are averages from 65 test measurements.

In order to calculate emission factors for ammonia, methanol, and carbon dioxide emitted in the steam stripper overheads, individual source test measurements (30) were used. A total of 65 source test measurements were used to calculate the ammonia and methanol emission factors, and 7 measurements were used for the carbon dioxide emission factor. Results are shown in Table 13. Uncertainty values were calculated using the Student "t" test for 95% confidence limits. Average height of the steam stripper vent is 24 m.

TABLE 13. EMISSION FACTORS FOR PROCESS CONDENSATE STEAM STRIPPER (30)

Emission species	Emission factor, g/kg
Ammonia	1.1 ± 4%
Methanol	0.60 ± 2%
Carbon dioxide	3.4 ± 60%

For comparison, emission factors can be calculated from the average species concentration in the process condensate (from Table 11), based on 7.89 x 10^{-3} m^3/s of process condensate that is generated at a 544 metric ton/day ammonia plant. Process condensate with 1,000 ppm ammonia and 95% removal efficiency results in an ammonia emission factor of 1.18 g/kg of ammonia produced. A methanol emission factor of 0.59 g/kg of ammonia produced is obtained from an average methanol concentration of 500 ppm and steam stripper removal efficiency of 95%. For 1,500 ppm of CO_2 in the process condensate, the resulting emission factor is 1.78 g/kg of ammonia produced. These values are within 10% of the results in Table 13 for ammonia and methanol, and within the 60% uncertainty given in Table 13 for CO_2.

Fugitive Emissions

Sources of intermittent fugitive ammonia emissions include ammonia compressors and pumps, ammonia storage tanks and their pressure relief valves, and ammonia spillages which occur during loading operations. The only continuous source of fugitive ammonia emissions is the building which houses the ammonia compressors. Ammonia may escape from various seals into the room and then escape from the doors, windows, and ventilation system.

No source test data exist for fugitive emissions. It should be noted that ammonia leakages within the plant are held to a minimum to avoid product loss, and also because government regulations limit the allowable concentration of ammonia in the workplace atmosphere to 18 mg/m^3, the threshold limit value (TLV) (44).

POTENTIAL ENVIRONMENTAL EFFECTS

Emissions released during the manufacture of ammonia enter the atmosphere and are dispersed through the environment. This section evaluates potential environmental effects from air emissions in terms of the effect of an average plant and also in terms of the impact of the entire industry.

Representative Ammonia Plant

In the United States, 84 of the 90 synthetic ammonia plants use the catalytic steam reforming process and natural gas feedstock. The other six plants, representing less than 2% of the ammonia production, obtain their hydrogen from brine electrolysis plants. Only the plants which use steam reforming of natural gas are studied in detail in this report.

Ammonia plants range in capacity from 8,000 to 655,000 metric tons/yr. The distribution of plant capacities is shown in Table Table 14. The influence of the large ammonia plants (>200 x 10^3 metric tons/yr) is illustrated in Table 14 because they dominate the industry with 62% of the production capacity. Average plant capacity is 186 x 10^3 metric tons/yr. Based on national production figures the average plant has an annual production rate of 170 x 10^3 metric tons. Average daily production rate, assuming 351 days per year operation (2 weeks downtime for schedule maintenance), is 480 metric tons/day. The trend in the ammonia industry is towards the larger plants, >900 metric tons/day.

Locations of the 90 ammonia plants are presented in Appendix A, which also shows the population densities of the counties where the ammonia plants are located. Population densities range from 0.5 to 1,103 persons/km^2. Average county population density is 117 persons/km^2.

A summary of the emission factors previously developed is shown in Table 15. Currently there are no air pollution control devices associated with these emission sources; therefore, these values are uncontrolled emission factors. Stack heights of the four emission sources are also listed.

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(44) TLVs© Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 97 pp.

TABLE 14. 1976 DISTRIBUTION OF AMMONIA SYNTHESIS PLANTS BY CAPACITY (16)

Annual capacity, 10^3 metric ton	Number of plants	Percent of total plants	Annual capacity,[a] 10^3 metric ton	Percent of total capacity
≤10	1	1.1	8	<0.1
>10 to 50	13	14.4	408	2.4
>50 to 100	15	16.7	1,184	7.1
>100 to 150	17	18.9	2,101	12.5
>150 to 200	15	16.7	2,707	16.2
>200 to 300	6	6.7	1,529	9.1
>300 to 400	16	17.8	5,257	31.4
>400 to 500	4	4.4	1,769	10.6
>500	3	3.3	1,793	10.7
TOTAL	90	100.0	16,756	100.0

[a] Summed from Appendix A

TABLE 15. STACK HEIGHTS AND UNCONTROLLED EMISSION FACTORS FOR REPRESENTATIVE AMMONIA PLANT

Emission point	Stack height, m	Emission factor, g/kg						
		Ammonia	NO_x	SO_x	CO	Particulate	Total hydrocarbons	Other
Desulfurization tank[a]	10	0[b]	0	0.019[c]	6.9	0	3.6	0
Primary reformer	28.6							
Natural gas fuel		0	2.7 ± 23%	0.0024	0.068	0.072	0.012	0
Number 2 fuel oil		0	2.7	1.3	0.12	0.45	0.15	0
Carbon dioxide regenerator	27.9	1.0	0	0	1.0	0	0.47	Monoethanolamine:[d] 0.05 Carbon dioxide: 1,200
Condensate steam stripper	24	1.1 ± 4%	0	0	0	0	0	Carbon dioxide: 3.4 ± 60% Methanol: 0.60 ± 2%

[a] Intermittent source of emissions; desulfurization tanks are regenerated once every 30 days for 10-hour period.

[b] Zero indicates species not emitted from this source.

[c] Assuming all sulfur is released as SO_2; if H_2S is emitted the emission factor would be 0.010 g/kg.

[d] Only at plants with monoethanolamine absorption system.

Source Severity

In order to evaluate the relative significance of emissions from synthetic ammonia plants, a source severity, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} \qquad (12)$$

where $\bar{\chi}_{max}$ = time-averaged maximum ground level concentration of an emission species

F = hazard factor

For the criteria pollutants NO_x, SO_x, CO, hydrocarbons and particulates, F is the primary ambient air quality standard. For other emission species F is defined by a reduced threshold limit value (TLV):

$$F = TLV \times \frac{8}{24} \times \frac{1}{100} \qquad (13)$$

where 8/24 normalizes the TLV to a 24-hr exposure and 1/100 is a safety factor.

Values of F are reported in Table 16. Equation 13 was not used to find the hazard factor for CO_2; instead F was defined as the average ambient concentration of 630 mg/m^3. The ratio $\bar{\chi}_{max}/F$ compares an ambient air concentration with a standard concentration where incipient deleterious effects may begin; it is thus a measure of environmental severity.

TABLE 16. VALUES OF F USED TO CALCULATE APPROPRIATE SOURCE SEVERITIES

Emission species	Primary ambient air quality standard, mg/m^3	TLV (44), mg/m^3	F, $\mu g/m^3$	$\left(\frac{t_o}{t}\right)^{0.17}$
Particulate	0.26	N.A.[a]	260	0.35
SO_x	0.365	N.A.	365	0.35
Hydrocarbon	0.16[b]	N.A.	160	0.50
CO	40	N.A.	4,000	0.60
Ammonia	none	18	60	0.35
Hydrogen sulfide	none	15	50	0.35
Monoethanolamine	none	6.0	20	0.35
Carbon dioxide	none	9,000	6.3×10^5[c]	0.35
Methanol	none	260	87	0.35

[a] Not applicable.

[b] There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is a recommended guideline for meeting the primary ambient air quality standard for photochemical oxidants.

[c] Average ambient CO_2 concentration.

Values of $\bar{\chi}_{max}$ are calculated from the equations suggested by Turner (45):

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_o}{t}\right)^{0.17} \qquad (14)$$

where $\chi_{max} = \dfrac{2\ Q}{\pi e u h^2}$

χ_{max} = instantaneous (i.e., 3-min average) maximum ground level concentration

t_o = instantaneous averaging time, 3 min

t = averaging time, min

Q = emission rate, g/s

h = stack height, m

π = 3.14

e = 2.72

u = wind speed, m/s

For criteria pollutants, the averaging time, t, is the same as that for the corresponding ambient air quality standard. For noncriteria emission species, t is 1,440 minutes (24 hours) (Table 16).

Since NO_x has a primary ambient air quality standard with a 1-yr averaging time, Equation 14 for $\bar{\chi}_{max}$ cannot be used. Instead, Equation 5.13 in Reference 45 was used for neutral atmospheric conditions to develop the following source severity equation (46):

$$S_{NO_x} = \frac{315\ Q}{h^{2.1}} \qquad (15)$$

Using Equations 12 through 15 and the data from Tables 15 and 16 values of $\bar{\chi}_{max}$ and S were calculated for a representative synthetic ammonia plant based on a production rate of 480 metric tons/day. Results are shown in Table 17. Source severity

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(45) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare. Cincinnati, Ohio, 1969. 62 pp.

(46) Reznik, R. B. Source Assessment: Flat Glass Manufacturing Plants. EPA-600/2-76-032b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 147 pp.

values for sulfur emissions from regenerating the desulfurization tank were individually calculated, assuming all sulfur was emitted in one of two forms: SO_2 or hydrogen sulfide. Sulfur emission factors based on a 24-hr average were used because the sulfur severity equations are derived for 24-hr averages.

TABLE 17. SOURCE SEVERITY VALUES FOR UNCONTROLLED EMISSIONS FROM REPRESENTATIVE AMMONIA PLANT

	Source severity (S)						
Emission point	Ammonia	NO_x	SO_x	CO	Particulate	Total hydrocarbon	Other
Desulfurization tank	0	0	0.053[a]	0.30	0	32.4	Hydrogen sulfide: 0.21[b]
Primary reformer							
Natural gas fuel	0	4.1	<0.001	<0.001	0.034	0.013	0
Number 2 fuel oil	0	4.1	0.44	<0.001	0.21	0.16	0
Carbon dioxide regenerator	2.2	0	0	0.006	0	0.54	Monoethanolamine: 0.33 Carbon dioxide: 0.25
Condensate steam stripper	3.2	0	0	0	0	0	Carbon dioxide: <0.001 Methanol: 0.12

[a] Assuming all sulfur is emitted as SO_2.

[b] Assuming all sulfur is emitted as hydrogen sulfide.

The source severity values in Table 17 were calculated for a single plant representative of the ammonia industry. In order to illustrate the potential environmental impact of emissions from each plant in the entire industry, severity ranges for each species and each emission point were calculated and are presented in Table 18. Sulfur emissions from the desulfurization tank were calculated by assuming all the sulfur was emitted either as sulfur dioxide or as hydrogen sulfide, normalized to a 24-hr emission factor.

Actual stack heights from the 90 ammonia plants for each emission point are not available; therefore the average stack heights previously determined for a representative plant were used in calculations. Average emission factors were employed for the same reason. As a result, the range in severity values reflects the range in individual plant production rates. The minimum severity value is for the plant with the smallest production rate and the maximum severity value corresponds to the plant with the highest production rate.

Table 18 also shows the percentage of plants having a severity exceeding 0.05 and 1.0. At severity value of 1.0, the estimated average maximum ground level concentration for a given emission species exceeds the corresponding ambient air quality standard or reduced TLV. For those emission points where the severity exceeds 1.0 at some plants, the entire severity distributions are presented in Figures 7 through 10. Source severity values were calculated from the emission factors and average plant stack heights in Table 15 and individual plant capacity data

TABLE 18. RANGE OF SOURCE SEVERITIES AND PERCENTAGE OF PLANTS HAVING SEVERITIES GREATER THAN 0.05 OR 1.0

Emission point	Species	Source severity		Percentage of plants	
		Minimum	Maximum	S > 0.05	S > 1.0
Desulfurization tank	SO_2	0.002	0.187	44	0
	Hydrogen sulfide	0.009	0.73	88	0
	CO	0.016	1.35	93	3
	Hydrocarbon	1.39	114.0	100	100
Primary reformer					
Natural gas	NO_x	0.18	14.5	100	86
	SO_x	0.00003	0.003	0	0
	CO	0.00002	0.001	0	0
	Hydrocarbon	0.0006	0.046	0	0
	Particulate	0.0015	0.12	13	0
Fuel oil	NO_x	0.18	14.5	100	86
	SO_x	0.019	1.55	96	7
	CO	0.00003	0.002	0	0
	Hydrocarbon	0.007	0.58	82	0
	Particulate	0.009	0.75	88	0
Carbon dioxide regenerator	Ammonia	0.094	7.68	100	74
	CO	0.0002	0.002	0	0
	Carbon dioxide	0.011	0.89	89	0
	Hydrocarbon	0.023	1.91	97	14
	Monoethanolamine	0.014	1.15	93	2
Condensate steam stripper	Ammonia	0.14	11.41	100	83
	Methanol	0.005	0.43	79	0
	Carbon dioxide	0.00004	0.003	0	0

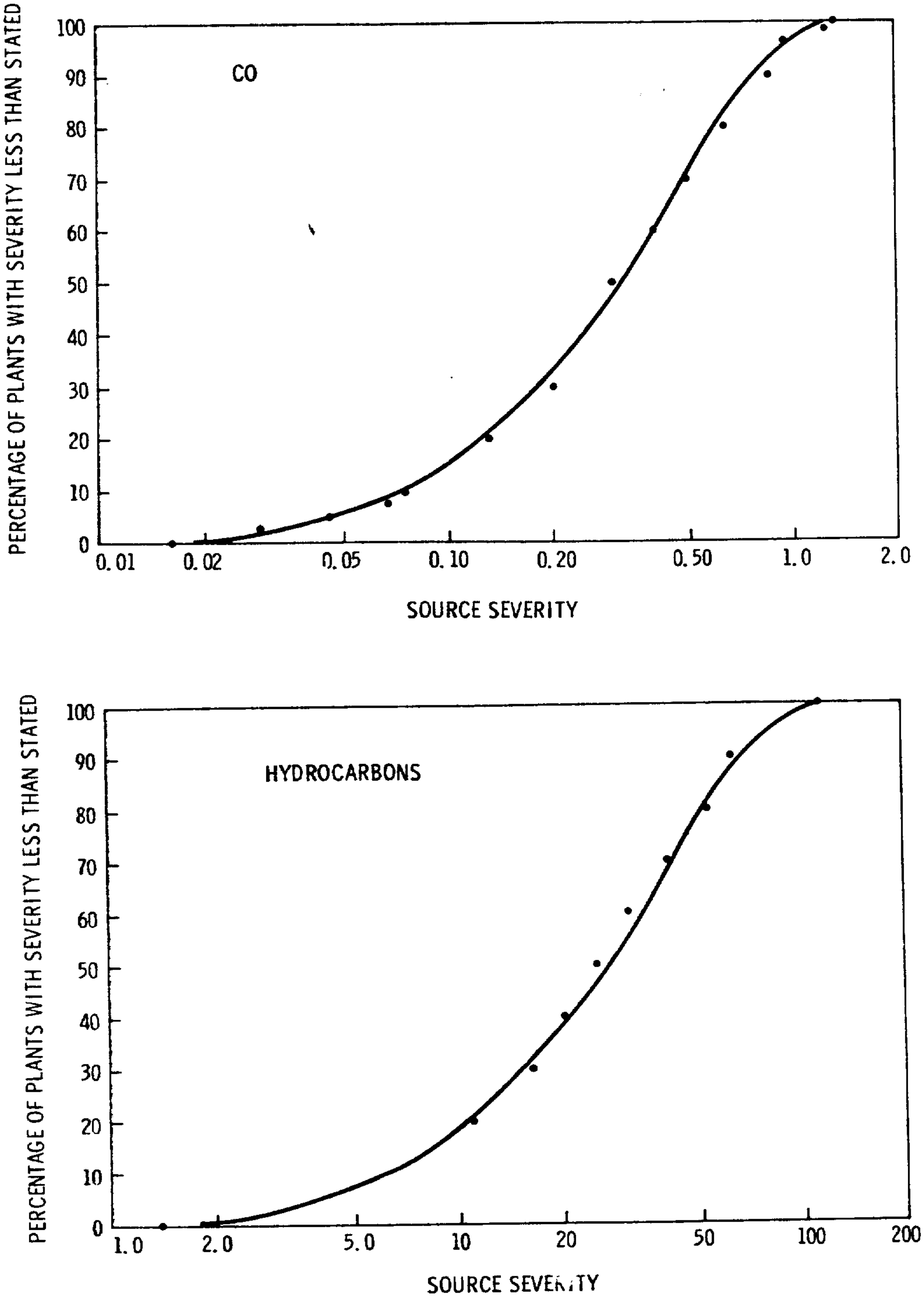

Figure 7. Source severity distributions for desulfurization tank.

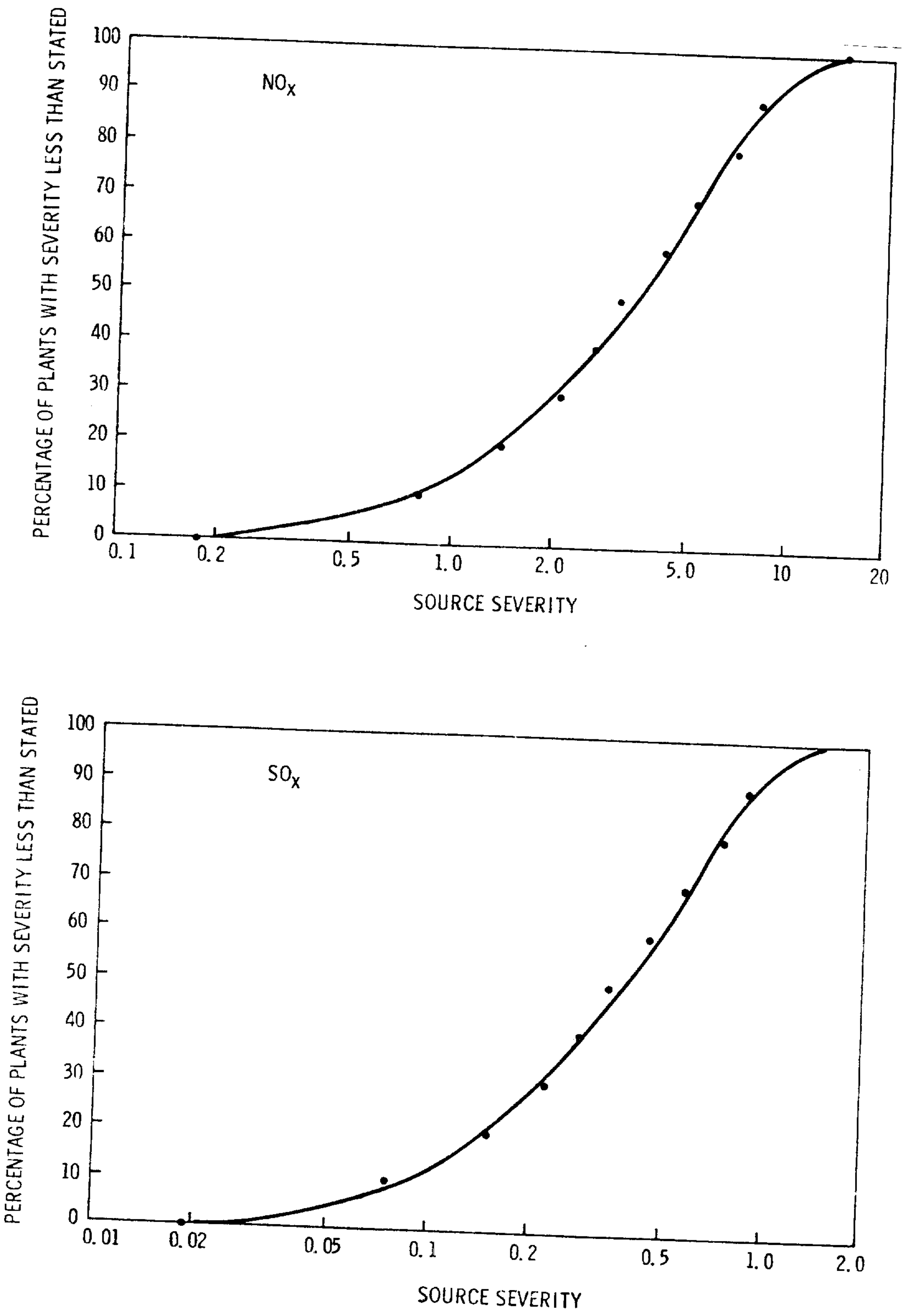

Figure 8. Source severity distributions for primary reformer using oil and gas fuel (emission factor calculation given in Appendix B).

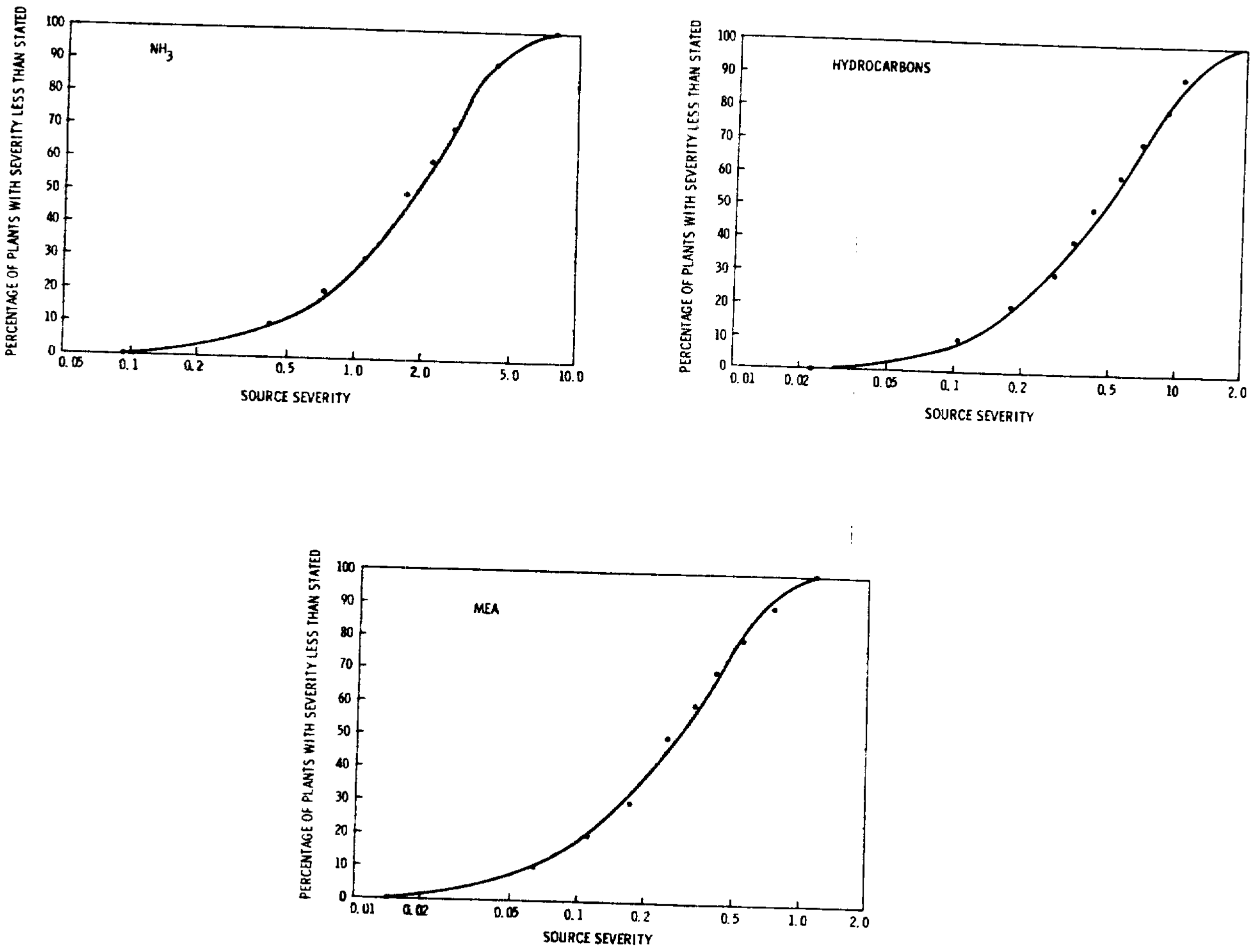

Figure 9. Source severity distributions for CO_2 regenerator.

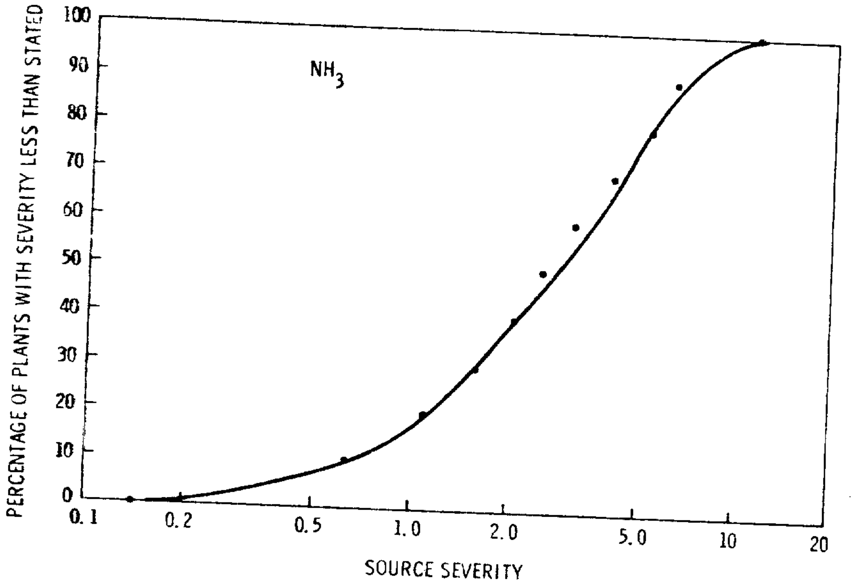

Figure 10. Source severity distributions for condensate steam stripper.

Appendix A. Daily production rates were found by assuming 351 days of operation per year and an annual production rate equal to 90.5% of capacity (the national average).

Total Industry Emissions

Another measure of the environmental impact from the production of ammonia is provided by the total amount of industry emissions. These can be compared to total state and national emissions from all sources to find the emission burden due to the ammonia industry. State and national emission burdens for the criteria pollutants (NO_x, SO_x, CO, particulates and hydrocarbons) are given in Table 19. Appendix B gives a detailed description of how the emission burdens were calculated, a table of the total emissions of each criteria pollutant by the ammonia industry on a state-by-state basis, and state-by-state listings of total emissions of criteria pollutants from all sources (47, 48).

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(47) 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

(48) Eimutis, E. C., and R. P. Quill. Source Assessment: State-by-State Listing of Criteria Pollutant Emissions. EPA-600/2-77-107b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1977. 138 pp.

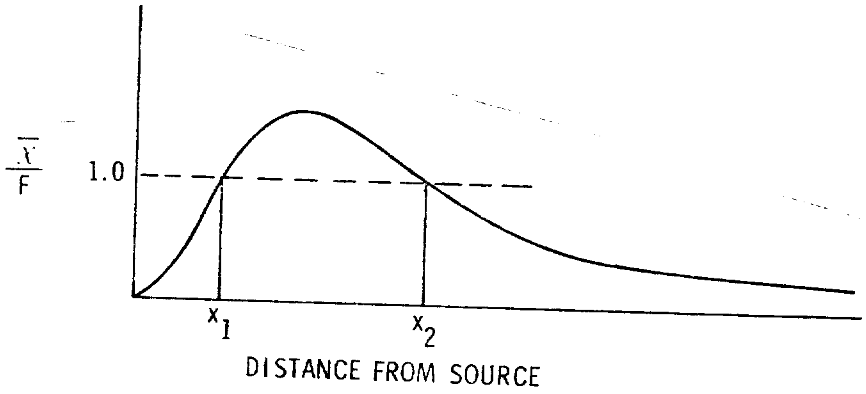
TABLE 19. CONTRIBUTION OF EMISSIONS FROM AMMONIA PLANTS TO STATE BURDENS

State	Percent of state burden				
	Particulate	NO_x	SO_x	CO	Hydrocarbons
Alabama	<0.10	0.22	<0.10	<0.10	0.10
Alaska	<0.10	6.3	0.10	7.0	1.4
Arizona	<0.10	0.31	<0.10	<0.10	<0.10
Arkansas	<0.10	1.2	0.10	0.25	0.22
California	<0.10	0.54	<0.10	<0.10	<0.10
Florida	<0.10	0.16	<0.10	<0.10	<0.10
Georgia	<0.10	0.30	<0.10	<0.10	<0.10
Idaho	<0.10	3.9	0.11	0.19	0.39
Illinois	<0.10	<0.10	<0.10	<0.10	<0.10
Indiana	<0.10	<0.10	<0.10	<0.10	<0.10
Iowa	<0.10	2.4	<0.10	2.5	0.49
Kansas	<0.10	1.3	<0.10	0.62	0.22
Louisiana	<0.10	3.2	0.22	0.42	0.35
Mississippi	<0.10	3.6	0.18	0.53	0.46
Missouri	<0.10	0.19	<0.10	0.14	<0.10
Nebraska	<0.10	2.8	0.13	2.0	0.52
New Mexico	<0.10	0.60	<0.10	2.1	0.24
New York	<0.10	<0.10	<0.10	<0.10	<0.10
North Carolina	<0.10	0.16	<0.10	<0.10	<0.10
Ohio	<0.10	0.29	<0.10	<0.10	0.10
Oklahoma	<0.10	1.8	0.24	0.74	0.35
Oregon	<0.10	0.47	<0.10	<0.10	<0.10
Pennsylvania	<0.10	0.14	<0.10	<0.10	<0.10
Tennessee	<0.10	0.38	<0.10	0.18	0.17
Texas	<0.10	0.90	<0.10	0.13	0.13
Utah	<0.10	0.18	<0.10	<0.10	<0.10
Virginia	<0.10	0.51	<0.10	0.15	0.11
Washington	<0.10	0.41	<0.10	<0.10	0.14
West Virginia	<0.10	0.27	<0.10	<0.10	0.23
Wyoming	<0.10	0.54	<0.10	1.6	0.17
United States	0.01	0.44	0.01	0.02	0.10

The contribution to total state emissions exceeds 1.0% for NO_x in nine states, for CO in five states, and for hydrocarbons in one state. On a national basis only NO_x emissions exceed 0.1%.

Affected Population

Dispersion equations predict that the average ground level concentration, $\bar{\chi}$, varies with the distance, x, downwind from a source. For elevated sources, $\bar{\chi}$ is zero at the source (where x = 0), increases to some maximum value, $\bar{\chi}_{max}$, as x increases, and then falls back to zero as x approaches infinity. Therefore, a plot of $\bar{\chi}/F$ vs x will have the following appearance:



Affected population is defined as the number of nonplant persons around a representative ammonia plant exposed to a $\bar{\chi}/F$ ratio greater than 1.0. The mathematical derivation of the affected population calculation is presented in Reference 46. Affected population values for emissions from a representative ammonia plant, located in a county with a population density of 117 persons/km^2, are shown in Table 20. Also presented is the population exposed to $\bar{\chi}/F \geq 0.05$.

TABLE 20. AFFECTED POPULATION FOR $\bar{\chi}/F \geq 0.05$ AND 1.0

Emission point	Emission species	Affected population, persons: $\frac{\bar{\chi}}{F} \geq 1.0$	Affected population, persons: $\frac{\bar{\chi}}{F} \geq 0.05$
Desulfurization tank	Total sulfur[a]	0[b]	8
	CO	0	42
	Hydrocarbons	130	7,764
Primary reformer			
Burning natural gas	NO_x	357	104,627
	SO_x	0	0
	CO	0	0
	Particulates	0	0
	Hydrocarbons	0	0
Burning fuel oil	NO_x	357	104,627
	SO_x	0	1,076
	CO	0	0
	Particulates	0	479
	Hydrocarbons	0	225
Carbon dioxide regenerator	Ammonia	197	5,626
	CO	0	0
	Carbon dioxide	0	0
	Hydrocarbons	0	869
	Monoethanolamine	0	736
Condensate stripper	Ammonia	237	6,220
	Carbon dioxide	0	0
	Methanol	0	168

[a] As SO_2; if emissions are H_2S, the affected population is 0 for $\bar{\chi}/F \geq 1.0$ and 51 for $\bar{\chi}/F \geq 0.05$.

[b] Zero affected population indicates $\bar{\chi}/F$ is always less than 1.0 or 0.05 around a representative plant.

SECTION 5

CONTROL TECHNOLOGY

To date, add-on air pollution control devices are not used at synthetic ammonia plants because their emissions are below current state emission standards. Process modifications have been implemented which reduce air emissions and improve the utilization of raw materials and energy. Control techniques currently being used and those proposed for the future are discussed in the following sections.

DESULFURIZATION

During regeneration of the desulfurization tank, stripping steam is vented directly to the atmosphere. Air pollution control devices are not used on this emission source because the regeneration lasts only about 10 hours and occurs from once per week to once per year depending on the plant, with an industry average of once every 30 days.

PRIMARY REFORMER

Natural gas is fired in the radiant heat section of the primary reformer to supply the energy needed to reform the feedstock. Flue gas containing combustion products first passes over a series of heat exchangers and is then vented to the atmosphere. No air pollution control devices are being used for this emission source because natural gas is considered a clean fuel. Nitrogen oxide and CO emissions from this source are below state emission standards.

Burning of the purge gas in the primary reformer is the most significant process modification used at all ammonia plants to reduce air pollution and recover energy. (In the past, the purge gas was vented to the atmosphere.) Purge gas is vented from the synthesis process to prevent the buildup of inerts such as argon. Purge gas contains about 60% hydrogen, 20% nitrogen, 3.5% argon, and 16.5% methane (39).

If present NO_x emission standards are made more stringent, it might be difficult for ammonia plants to meet them because of a lack of proven NO_x emissions control technology. The most promising applicable control system is the ammonia injection technique (49). At temperatures ranging from 250°C to 450°C, 1.0 moles to 1.3 moles of ammonia per mole of NO_x are injected into the flue gas and, aided by a catalyst, 90+% of the nitrogen oxides are reduced to nitrogen and water. However, if No. 2 fuel oil is used in the reformer, the increased particulates and sulfur would poison the catalyst needed in the ammonia injection control technique. Other research is considering ammonia injection into the combustion chamber.

CARBON DIOXIDE REMOVAL SYSTEM

Carbon dioxide gas liberated during regeneration of the scrubbing solution is either vented directly to the atmosphere (67% of plants) or used as a chemical feedstock (33% of plants) for other processes at the plant complex. Since 98.5% of the gas is carbon dioxide and 1.0% is water vapor, air pollution control devices are not installed on this process.

CONDENSATE STRIPPER

To comply with effluent standards, the ammonia production process includes a condensate stripper that reduces the concentration of ammonia and methanol in the wastewater stream. The simple condensate stripper, used at 95% of the plants, passes low-pressure steam countercurrent to the condensate in a packed or tray tower. Stripped condensate is either discharged into a receiving stream or used as cooling water makeup or as boiler feedwater. Uncondensed steam and 95% to 99% of the ammonia and methanol are then vented directly to the atmosphere. Currently, add-on control devices are not used at these plants to reduce emissions of ammonia and methanol.

The few ammonia plants without condensate strippers are currently researching alternative procedures for handling process condensate because the simple condensate stripper, though it performs satisfactorily, has four major disadvantages: 1) it does not permit complete reuse of condensate; 2) it requires a substantial amount of steam; 3) it has no provision for waste heat recovery; and 4) it does not eliminate air emissions of ammonia and methanol (15). An alternative procedure for recovering process condensate and reducing air emissions is described below.

The process shown in Figure 11 can be used for improving overall performance and eliminating atmospheric pollution (32). This scheme has a modified overhead reflux and product recovery system, and it provides for the use of low level heat in conjunction with the operation of the carbon dioxide scrubbing system regenerator. All process condensate is preheated from the hotter

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(49) Ushio, S. Japan's NO_x Cleanup Routes. Chemical Engineering, 82(15):70-71, 1975.

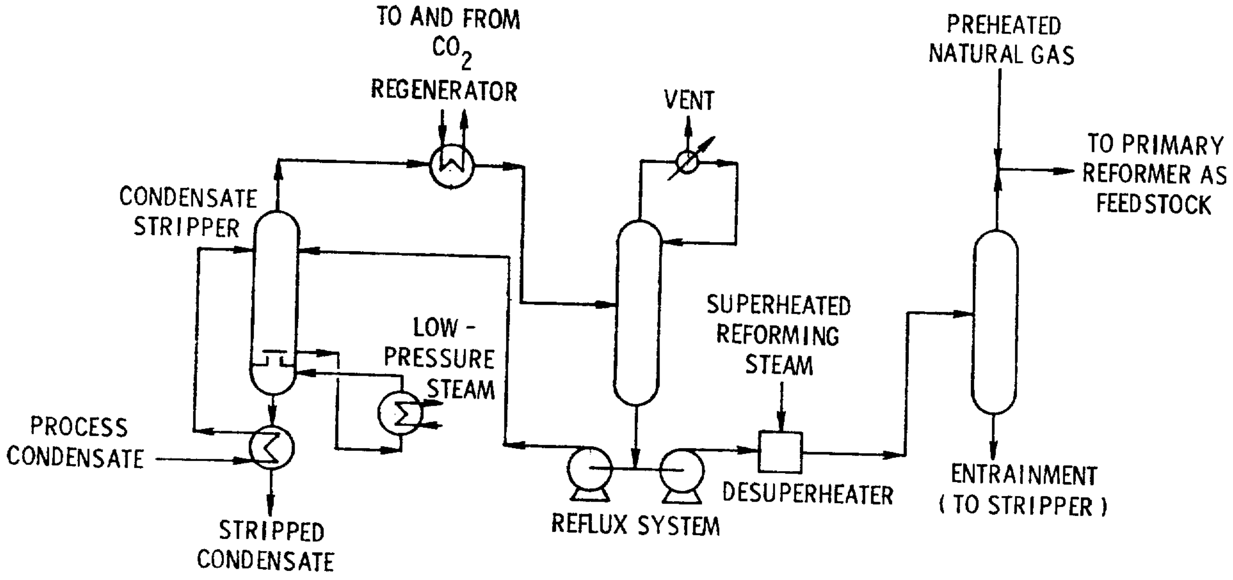

Figure 11. Modified process condensate strip system (32).

stripper effluent. Stripper overhead is reboiled in a reflux condenser to minimize the quantity of water in the overhead and to recover clean condensate. Liquid product taken from the overhead of the condensate stripper is recycled by injection into the reforming facility. Superheated reforming steam heats the overhead product and the resulting gas is combined with preheated reforming feedstock. All contaminants - carbon dioxide, ammonia, and methanol - are reformable and should cause no problems in the catalyst tubes. Condensate stripper bottoms may be used for cooling tower makeup or may be returned to the boiler feedwater facility for further treatment.

In a similar but much simpler scheme researched by GSRI (43), the overhead is simply heated to ∿475°C, and a reciprocating pump is used to pressurize the stream to 3.7 MPa. This stream is then combined with preheated reforming feedstock and sent to the primary reformer. Results indicate that this process is not economically feasible because reinjecting the overhead reduces production and disrupts the delicate steam balance at the ammonia plant (30).

In the same study (30) four other techniques for disposing of stripper overheads were investigated:

- Direct discharge to the atmosphere.
- Precipitation of ammonia with magnesium phosphate to produce a magnesium ammonium phosphate.

- Adsorption of ammonia on a vanadium pentoxide catalyst.
- Injection of overheads into the primary reformer stack along with the combustion gases.

The direct discharge of stripper overheads to the atmosphere was obviously the least expensive disposal technique, but certainly did not reduce emissions of ammonia and methanol to the environment. GSRI found that the precipitation with magnesium phosphate was impractical because of the larger capital cost and minimum cost-benefit expectations. Adsorption by vanadium pentoxide was not fully developed as a viable process and the cost-benefit ratio was the poorest of the five systems GSRI investigated. The fifth process, injecting the overheads into the primary reformer stack, not only had the best cost-benefit ratio, but according to test measurements, it also reduced ammonia and methanol emissions to the environment by 59.3% and 74.7%, respectively (30). In terms of potential environmental effects, this technique decreased the source severity for ammonia and methanol emissions from the condensate stripper by 95% and 97%, respectively. The reduction in severity was greater than the reduction in the amount of material released because the stack height for the primary reformer is 28.6 m versus 10 m for the condensate stripper exhaust. However, although both ammonia and methanol emissions decreased, nitrogen oxide emissions from the primary reformer increased by 41%. The source severity for NO_x also increased by 41%.

Stack test data in Reference 30 imply that approximately 50% of the ammonia in the stripper overhead reacts with the NO_x in the reformer stack gases to produce N_2 and water. Remaining ammonia is converted to NO_x. Other research studies indicate that the reduction of ammonia to form N_2 and water requires higher temperatures than those in the reformer and also requires a catalyst (49).

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

PRESENT TECHNOLOGY

In the U.S. 98% of the synthetic ammonia is produced by steam reforming natural gas. Six plants representing <2% of domestic production use hydrogen feedstock obtained from salt water electrolysis plants. Other foreign processes for ammonia production include: use of naphtha and other light hydrocarbons for feedstock, partial oxidation of heavier hydrocarbons (petroleum oil for distillates), cryogenic recovery of hydrogen from petroleum refinery gases, and gasification of coal or coke. These production techniques are not used in the U.S. because of their high capital and operating costs compared to the low prices and availability of natural gas in this country.

Within the last 15 years a dramatic change in the ammonia industry was brought about by the replacement of reciprocal compressors with newly designed centrifugal compressors (37). Centrifugal compressors are designed to handle synthesis gas at pressures ranging from 14 MPa to 70 MPa, resulting in much higher production capacities, lower synthesis loop pressures, and reduced investment and operating costs (38). As a result, older design plants were rapidly replaced by new plants with larger capacity. In 1955, a plant producing 270 metric tons/day was considered large (21). Today, 53% of the ammonia is produced by plants with a production capacity >900 metric tons/day. A large plant today produces 1,300 to 2,000 metric tons/day.

EMERGING TECHNOLOGY

As long as natural gas is available and cheaper than oil, plants in the U.S. will continue to use the catalytic steam reforming process. However, because of the uncertainty in natural gas supply and prices, several companies are considering other production techniques, such as the use of naphtha for feedstock, partial oxidation of heavier hydrocarbons, and coal gasification.

Because of natural gas curtailments, ∿50% of the plants are beginning to fire No. 2 fuel oil in the radiant heat section of the primary reformer during the winter months (28, 43, 50). If gas supplies continue to dwindle, this practice probably will be extended to full annual operation, resulting in a two orders of magnitude increase in sulfur oxide emissions and a threefold increase in particulate emissions from the primary reformer.

In terms of feedstock substitution, estimates indicate that conversion from natural gas to naphtha would cost 50% to 100% of the original expense of a new plant (40, 51). For example, a new 900-metric ton/day ammonia plant built to use naphtha would cost 15% more than one built to operate on natural gas because additional desulfurization and carbon removal equipment would have to be installed to treat the dirtier feedstock (40).

For situations where light hydrocarbon feedstocks are expensive or unavailable, the partial oxidation of heavier hydrocarbons is one process alternative. This process generates raw synthesis gas noncatalytically at relatively high temperature and pressure, and uses high-purity oxygen in the combustion step. As shown in Figures 12 and 13, a partial oxidation plant requires an air separation plant and additional carbon removal and recycle, desulfurization, and other facilities (17). The increased investment for a partial oxidation plant over a steam reforming plant ranges from 20% to 50% (17, 51).

Prior to World War II, practically all ammonia plants outside of the U.S. used coal as a source of synthesis gas. Coal-based plants slowly gave way to natural gas and liquid hydrocarbons, primarily because of the lower investment and favorable price structure of these feeds. However, with the current energy supply problem and prospects of rising costs for both natural gas and petroleum, the use of coal has reentered the picture and is again being given serious consideration. Several German processes such as Lurgi, Koppers-Totzek, and Winkler have been used for many years to produce synthesis gas for steam generation and heating and as a feedstock for ammonia, methanol, and synthetic liquid fuels. These three processes differ somewhat in mechanical design and operating conditions.

The Koppers-Totzek (K-T) process reacts coal, steam, and oxygen in an entrained bed at atmospheric pressure (Figure 14). Because synthesis gas leaves the gasifier at relatively high temperatures

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(50) Sloan, C. R., and A. S. McHone. The Effect of the Energy Crisis on Ammonia Producers. In: Ammonia Plant Safety, Vol. 15, Chemical Engineering Progress Technical Manual, American Institute of Chemical Engineers, New York, New York, 1973. pp. 91-95.

(51) Strelzoff, S. Make Ammonia from Coal. Hydrocarbon Processing, 53(10):133-135, 1974.

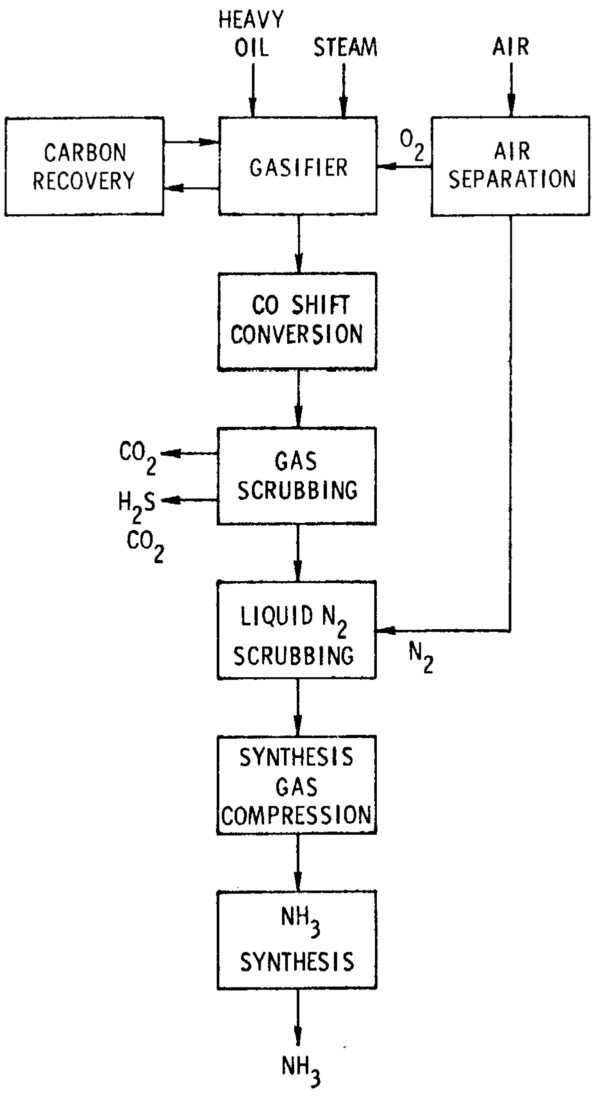

Figure 12. Ammonia process based on partial oxidation of heavy hydrocarbons (alternative A) (17, 51).

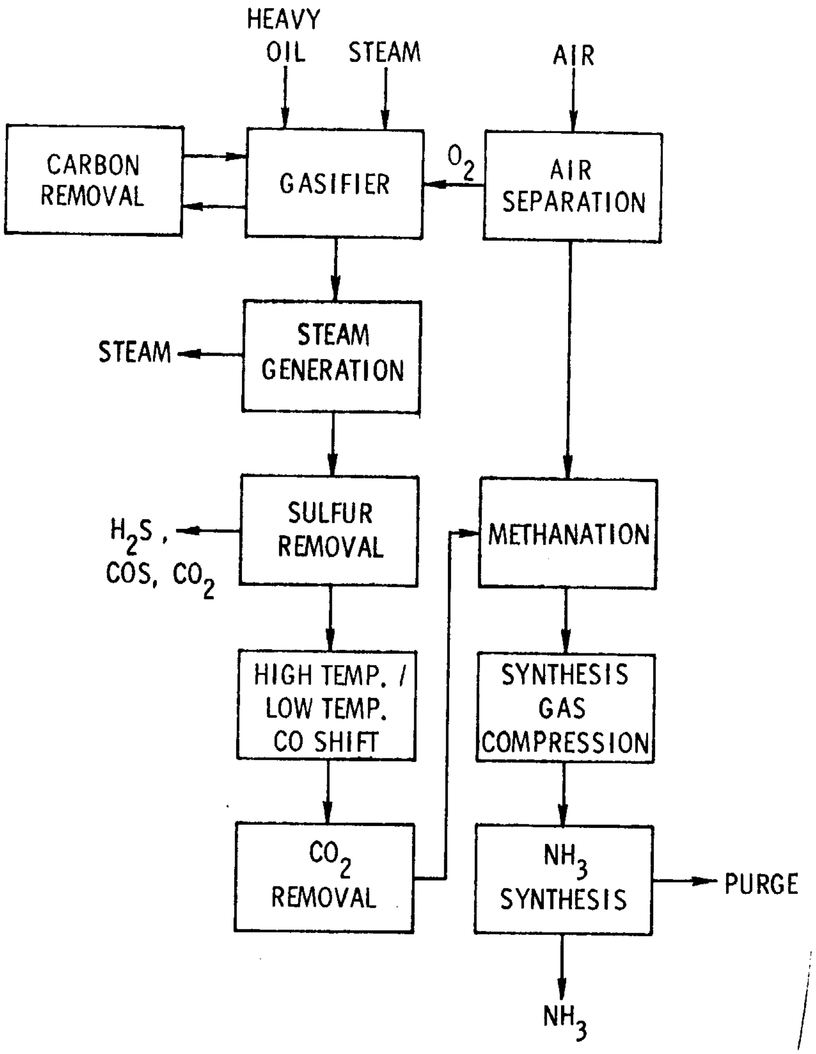

Figure 13. Ammonia process based on partial oxidation of heavy hydrocarbons (alternative B) (17, 51).

(>1,800°C), the gasifier effluent contains no hydrocarbons higher in molecular weight than methane. Methane content is <0.2% and the CO/H_2 content is ∿85%, making it an ideal gas mixture for ammonia synthesis (52). Outside the U.S., 49 K-T gasifiers are used to produce synthesis gas for ammonia production.

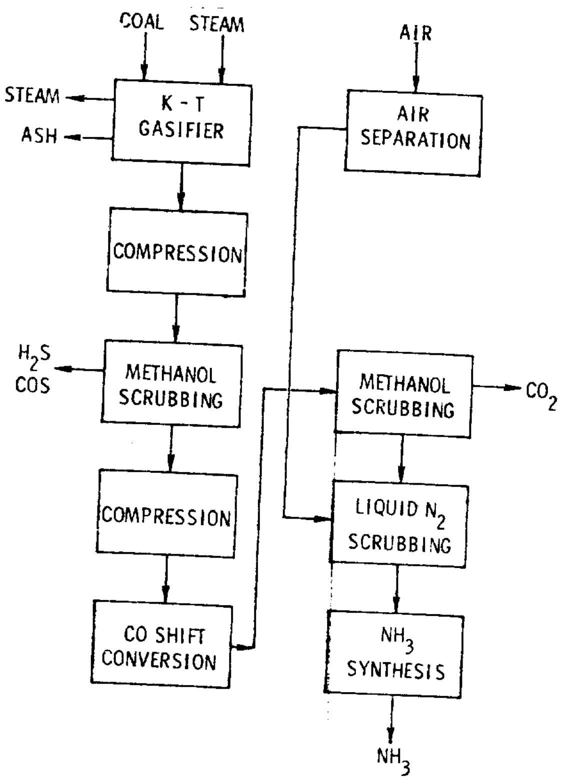

Figure 14. Ammonia production based on Koppers-Totzek coal gasification (52).

In the Lurgi process, coal is gasified at ∿2 MPa to 3 MPa using oxygen and steam in a fixed bed (Figure 15). Because the gasification temperature (560°C to 620°C) is in the intermediate range and operating pressure is high, the content of methane (10%) and carbon dioxide (28%) in the crude gas is considerably greater than that in the conventional reforming and partial oxidation processing (17). Methane can be removed by liquid nitrogen scrubbing in a downstream processing operation and subsequently reprocessed for the additional production of hydrogen and carbon monoxide. High-pressure, low temperature gasifier operation

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(52) Rothman, S. N., and M. E. Frank. Opportunities in Ammonia from Coal. In: Ammonia Plant Safety, Vol. 17, Chemical Engineering Progress Technical Manual, American Institute of Chemical Engineers, New York, New York, 1975. pp. 19-23.

results in the production of other components in the crude gas such as tars, naphtha, phenols, and light oils; they must be removed from the gas stream and can possibly be recovered as salable product (53).

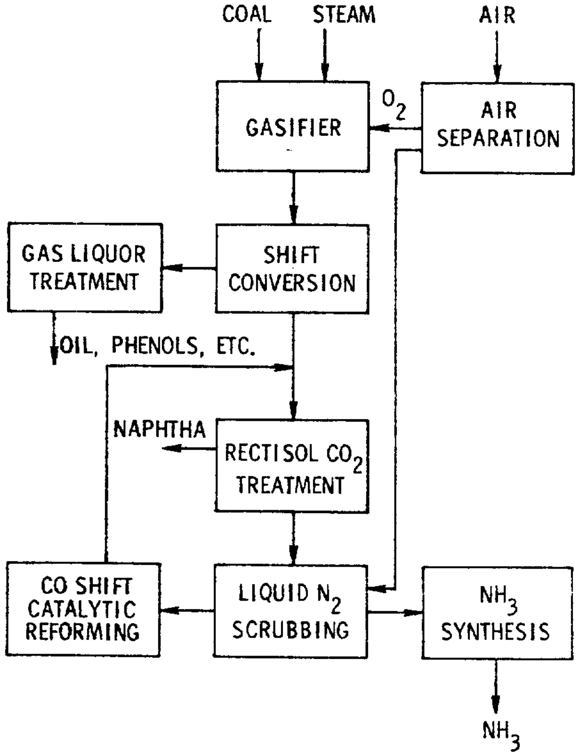

Figure 15. Ammonia process based on Lurgi coal gasification.

The Winkler gasifier falls between the Koppers-Totzek and Lurgi processes, turning out methane but no liquid byproducts. This process is an atmospheric fluidized bed in which the gasifying media are oxygen and steam. The fluid bed operates at 800°C to 1,000°C, and most of the ash is carried over with the product gas. All size ranges of coal can be used in the Winkler process, but not that which is strongly coking. Oxygen consumption is intermediate between that of the fixed-bed Lurgi and the entrained Koppers-Totzek (53).

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(53) Perry, H. Coal Conversion Technology. Chemical Engineering, 81(14):88-93, 1974.

Other coal gasification processes currently being developed that could potentially be used to produce synthesis gas for ammonia plants include the Hygas, CO_2-Acceptor, Synthane, Bigas, Cogas, Union Carbide-Battelle, and Hydrane processes (54). However, it is anticipated that coal gasification will not be used to produce ammonia until after 1980 (53). At current feedstock and construction prices, a coal gasification-based ammonia plant would cost 200% to 300% more than a new steam reforming plant (17, 18, 52, 54).

INDUSTRY PRODUCTION TRENDS

The trend in synthetic ammonia production from 1960 to the present and projected to 1980 is shown in Figure 16. The dramatic upturn in production during the 1960's was a result of new developments in centrifugal compressor plants (21). Production rates leveled off in early 1970 because no new plants were constructed. Demand for ammonia now exceeds present capacity. Several new plants are being built and older plants are being expanded (55). Figure 17 shows the locations of new and expanding plants.

As a result of the increased capacity, it is estimated that production of ammonia will increase at a rate of 4% to 8% per year for the next 5 years (55, 56). This will result in a corresponding increase of 22% to 47% in emissions from 1975 to 1980.

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(54) Iammartino, N. R. Coal Chemicals are Making a Comeback. Chemical Engineering, 82(18):57-59, 1975.

(55) Wett, T. Outlook for Ammonia Seen Rosy Through the 1970's. The Oil and Gas Journal, 73(29):21-23, 1975.

(56) Ammonia Capacity Projections Down in 1975. Nitrogen, 98:6-7, November/December 1975.

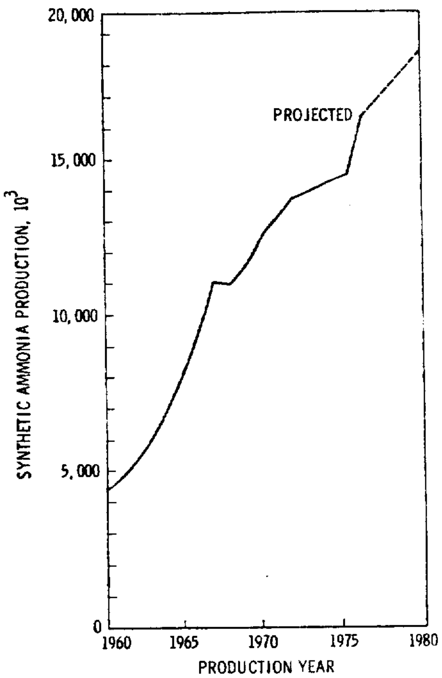

Figure 16. Production of synthetic anhydrous ammonia (16).

Figure 17. New and expanding ammonia plant locations (55).

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APPENDIX A

SYNTHETIC AMMONIA PLANTS IN THE U.S. IN 1976

Table A-1 describes the 90 synthetic ammonia plants in operation in the U.S. in 1976, listing the company name and location, an estimate of annual plant capacity, and the population density of the county where the plant is located.

TABLE A-1. SYNTHETIC AMMONIA PLANTS IN THE UNITED STATES IN 1976 (16)

Company	Location	Estimated capacity, 10^3 metric tons/yr	County population density, persons/km^2	EPA Region
Air Products and Chemicals, Inc.	New Orleans, LA	190	1,103.0	6
	Pace, FL	68	116.8	4
Allied Chemical Corp., Agricultural Division	Geismar, LA	308	46.7	6
	Hopewell, VA	308	39.6	3
	South Point, OH	290	47.0	5
	Omaha, NE	180	446.3	7
American Cyanamid Co., Agricultural Division	New Orleans, LA	308	1,103.0	6
Apache Powder Co.	Benson, AZ	14	3.8	9
Beker Industries, Inc.	Conda, ID	127	1.4	10
	Carlsbad, NM	190	3.7	6
Borden Inc., Chemical Division	Geismar, LA	258	46.7	6
Camex, Inc.	Borger, TX	363	10.6	6
Central Farmers Fertilizer Co.	Donaldsonville, LA	{308 {308	46.7	6
	Fremont, NE	43	13.3	7
	Terre Haute, IN	122	105.2	5
Colorado Oil and Gas Corp., Wycon Chemical Co., Subsidiary	Cheyenne, WY	166	7.9	8
Columbia Nitrogen Corp.	Augusta, GA	118	192.2	4
Commercial Solvents Corp.	Sterlington, LA	308	7.6	6
Cooperative Farm Chemicals Assoc.	Lawrence, KS	308	38.6	7
Diamond Shamrock Corp.	Dumas, TX	145	5.9	6
The Dow Chemical Co.	Freeport, TX	104	28.8	6
E. I. Du Pont de Nemours and Co., Inc.				
Explosives Dept.	Beaumont, TX	308	75.7	6
Industrial and Biochemicals Dept.	Belle, WV	308	95.4	3
Plastics Dept.	Victoria, TX	90	22.8	6
El Paso Natural Gas Co.	Odessa, TX	104	38.4	6
FMC Corp., Inorganic Chemicals Div.	South Charleston, WV	22	95.4	3
Farmers Chemical Assoc., Inc.	Tunis, NC	190	24.5	4
	Tyner, TN	149	170.4	4
Farmers National Chemical Co.	Plainview, TX	54	13.2	6
Farmland Industries, Inc.	Dodge City, KS	181	7.8	7
	Ft. Dodge, IA	181	25.7	7
	Hastings, NE	127	20.7	7
	Enid, OK	362	20.3	6
	Plainview, TX	24	13.2	6
Felmont Oil Corp.	Olean, NY	77	23.4	2
First Mississippi Corp.	Ft. Madison, IA	308	30.7	7
Gardinier, Inc.	Tampa, FL	118	180.2	4
W. R. Grace and Co., Agricultural Products Group	Big Spring, TX	113	15.7	6
	Memphis, TN	300	367.5	4
Goodpasture, Inc.	Dimmitt, TX	77	4.5	6
Green Valley Chemical Corp.	Creston, IA	32	12.0	7
Gulf and Western Industries, Inc.	Palmerton, PA	36	47.7	3
Hawkeye Chemical Co.	Clinton, IA	123	31.4	3
Hercules, Inc.	Hercules, CA	63	557.8	9
	Louisiana, MO	63	9.4	7

(continued)

TABLE A-1 (continued)

Company	Location	Estimated capacity, 10^3 metric tons/yr	County population density, persons/km^2	EPA Region
Hooker Chemical Corp., Industrial Chemical Div.	Tacoma, WA	20	93.3	10
Kaiser Aluminum and Chemical Corp.	Savannah, GA	136	158.6	4
Jupiter Chemicals, Inc.	Lake Charles, LA	120	49.7	6
Lone Star Producing Co., NIPAK, Inc., Subsidiary	Kerens, TX	113	10.8	6
	Pryor, OK	95	12.8	6
MISCOA (Mississippi Chemical Corp. and Coastal Chemical Corp.)	Pascagoula, MS	159	44.8	4
	Yazoo City, MS	358	11.2	4
Triad Chemical	Donaldsonville, LA	345	46.7	6
Mobil Oil Corp., Petrochemicals Div.	Beaumont, TX	236	98.5	6
Monsanto Co., Agricultural Div.	Luling, LA	408	37.1	6
Occidental Petroleum Corp., Best Fertilizer Div.	Lathrop, CA	87	77.6	9
	Plainview, TX	47	13.2	6
Olin, Agricultural Chemicals Div.	Lake Charles, LA	435	49.7	6
PPG Industries, Inc.	New Martinsville, WV	45	21.2	3
Pennwalt Chemicals Corp.	Portland, OR	8	500.1	10
Phillips Pacific Chemical Co.	Finley, WA	141	14.9	10
Phillips Petroleum Co.	Beatrice, NE	190	11.6	7
	Pasadena, TX	209	385.9	6
Reichhold Chemical, Inc.	St. Helens, OR	81	17.2	10
Rohm and Haas Co.	Deer Park, TX	45	385.9	6
St. Paul Ammonia Products, Inc.	East Dubuque, IL	190	13.5	5
J. R. Simplot Co., Minerals and Chemical Div.	Pocatello, ID	100	17.5	10
Standard Oil of Ohio	Joplin, MO	123	47.3	7
Vistron	Lima, OH	522	104.4	5
Standard Oil Co. of California	El Segundo, CA	12	5.6	9
	Richmond, CA	118	151.7	9
Chevron Chemical Co.	Fort Madison, IA	95	30.7	7
Standard Oil of Kentucky	Pascagoula, MS	463	44.8	4
Standard Oil Co. of Indiana	Texas City, TX	92 463	160.3	6
Tenneco, Inc.	Houston, TX	190	385.9	6
Tennessee Valley Authority	Wilson Dam, AL	81	31.8	4
Terra Chemicals International, Inc.	Sioux City, IA	190	44.6	7
Tipperary Corp.	Lovington, NM	90	4.3	6
Union Oil Co. of California, Collier Carbon and Chemical Corp.	Brea, CA	118 118	695.8	9
	Kenai, AK	463	0.5	6
United States Steel Corp., USS Agri-Chemicals, Inc.	Cherokee, AL	160	31.7	4
	Clairton, PA	363	841.4	3
	Geneva, UT	63	26.4	8
Valley Nitrogen Producers, Inc.	El Centro, CA	190	6.7	9
	Chandler, AZ	32	40.2	9
	Helm, CA	160	26.3	9
Vulcan Materials Co., Chemicals Div.	Wichita, KS	36	133.4	7
The Williams Companies, Agrico Chemicals	Donaldsonville, LA	308	46.7	6
	Tulsa, OK	386	267.7	6
	Blytheville, AR	308	26.3	6

APPENDIX B

TOTAL MASS OF EMISSIONS

The total mass of emissions from ammonia plants was calculated on a state-by-state basis and compared to total state emissions from all sources. Only criteria pollutant emissions can be compared because a comprehensive data base is available for only these materials. Table B-1 shows the production rate and masses of emissions for each state. State production rates were determined by multiplying the state capacities, as summed from the appropriate values in Appendix A, by the ratio of national production in 1976 to total national capacity as given in Appendix A; i.e., multiplying state capacities by 0.9053.

TABLE B-1. MASS OF EMISSIONS FROM SYNTHETIC AMMONIA PLANTS IN 1976

State	Estimated ammonia production, 10^3 metric tons/yr	Mass of emissions, metric tons/yr				
		Particulate	NO_x	SO_x	CO	Hydrocarbons[a]
Alabama	218	29	589	48	210	238
Alaska	419	57	1,131	92	404	457
Arizona	42	6	113	9	40	46
Arkansas	279	38	753	61	269	305
California	784	106	2,117	172	755	856
Florida	168	23	454	37	162	183
Georgia	230	31	621	50	222	251
Idaho	206	28	556	45	198	225
Illinois	172	23	464	38	166	188
Indiana	110	15	297	24	106	120
Iowa	841	114	2,271	184	810	918
Kansas	475	64	1,283	104	458	519
Louisiana	3,263	441	8,810	716	3,144	3,562
Mississippi	887	120	2,395	195	855	968
Missouri	168	23	454	37	162	183
Nebraska	489	66	1,320	107	471	534
New Mexico	253	34	683	55	244	276
New York	70	9	189	15	67	76
North Carolina	172	23	464	38	166	188
Ohio	735	99	1,985	161	708	802
Oklahoma	763	103	2,060	167	735	833
Oregon	81	11	219	18	78	88
Pennsylvania	361	49	975	79	348	394
Tennessee	406	55	1,096	89	391	443
Texas	2,605	352	7,034	571	2,510	2,844
Utah	57	8	154	13	55	62
Virginia	279	38	753	61	269	305
Washington	146	20	394	32	141	159
West Virginia	339	46	915	74	327	370
Wyoming	150	20	405	33	145	164
United States[b]	15,168	2,051	40,954	3,325	14,616	16,557

[a] Includes monoethanolamine and methanol. [b] Totals may not agree due to rounding errors.

Statewide mass emissions were computed by multiplying the appropriate emission factors from Table 15 by the quantity of ammonia produced in each state. Since total state emissions are reported for only criteria pollutants, the masses of ammonia, MEA, methanol, or carbon dioxide emitted on a state basis were not calculated. Methanol and MEA emissions were included with total hydrocarbons. In certain cases, calculations had to be modified as follows:

- Because the desulfurization tank is regenerated once every 30 days, annual emissions of SO_2, CO, and hydrocarbons from this emission point were determined by applying a correction factor of 12 days/365 days = 0.0329.
- Total emissions from the primary reformer were computed based on the assumption that 50% of the ammonia plants burned No. 2 fuel oil for 4 months/yr. Natural gas was used in the others. The ratio of fuel oil burned to natural gas burned is then 1:5.
- As previously stated, 80% of the ammonia plants use the MEA process for scrubbing carbon dioxide from the synthesis gas, and 20% use the hot potassium carbonate process. Also, about 30% of the MEA plants and 50% of the hot potassium carbonate plants do not vent the regeneration gases, but sell them as a chemical feedstock. Therefore, the fraction of synthetic ammonia plants that have an atmospheric discharge from this process is (8/10 x 7/10 + 2/10 x 5/10) = 0.66.

With these considerations in mind, total emission factors were established for each criteria pollutant. Since NO_x is only emitted from the primary reformer, its emission factor was 2.7 g/kg. The total SO_x emission factor was determined as follows:

$$\text{Total emission factor} = \underbrace{\frac{12}{365}\,(0.019\ \text{g/kg})}_{\text{Desulfurization tank}} + \underbrace{\frac{5}{6}\,(0.0024\,\text{g/kg})}_{\text{Reformer, natural gas}} + \underbrace{\frac{1}{6}\,(1.3\ \text{g/kg})}_{\text{Reformer, fuel oil}}$$

$$= 0.22\ \text{g/kg of ammonia}$$

In the case of CO emissions, a similar calculation was used:

$$\text{Total emission factor} = \underbrace{\frac{12}{365}\,(6.9\ \text{g/kg})}_{\text{Desulfurization tank}} + \underbrace{\frac{5}{6}\,(0.068\ \text{g/kg})}_{\text{Reformer, natural gas}} + \underbrace{\frac{1}{6}\,(0.12\ \text{g/kg})}_{\text{Reformer, fuel oil}} + \underbrace{0.66\ (1.0\ \text{g/kg})}_{CO_2\ \text{regenerator}}$$

$$= 0.96\ \text{g/kg of ammonia}$$

The total particulate emission factor was determined as follows:

$$\text{Total emission factor} = \underset{\substack{\text{Reformer,}\\ \text{natural gas}}}{\frac{5}{6}\,(0.072\text{ g/kg})} + \underset{\substack{\text{Reformer,}\\ \text{fuel oil}}}{\frac{1}{6}\,(0.45\text{ g/kg})}$$

$$= 0.14\text{ g/kg of ammonia}$$

MEA and methanol emissions were added to the total hydrocarbon emission factors in the following manner:

$$\text{Total emission factor} = \underset{\substack{\text{Desulfurization}\\ \text{tank}}}{\frac{12}{365}\,(3.6\text{ g/kg})} + \underset{\substack{\text{Reformer,}\\ \text{natural gas}}}{\frac{5}{6}\,(0.012\text{ g/kg})} + \underset{\substack{\text{Reformer,}\\ \text{fuel oil}}}{\frac{1}{6}\,(0.15\text{ g/kg})} + \underset{\substack{CO_2\text{ regenerator,}\\ \text{hydrocarbons}}}{(0.66)(0.47\text{ g/kg})} + \underset{\substack{CO_2\text{ regenerator,}\\ \text{MEA}}}{(0.8)(0.7)(0.05\text{ g/kg})} + \underset{\substack{\text{Steam}\\ \text{stripper,}\\ \text{methanol}}}{0.6\text{ g/kg}}$$

$$= 1.09\text{ g/kg of ammonia}$$

Table B-2 gives total state emissions for the five criteria pollutants as reported in the National Emissions Data System (47). Table B-3, a recent emissions listing prepared by Monsanto Research Corporation under U.S. EPA contract (48), was used to compute the ratios which are shown in Table 19.

TABLE B-2. NEDS EMISSION SUMMARY BY STATE (47)

	Mass of emissions, metric tons/yr				
State	Particulates	SO_x	NO_x	Hydrocarbon	CO
Alabama	1,178,643	882,731	397,068	643,410	1,885,657
Alaska	13,913	5,874	32,757	28,389	167,357
Arizona	72,685	1,679,768	123,871	189,981	815,454
Arkansas	137,817	39,923	168,989	195,538	843,204
California	1,006,452	393,326	1,663,139	2,160,710	8,237,667
Colorado	201,166	49,188	147,496	193,456	875,781
Connecticut	40,074	168,068	155,832	219,661	897,580
Delaware	36,808	209,310	58,407	63,886	204,227
District of Columbia	19,451	60,630	46,824	41,789	190,834
Florida	226,460	897,381	644,794	619,872	2,695,817
Georgia	404,574	472,418	369,817	458,010	2,036,010
Hawaii	61,621	45,981	44,221	89,530	275,566
Idaho	55,499	54,387	48,552	84,230	343,720
Illinois	1,143,027	2,043,020	974,372	1,825,913	6,412,718
Indiana	748,405	2,050,541	1,371,233	600,477	2,933,780
Iowa	216,493	283,416	242,524	316,617	1,440,621
Kansas	348,351	86,974	233,987	309,633	1,002,375
Kentucky	546,214	1,202,827	419,142	326,265	1,189,932
Louisiana	380,551	166,664	442,817	1,919,662	5,633,827
Maine	49,155	144,887	76,741	122,918	376,196
Maryland	494,921	420,037	265,204	295,867	1,261,804
Massachusetts	96,160	636,466	334,379	440,481	1,682,218
Michigan	705,921	1,466,935	2,222,438	717,891	3,243,526
Minnesota	266,230	391,633	311,834	410,674	1,760,740
Mississippi	168,355	50,591	172,519	195,950	829,094
Missouri	202,435	1,152,373	448,300	413,130	1,854,901
Montana	272,688	871,235	148,405	271,824	611,061
Nebraska	95,338	58,014	101,948	127,821	569,522
Nevada	94,040	304,851	88,933	53,673	215,751
New Hampshire	14,920	86,596	67,309	88,469	256,380
New Jersey	151,768	463,736	489,216	819,482	2,877,319
New York	160,044	345,979	572,451	1,262,206	4,881,922
North Carolina	481,017	473,020	412,599	447,238	1,734,398
North Dakota	78,978	78,537	85,708	70,289	318,679
Ohio	1,766,056	2,980,333	1,101,470	1,153,493	5,205,719
Oklahoma	93,595	130,705	222,687	341,358	1,456,627
Oregon	169,449	36,776	135,748	234,669	92,247
Pennsylvania	1,810,598	2,929,137	3,017,345	891,763	3,729,830
Rhode Island	13,073	65,761	46,921	65,833	283,650
South Carolina	198,767	247,833	521,544	907,833	4,222,168
South Dakota	52,336	17,354	49,490	90,478	387,356
Tennessee	409,704	1,179,982	42,454	362,928	1,469,253
Texas	549,399	753,098	1,303,801	2,218,891	6,897,748
Utah	71,692	152,526	80,998	98,2,2	40,527
Vermont	14,587	17,751	24,286	41,980	150,510
Virginia	477,494	447,394	329,308	36,416	1,548,031
Washington	161,934	272,991	187,923	344,643	1,659,117
West Virginia	213,715	678,348	229,598	116,155	494,214
Wisconsin	411,558	712,393	408,525	523,930	1,582,869
Wyoming	75,427	69,394	72,572	55,319	303,297
U.S. TOTALS	16,762,000	28,873,000	21,722,000	23,994,000	91,782,000

Adjustments to grand total

The U.S. summary does not include certain source categories. The following additions should be considered part of the U.S. grand total for a more accurate picture of nationwide emissions.

New York point sources	311,000	993,000	382,000	127,000	44,000
Forest wild fires	375,000	0	88,000	529,000	3,089,000
Agricultural burning	272,000	15,000	29,000	272,000	1,451,000
Structural fires	52,000	0	6,000	61,000	200,000
Coal refuse fires	100,000	128,000	31,000	62,000	308,000
TOTAL	1,110,000	1,076,000	536,000	1,051,000	5,086,000
U.S. SUBTOTAL	16,762,000	28,873,000	21,722,000	23,994,000	91,782,000
U.S. GRAND TOTAL	17,872,000	29,949,000	22,258,000	25,045,000	96,868,000

TABLE B-3. STATE LISTING OF EMISSIONS AS OF MAY 13, 1977 (48)

	Mass of emissions, 1,000 kg/yr Percent of U.S. totals				
State	Particulate	SO_2	NO_x	Hydrocarbon	CO
Alabama	2,118,000 1.64000	802,300 3.30000	268,000 2.89000	226,700 1.37000	3,703,000 4.20000
Alaska	16,270,000 12.60000	88,740 0.36400	17,830 0.19200	33,000 0.19900	5,760 0.00654
Arizona	3,296,000 2.55000	57,280 0.23500	36,480 0.39400	98,840 0.59600	147,600 0.16700
Arkansas	1,641,000 1.27000	61,440 0.25200	62,150 0.67000	136,400 0.82200	107,600 0.12200
California	5,833,000 4.50000	607,000 2.49000	391,700 4.23000	1,423,000 8.58000	2,796,000 3.17000
Colorado	3,198,000 2.47000	226,500 0.93000	95,430 1.03000	145,600 0.87800	1,436,000 1.63000
Connecticut	318,400 0.24600	200,700 0.82400	72,420 0.78100	207,400 1.25000	106,200 0.12100
Delaware	142,500 0.11000	131,000 0.53800	39,190 0.42300	65,960 0.39800	97,410 0.11100
Florida	2,352,000 1.82000	699,500 2.87000	277,500 2.99000	426,900 2.57000	3,113,000 3.53000
Georgia	2,148,000 1.66000	484,600 1.99000	205,400 2.22000	321,800 1.94000	601,300 0.68200
Hawaii	235,800 0.18200	37,620 0.15500	17,240 0.18600	52,910 0.31900	64,920 0.07370
Idaho	2,411,000 1.86000	40,820 0.16800	14,120 0.15200	57,480 0.34700	103,000 0.11700
Illinois	3,144,000 2.43000	1,593,000 6.54000	564,200 6.09000	828,600 5.00000	6,401,000 7.26000
Indiana	2,266,000 1.75000	1,348,000 5.53000	433,000 4.67000	419,700 2.53000	13,130,000 14.90000
Iowa	2,155,000 1.66000	209,200 0.85900	93,220 1.01000	187,400 1.13000	32,660 0.03710
Kansas	3,191,000 2.46000	119,900 0.49300	99,910 1.08000	239,700 1.45000	74,330 0.08430
Kentucky	1,713,000 1.32000	871,300 3.58000	289,400 3.12000	229,500 1.38000	1,099,000 1.25000
Louisiana	1,698,000 1.31000	323,400 1.33000	272,100 2.94000	1,008,000 6.08000	745,500 0.84600
Maine	1,002,000 0.77400	151,900 0.62400	33,010 0.35600	57,100 0.34400	41,000 0.04650
Maryland	764,700 0.59100	392,500 1.61000	136,700 1.47000	244,500 1.47000	4,633,000 5.26000
Massachusetts	553,100 0.42700	442,500 1.82000	145,200 1.57000	368,400 2.22000	41,740 0.04740
Michigan	2,764,000 2.13000	1,131,000 4.65000	390,800 4.22000	537,300 3.24000	5,390,000 6.10000
Minnesota	2,911,000 2.25000	386,900 1.59000	140,500 1.52000	251,100 1.51000	1,069,000 1.21000
Mississippi	1,516,000 1.17000	109,400 0.44900	66,500 0.71700	209,500 1.26000	160,400 0.18200
Missouri	3,209,000 2.48000	711,900 2.92000	241,300 2.60000	309,900 1.87000	113,400 0.12900
Montana	4,988,000 3.85000	74,020 0.30400	28,840 0.31100	82,820 0.49900	139,400 0.15800
Nebraska	2,862,000 2.21000	79,660 0.32700	47,850 0.51600	102,400 0.61800	24,030 0.02730
Nevada	3,143,000 2.43000	142,900 0.58700	56,310 0.60700	23,370 0.14100	14,720 0.01670
New Hampshire	313,700 0.24200	84,650 0.34800	22,820 0.24600	37,210 0.22400	16,030 0.01920
New Jersey	688,100 0.53100	495,400 2.03000	194,600 2.10000	634,100 3.82000	115,800 0.13100
New Mexico	3,524,000 2.72000	294,700 1.21000	114,000 1.23000	115,600 0.69700	11,740 0.01330
New York	2,694,000 2.08000	1,232,000 5.06000	397,500 4.29000	1,096,000 6.61000	3,610,000 4.10000
North Carolina	2,055,000 1.59000	854,000 3.51000	293,600 3.17000	339,700 2.05000	248,300 0.28200
North Dakota	2,732,000 2.11000	97,410 0.40000	40,640 0.43800	39,810 0.24000	12,690 0.01440
Ohio	3,157,000 2.44000	2,081,000 8.55000	684,200 7.38000	838,700 5.06000	14,370,000 16.30000
Oklahoma	2,317,000 1.79000	69,170 0.28400	116,500 1.26000	241,100 1.45000	99,030 0.11200
Oregon	2,896,000 2.24000	93,250 0.38300	46,610 0.50300	155,100 0.93500	182,900 0.20800
Pennsylvania	3,267,000 2.52000	2,158,000 8.86000	674,500 7.28000	902,200 5.44000	17,940,000 20.40000
Rhode Island	85,950 0.06640	55,420 0.22800	15,770 0.17000	73,060 0.44100	10,240 0.01160
South Carolina	1,160,000 0.89600	310,600 1.28000	109,900 1.19000	176,100 1.06000	430,200 0.48800
South Dakota	2,787,000 2.15000	38,730 0.15900	12,060 0.13000	35,780 0.21600	5,705 0.00647
Tennessee	1,763,000 1.36000	882,300 3.62000	289,600 3.12000	258,200 1.56000	222,000 0.25300
Texas	9,279,000 7.17000	937,500 3.85000	785,800 8.48000	2,184,000 13.20000	1,913,000 2.17000
Utah	2,570,000 1.98000	320,100 1.31000	85,200 0.91900	69,930 0.42200	862,900 0.97900
Vermont	291,300 0.22500	17,640 0.07240	5,694 0.06140	21,100 0.12700	6,071 0.00689
Virginia	1,539,000 1.19000	433,000 1.78000	148,000 1.60000	270,600 1.63000	179,100 0.20300
Washington	2,266,000 1.75000	401,300 1.65000	97,230 1.05000	259,200 1.56000	302,000 0.34300
West Virginia	1,328,000 1.03000	1,122,000 4.61000	337,800 3.64000	162,300 0.97900	2,091,000 2.37000
Wisconsin	2,127,000 1.64000	601,000 2.47000	186,300 2.01000	280,600 1.69000	104,400 0.11800
Wyoming	2,809,000 2.17000	243,300 0.99900	74,540 0.80400	97,100 0.58600	9,158 0.01040
U.S. TOTALS	129,500,000	24,350,000	9,269,000	16,580,000	88,130,000

GLOSSARY

carbon monoxide shift: High and low temperature catalytic reaction in which steam is added to transform carbon monoxide to carbon dioxide and hydrogen.

desulfurization: Removal of hydrogen sulfide from natural gas feedstock, prior to reforming, by use of an activated carbon or zinc oxide bed.

methanation: Catalytic reaction in which hydrogen in process gas converts trace amounts of carbon monoxide and carbon dioxide to methane and water.

primary reformer: Set of catalyst-filled tubes in which natural gas (methane) reacts with steam to form carbon monoxide and hydrogen.

secondary reformer: Catalytic reactor in which compressed air is mexed with process gas from primary reformer to produce a synthesis gas with a hydrogen-to-nitrogen mole ratio of 3:1.

steam stripper: Column in which process condensate flows down the column countercurrent to steam which extracts ammonia and methanol from condensate.

CONVERSION FACTORS AND METRIC PREFIXES (57)

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius (°C)	degree Fahrenheit (°F)	$t_{°F} = 1.8\, t_{°C} + 32$
joule (J)	British thermal unit (Btu)	9.479×10^{-4}
kilogram (kg)	pound-mass (lb-mass avoirdupois)	2.205
kilogram (kg)	ton (short, 2000 lb mass)	1.102×10^{-3}
kilogram/meter^3 (kg/m^3)	pound-mass/gallon (lb-m/gal)	8.348×10^{-3}
kilometer^2 (km^2)	mile^2	3.861×10^{-1}
meter (m)	foot	3.281
meter^3 (m^3)	foot^3	3.531×10^{1}
meter^3/second (m^3/s)	gallon/minute (gpm)	1.585×10^{4}
metric ton	ton (short, 2000 lb-m)	1.102
pascal (Pa)	atmosphere	9.869×10^{-6}
pascal (Pa)	pound-force/inch^2 (psi)	1.450×10^{-4}
second (s)	minute	1.667×10^{-2}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
giga	G	10^9	5 GJ = 5×10^9 joules
mega	M	10^6	5 MPa = 5×10^6 pascals
kilo	k	10^3	5 kg = 5×10^3 grams
milli	m	10^{-3}	5 mg = 5×10^{-3} gram
micro	µ	10^{-6}	5 µg = 5×10^{-6} gram

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(57) Standard for Metric Practice. ANSI/ASTM Designation E 380-76^{ε}, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

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16. ABSTRACT The report describes a study of air emissions from the production of synthetic ammonia. In 1976, 90 synthetic ammonia plants in 30 states produced 15.2 million metric tons of anhydrous ammonia. Ammonia is synthesized by the reaction of nitrogen and hydrogen. Most plants produce hydrogen by the catalytic steam reforming of natural gas. An average ammonia plant has a capacity of 180,000 metric tons/year. Plant air emissions result from regeneration of the desulfurization tank, from combustion in the primary reformer, from regeneration of the CO2 scrubbing solution, and from steam stripping of process condensate. On the average, emissions from the regeneration of the desulfurization tank are released for 10 hours, but only once every 30 days; emissions from the other sources are continuous during plant operation. These emission points are not controlled because no state or federal standards are exceeded. Process modifications have reduced air emissions and improved utilization of raw materials and energy. Potential environmental effects from ammonia plant emissions were measured: highest continuous source severities result from NOx emissions from the primary reformer (4.1), and ammonia emissions from the regeneration of the CO2 scrubbing solution (2.2) and from the condensate steam stripper (3.2). Annual ammonia production should increase by 4-8 % through 1980. Industry emissions should also increase at this rate.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Hydrogen	Air Pollution Control	13B	
Industrial Processes	Natural Gas	Stationary Sources	13H	21D
Assessments	Steam	CO2 Scrubber	14B	07D
Ammonia	Reforming		07B	
Synthesis	Catalysis			
Nitrogen	Desulfurization			07A
Carbon Dioxide	Scrubbers			

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