Handbook of Pollution Prevention and Cleaner Production

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Paul E. Rosenfeld

Best Practices in the Agrochemical Industry



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Edited by

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1.1 Introduction

The fertilizer, pesticide, and agricultural chemical industry sector is diverse. The justification for this industry is that as the world population increases, crop lands are increasingly strained and unable to meet the growing demand for food without employing some method of crop enhancement. There are generally believed to be five common practices capable of meeting the growing demand:

- increasing tilled acreage
- improving plant strains
- introducing or expanding irrigation
- controlling pests by chemical or biological methods, and
- initiating or increasing fertilizer usage.

The last two methods have created a large agrichemical industry which produces a wide variety of products designed to increase crop production and protect crops from disease and pests. Along with the benefits there have been increasingly negative impacts on the environment, various natural resources, and to human health.

Plant life requires 18 elements to grow, with the most important ones being oxygen, carbon, hydrogen, nitrogen, phosphorous, and potassium. Oxygen, carbon, and hydrogen are obtained from the atmosphere and water, while nitrogen, phosphorous, and potassium are naturally obtained from soils. Under current high-yield production methods, soils are stripped of the essential nutrients, thereby requiring the addition of fertilizers, particularly those comprised of nitrogen, phosphorous, and potassium in order to resupply the land. The additional 12 essential nutrients are generally maintained in soil at sufficient levels for plant growth, but they may be added to some fertilizer formulations to improve crop yields.

There are more than 8000 establishments identified by the United States EPA that manufacture, formulate, and package pesticides and other agricultural chemicals. Many of these are relatively small establishments and are comprised of facilities that have a primary line of business other than producing pesticides and other miscellaneous agricultural chemicals. The industry is therefore diverse with a significant number of stakeholders.

This chapter provides an overview of the industry and various chemical products and building blocks used in the manufacture of agrochemicals. From this general overview, we will build on an understanding of the pollution issues stemming from

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the industry and then discuss pollution prevention and responsible care practices in subsequent chapters.

1.2 Fertilizers

There are two important classes: nitrogenous and phosphatic fertilizers.

1.2.1 Nitrogenous Fertilizers

The nitrogenous fertilizer industry includes the production of synthetic ammonia, nitric acid, ammonium nitrate, and urea. Synthetic ammonia and nitric acid are used primarily as intermediates in the production of ammonium nitrate and urea fertilizers. The following is a list of primary specific products classified as nitrogenous fertilizers:

- ammonia liquor
- ammonium nitrate
- ammonium sulfate
- anhydrous ammonia
- aqua ammonia
- fertilizers, mixed, produced in nitrogenous fertilizer plants
- fertilizers, natural
- nitric acid
- nitrogen fertilizer solutions
- plant foods, mixed in nitrogenous fertilizer plants
- urea.

Synthetic ammonia is ammonia that has been synthesized from natural gas in which natural gas molecules are reduced to carbon and hydrogen. The hydrogen is then purified and reacted with nitrogen to produce ammonia. About 75% or more of the synthetic ammonia produced in the United States is used as fertilizer, either directly as ammonia or indirectly after fertilizer synthesis into urea, ammonium nitrate, and monoammonium or diammonium phosphates. Roughly one-third of the fertilizer nitrogen is applied directly to the land as anhydrous ammonia. The remaining 25% of ammonia produced is used as raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products.

Nitric acid is formed by concentration, absorption, and oxidation of anhydrous ammonia. About 70% of the nitric acid produced is consumed as an intermediate in the manufacture of ammonium nitrate (NH_4NO_3), which is largely used in fertilizers. Up to 10% of the nitric acid produced is used in adipic acid manufacturing which is an intermediate in nylon production. Explosive manufacturing uses nitric acid for organic nitrations to produce nitrobenzene, dinitrotoluenes, and other chemical intermediates. Other end uses of nitric acid are gold and silver separation, military munitions, steel and brass pickling, photoengraving, and acidulation of phosphate rock.

Ammonium nitrate is produced by neutralizing nitric acid with ammonia. Up to 20% of ammonium nitrate is used for explosives and the remainder for fertilizer production. Liquid ammonium nitrate may be sold as a fertilizer, generally in combination with urea. Liquid ammonium nitrate may also be concentrated to form an ammonium nitrate 'melt' for use in solids formation processes. Solid ammonium nitrate may be produced in the form of prills, grains, granules, or crystals. Prills, round or needle-shaped aggregates, can be produced in either high- or low-density form, depending on the concentration of the melt. High-density prills, granules, and crystals are used as fertilizer, grains are used solely in explosives, and low-density prills can be used as either fertilizer or explosives.

Urea (also known as carbamide or carbonyl diamide) is produced by reacting ammonia with carbon dioxide. Roughly 85% of urea solution produced is used in fertilizer mixtures, with 3% used as animal feed supplements and 12% used for plastics and other uses. Urea is marketed as a solution or in solid form. Most solids are produced as prills or granules for use as fertilizer or protein supplement in animal feed, and in plastics manufacturing.

Ammonium sulfate is not economically feasible to produce for use as a fertilizer. However, it is formed as a by-product of other process such as acid scrubbing of coke oven gas, synthetic fiber production, and the ammoniation of process sulfuric acid.

1.2.2 Phosphatic Fertilizers

The phosphatic fertilizer industry is organized into three major segments: phosphoric acid, granular ammonium phosphate, and normal and triple superphosphate. The following is a list of important products:

- ammonium phosphates
- calcium meta-phosphates
- defluorinated phosphates
- diammonium phosphates
- fertilizers, mixed, produced in phosphatic fertilizer plants
- phosphoric acid
- plant foods, mixed in phosphatic fertilizer plants
- superphosphates, ammoniated and not ammoniated.

Phosphoric acid (H_3PO_4) can be manufactured using either a wet or a thermal process to react phosphate rock with sulfuric acid. Approximately 96% of the domestic phosphoric acid produced is made using the wet process. Wet process phosphoric acid has a phosphorous concentration typically ranging from 26–30% as phosphorous pentoxide (P_2O_5) and is used in the production of ammonium phosphates and triple superphosphates. Thermal process phosphoric acid is used in the manufacture of high-grade chemicals which require high purity.

Ammonium phosphate ($NH_4H_2PO_4$) is produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphatic fertilizers are produced. The most common ammonium phosphatic fertilizer grades are monoammonium phosphate (MAP) and diammonium phosphate (DAP). DAP is among the most commonly used fertilizers because it provides a large quantity of plant food, is compatible with most mix fertilizer ingredients, and is nonexplosive. It may be directly applied in irrigation systems because it is completely soluble in water. DAP is also preferred over MAP because it is capable of fixing twice as much ammonia per phosphorous pentoxide in solid form. MAP contains a higher concentration of phosphorous pentoxide than DAP. It is favored for use with alkaline soils and may be applied either directly or in a dry blend.

Normal, or 'ordinary,' superphosphate fertilizers are produced by reacting phosphate rock with sulfuric acid. Normal superphosphate (NSP) retains calcium sulfate which forms by the reaction between phosphate rock and sulfuric acid. For this reason NSP retains its importance wherever sulfur deficiency limits crop yields. NSP refers to fertilizer material containing 15–21% phosphorous as phosphorous pentoxide (P_2O_5). NSP contains no more than 22% of available P_2O_5. Production of NSP has given way to the higher-yielding triple superphosphates and ammonium phosphates since the 1990s. Because of its low P_2O_5 concentration, shipping can be prohibitively expensive due to the large volumes required. NSP is favored in low-cost nitrogen-phosphorous-potassium (NPK) mixes because it is a less expensive form of phosphorous; however, it is unacceptable for higher-grade mixes.

Triple superphosphates (TSP) are produced by reacting ground phosphate rock with phosphoric acid. Triple superphosphate is also known as double, treble, or concentrated superphosphate. The phosphorus content of TSP is over 40% measured as phosphorus pentoxide (P_2O_5), which is its main advantage over other phosphatic fertilizers. TSP began to be produced in large quantities when wet process phosphoric acid production became available commercially. It is commonly produced along with phosphoric acid near phosphate rock supplies. TSP may be applied directly or as a bulk blend.

Table 1.1 provides a product characterization summary of nitrogenous and phosphatic fertilizers.

1.2.3 Fertilizers, Mixing Only

A significant part of the fertilizer industry only purchases fertilizer materials in bulk from fertilizer manufacturing facilities and mixes them to sell as a fertilizer formulation. Phosphorous is the single nutrient most likely to be applied in a typical fertilizer mixture.

1.3 Pesticides and Other Agricultural Chemicals

The pesticides and agricultural chemicals industry group formulates and prepares ready-to-use agricultural and household pesticides and various other agricultural chemicals. There are more than 850 different pesticide formulations and preparations. Most pesticides can be classified as either insecticides, herbicides, or fungicides, although many other minor classifications exist. Also included in this

Table 1.1 Product Characterization Profiles

Product	Profile
Nitrogenous Fertilizer Products	
Synthetic ammonia	This is ammonia that has been synthesized from natural gas. In this process, natural gas molecules are reduced to carbon and hydrogen. The hydrogen is then purified and reacted with nitrogen to produce ammonia. Approximately 75% of the synthetic ammonia produced in the US is used as fertilizer, either directly as ammonia or indirectly after fertilizer synthesis into urea, ammonium nitrate, and monoammonium or diammonium phosphates. One-third of the fertilizer nitrogen is applied directly to the land as anhydrous ammonia. The remaining 25% of ammonia produced is used as raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products
Nitric acid	Nitric acid is formed by concentration, absorption, and oxidation of anhydrous ammonia. About 70% of the nitric acid produced is consumed as an intermediate in the manufacture of ammonium nitrate (NH_4NO_3), which is largely used in fertilizers. Another 5–10% of the nitric acid produced is used in adipic acid manufacturing, an intermediate in nylon production. Explosive manufacturing utilizes nitric acid for organic nitrations to produce nitrobenzene, dinitro-toluenes, and other chemical intermediates. Other end uses of nitric acid are gold and silver separation, military munitions, steel and brass pickling, photoengraving, and acidulation of phosphate rock
Ammonium nitrate	Ammonium nitrate is produced by neutralizing nitric acid with ammonia. Approximately 15–20% of ammonium nitrate is used for explosives and the balance for fertilizer. Ammonium nitrate is marketed in several forms, depending upon its use. Liquid ammonium nitrate may be sold as a fertilizer, generally in combination with urea. Liquid ammonium nitrate may also be concentrated to form an ammonium nitrate 'melt' for use in solids formation processes. Solid ammonium nitrate may be produced in the form of prills, grains, granules, or crystals. Prills, round or needle-shaped aggregates, can be produced in either high- or low-density form, depending on the concentration of the melt. High-density prills, granules, and crystals are used as fertilizer, grains are used solely in explosives, and low-density prills can be used as either fertilizer or explosives

(*Continued*)

Table 1.1 (Continued)

Product	Profile
Urea	Urea, also known as carbamide or carbonyl diamide, is produced by reacting ammonia with carbon dioxide. Eighty-five percent of urea solution produced is used in fertilizer mixtures, with 3% going to animal feed supplements and 12% is used for plastics and other uses. Urea is marketed as a solution or in solid form. Most solids are produced as prills or granules for use as fertilizer or protein supplement in animal feed, and in plastics manufacturing
Ammonium sulfate	It is not economically feasible to produce ammonium sulfate for use as a fertilizer. However, ammonium sulfate is formed as a by-product of other process such as acid scrubbing of coke oven gas, synthetic fiber production, and the ammoniation of process sulfuric acid
Phosphatic Fertilizers	
Phosphoric acid	Phosphoric acid (H_3PO_4) can be manufactured using either a wet or a thermal process to react phosphate rock with sulfuric acid. Approximately 96% of the phosphoric acid produced in the US is produced using the wet process. Wet process phosphoric acid has a phosphorous concentration typically ranging from 26–30% as phosphorous pentoxide (P_2O_5) and is used in the production of ammonium phosphates and triple superphosphates. Thermal process phosphoric acid is commonly used in the manufacture of high-grade chemicals requiring a much higher purity
Ammonium phosphates	Ammonium phosphate ($NH_4H_2PO_4$) is produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphatic fertilizers are produced in the United States. The most common ammonium phosphatic fertilizer grades are monoammonium phosphate (MAP) and diammonium phosphate (DAP). DAP

	has become one of the most commonly used fertilizers because it provides a large quantity of plant food, is compatible with most mix fertilizer ingredients, and is nonexplosive. It may be directly applied or used in irrigation systems as it is completely soluble in water. DAP is also preferred over MAP because it is capable of fixing twice as much ammonia per phosphorous pentoxide in solid form. MAP contains a higher concentration of phosphorous pentoxide than DAP. It is favored for use with alkaline soils and may be applied either directly or in a dry blend
Normal superphosphates	Like phosphoric acid, normal, or 'ordinary,' superphosphate fertilizers are produced by reacting phosphate rock with sulfuric acid. However, normal superphosphate (NSP) retains calcium sulfate which forms by the reaction between phosphate rock and sulfuric acid. For this reason NSP retains its importance wherever sulfur deficiency limits crop yields. NSP refers to fertilizer material containing 15–21% phosphorous as phosphorous pentoxide (P_2O_5). As defined by the Census Bureau, NSP contains not more than 22% of available P_2O_5. Production of NSP has given way to the higher-yielding triple superphosphates and ammonium phosphates. Because of its low P_2O_5 concentration, shipping can be prohibitively expensive due to the large volumes required. NSP is favored in low-cost nitrogen-phosphorous-potassium (NPK) mixes because it is a less expensive form of phosphorous, however, it is unacceptable for higher-grade mixes
Triple superphosphates	Triple superphosphates (TSP) are produced by reacting ground phosphate rock with phosphoric acid. Triple superphosphate is also known as double, treble, or concentrated superphosphate. The phosphorus content of triple superphosphates is over 40%, measured as phosphorus pentoxide (P_2O_5), which is its main advantage over other phosphatic fertilizers. TSP began to be produced in large quantities when wet process phosphoric acid production became available commercially. It is commonly produced along with phosphoric acid near phosphate rock supplies. TSP may be applied directly or as a bulk blend.

category are blends of fertilizers and pesticides produced at pesticide formulating and mixing facilities. The following is a list of common pesticides and important products:

- agricultural disinfectants
- agricultural pesticides
- arsenates and arsenites
- Bordeaux mixture
- cattle dips and sheep dips
- DDT
- defoliants
- fly sprays
- fungicides
- growth regulants
- herbicides
- insecticides, agricultural and household
- lime-sulfur, dry and solution
- lindane, formulated
- moth repellants
- nicotine and salts
- Paris green
- pesticides, household
- phytoactin
- plant hormones
- poison, household
- pyrethrin
- rodenticides
- rotenone
- soil conditioners
- sulfur dust
- thiocyanates
- trace elements (agrichemical)
- xanthone.

1.3.1 Herbicides

Herbicides are the largest class of pesticides used in the world. This class of pesticides comprises 50% of the value of aggregate world pesticide usage. Products are used to destroy or control a wide variety of weeds and other unwanted plants. Because of its demonstrated farm labor savings, nearly all the agricultural land in the United States is currently being treated with some type of herbicide. About 50% of total United States pesticide consumption (by value) is comprised of herbicides.

1.3.2 Insecticides

Insecticides are the second largest pesticide category (by value) used throughout the world. Historically, the category of synthetic organic insecticides has been divided into one of four major chemical groups: organochlorines (e.g., DDT and chlordane), organophosphates (e.g., parathion and diazinon), carbamates (e.g., carbaryl), and pyrethroids (e.g., natural and synthetic).

Several compounds, discovered during the 1950s, found widespread use in agriculture because of their high toxicity to a variety of insects. However, the qualities that made these chemicals so desirable also led to their eventual removal from the market, as these products also proved extremely harmful to humans. A new series of less toxic synthetic compounds called pyrethroids replaced these chemicals. These compounds are based on the natural pyrethroids, which are found in such plants as the chrysanthemum.

1.3.3 Fungicides

Fungicides are used primarily to protect agricultural crops and seeds from various fungi; farmers previously used inorganic products, such as elemental sulfur and copper sulfate. Initially, synthetic products were commercially unsuccessful, because of their high manufacturing costs. By the 1940s, however, newer, less expensive products became commercially successful. Today, fungicides are manufactured from a variety of chemical classes. Commercially, the most important fungicides are halogenated compounds, the carbamates and dithiocarbamates, and organophosphates.

1.3.4 Other Pesticides

A number of other classes of pesticide products are employed. Some well-known examples are listed below:

- Biological pesticides, also known as biopesticides, include true biological agents, living or reproduced biological entities such as viruses or bacteria, and naturally occurring biochemicals such as plant growth regulators, hormones, and insect sexual attractants (pheromones) that function by modes of action other than innate toxicity. Generally, biological pesticides pose little or no risk to human health or the environment. EPA generally requires much less data to register a biopesticide than to register a conventional pesticide. In 1994, EPA established the Biopesticides and Pollution Prevention Division in the Office of Pesticide Programs to aid in rapid registration of these products.
- Plant growth regulators have been developed to improve crop production. Plant growth regulators are produced for a variety of purposes, including loosening ripened fruits for faster harvest; controlling the size and firmness of fruits; and regulating the size of a plant to increase branching.
- Sex attractants may be used to attract insects to traps or to confuse specific male insects, making it difficult to locate females for mating. Commercially available sexual attractants are synthetically produced compounds. Insect growth regulators, such as juvenile growth hormones, are synthetic compounds similar to the natural chemicals that regulate insect growth.
- Genetically modified plants are plants developed through the use of biotechnology. There are three types of plants that are relevant to pest control: herbicide-tolerant plants (which can tolerate certain types of herbicides), insect-resistant plants (which can withstand attacks by certain insects), and virus- and other pest-resistant plants (which are immune to some types of plant viruses and other plant pests).

1.3.5 Pesticide Formulations

Pesticide formulations may exist as liquid, dry, and pressurized gas. The liquid formulation may be applied directly in liquid form or propelled as an aerosol. Some common dry-based formulations are dusts, wettable powders, granules, treated seed, bait pellets, encapsulated, and cubes. Pressurized gas formulations are used primarily for soil fumigation. Gaseous pesticides can be subjected to high pressures which often convert the formulation to a liquid which can be stored, transported, and applied from gas cylinders. Repackaging of pesticide formulations is common when materials are to be transferred from bulk storage to a smaller scale of packaging for use by a consumer. Products are typically repackaged in smaller containers and consumer-specific labeling is added.

1.4 Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requires that all establishments that produce pesticides in the United States or that import pesticides into the country register and report their production volume to the EPA. The term, 'produce' has been defined under FIFRA and 40 CFR Part 167 to mean 'to manufacture, prepare, propagate, compound, or process any pesticide, including any pesticide produced pursuant to Section 5 of FIFRA, any active ingredient, or device, or to package, repackage, label, relabel, or otherwise change the container of any pesticide or device.' Repackaging or otherwise changing the container of any pesticide or device in bulk amounts constitutes pesticide production. Under FIFRA Section 7, products are reported under one of four product types:

1. technical material or active ingredient
2. end-use blend, formulation, or concentrate
3. repackaged or relabeled product or
4. device.

There are approximately 12 000–13 000 Active Registered Pesticide-Producing Establishments, however not all produce pesticides but rather maintain registration. Also facilities producing a variety of products might not be classified under all applicable NAIC codes.

1.5 Manufacturing Technologies

The three most important nutrients for plant growth are nitrogen, phosphorous, and potassium. However, the production of the major potassium fertilizer salts, or potash as they are commonly known, is considered an inorganic chemical process. The fertilizer, pesticide, and agricultural chemical industry can be classified into nitrogenous fertilizers, phosphatic fertilizers, fertilizers (mixing-only), and the formulating and preparing of pesticides and other agricultural chemicals.

1.5.1 Nitrogenous Fertilizers

The major nitrogenous fertilizers include synthetic ammonia, ammonium nitrate, and urea.

Synthetic ammonia (NH_3) is produced by reacting hydrogen with nitrogen at a molar ratio of 3:1. Nitrogen is obtained from the air, which is primarily comprised of nitrogen (78%) and oxygen (21%). Hydrogen is obtained from either the catalytic steam reforming of natural gas (methane) or naptha, or as the byproduct from the electrolysis of brine at chlorine plants. In the US, about 98% of the hydrogen used to synthesize ammonia is produced by catalytic steam reforming of natural gas, and about 2% is obtained from chlorine plants. There are six process steps used to produce synthetic ammonia using 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 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 mixed with air (nitrogen). The last step produces anhydrous ammonia from the synthetic gas. An anhydrous compound is inorganic and does not contain water either adsorbed on its surface or combined as water of crystallization. While almost all ammonia plants use these basic process steps, details such as operating pressures, temperatures, and quantities of feedstock vary from plant to plant. Figure 1.1 provides a schematic of a generic ammonia plant. Table 1.2 provides a summary description of each process step.

1.5.2 Nitric Acid Production

Nitric acid (HNO_3) is produced by two methods. The first method utilizes oxidation, condensation, and absorption of ammonia to produce a 'weak' nitric acid. Weak nitric acid has a concentration ranging from 30–70% nitric acid. The second method combines dehydrating, bleaching, condensing, and absorption to produce 'high-strength' nitric acid from weak nitric acid. High-strength nitric acid generally contains more than 90% nitric acid. Table 1.3 provides a brief description of the manufacturing steps.

1.5.3 Ammonium Nitrate and Urea

The manufacture steps for ammonium nitrate (NH_4NO_2) and urea ($CO(NH_2)_2$) are similar. In both processes the unit operations are:

- solution formation
- concentration
- solids formation

- finishing
- screening
- coating
- product bagging and/or bulk shipping.

Not all of the steps are always necessary depending on the end product desired. For example, plants producing ammonium nitrate or urea liquid solutions alone use only the solution formation, solution blending, and bulk shipping operations. Plants producing a solid product may employ all of the unit operations. Table 1.4 provides summary descriptions of the process steps.

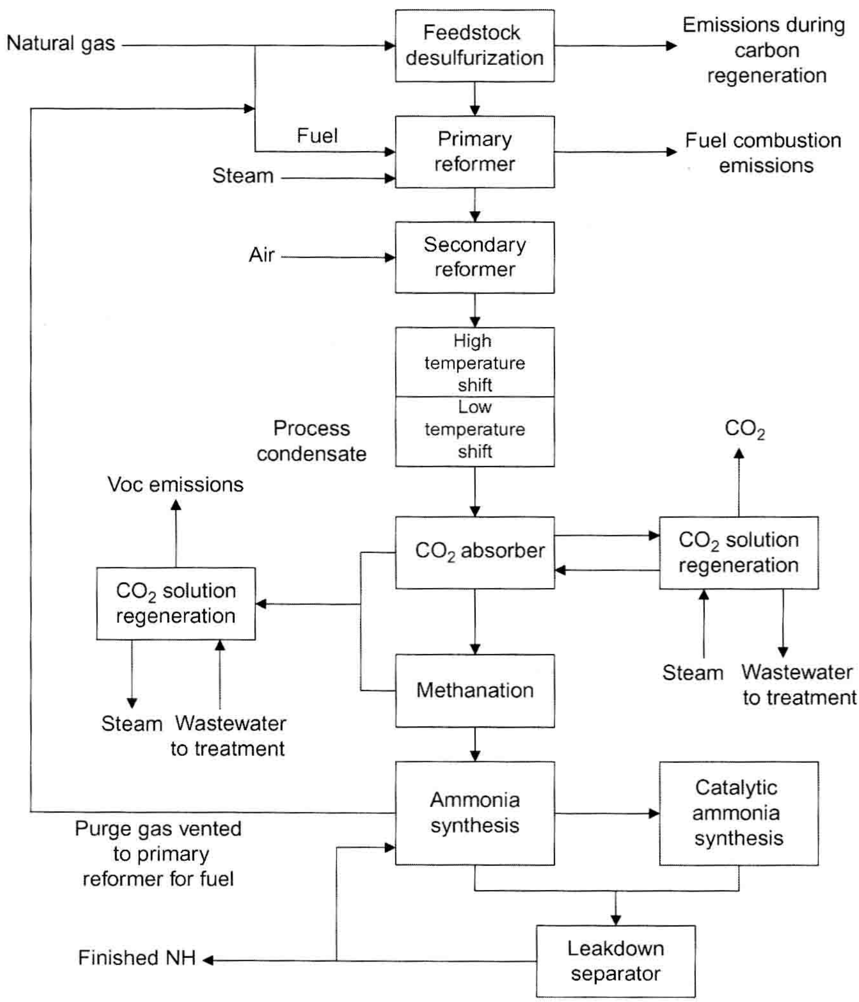

Figure 1.1 Process schematic of an ammonia plant.