

CHAPTER II

AMMONIA SYNTHESIS



2.1 History of Ammonia

In the past before 1800 the principle nitrogen source for agriculture were by-product organic materials of various types including animal manure, seed meals, fish scrap, leather scrap and various wastes from meat-animal slaughtering. However the supply of these was limited. The cultivation of leguminous plants capable of fixing nitrogen from air also was a means of supplying nitrogen fertilizer.

In 1809, a large deposit of sodium nitrate was discovered in a desert area in Chile. Mining soon began and by 1850 this material was supplying a major portion of the world nitrogen supply. It is estimated that it supplied 70 per cent of the world fertilizer from 1850-1900 and 50 per cent of nitrogen fertilizer up to 1914.

The remoteness of the Chilean nitrate deposit plus other factors cause a rapid decline. One adverse factor was the growing production of by-product ammonium sulphate and aqua ammonia by the coke industry and also was due to the nitrogen fixation from air into ammonia which had begun by that time.

Ammonia was first produced by Priestley in 1754 (Slack, 1973) by heating "sal ammoniac" (ammonium chloride) with lime. Thirty years later

Berthollet found out the composition of ammonia. The attempt to synthesize ammonia from nitrogen and hydrogen was first done by Hilderbrand in 1795 (Slack, 1973) at atmospheric pressure. Others have tried pressures up to 50 atm. but were unsuccessful (Slack, 1973). Dobereiner in 1823 seems to be the first to realize that a catalyst would be needed for a practical method.

The first practical industrial process for nitrogen fixation was developed by Birkeland and Eyde (Slack, 1973) by passing air through an electric arc to attain high temperature, forming nitric oxides which later react with lime to form calcium nitrate. However this arc process lost ground to ammonia synthesis process which stepped into industry in the period of 1910-1930.

The second process to fix nitrogen was the Cyanamide route process which Frank, Caro and Rothe (Slack, 1973) found that nitrogen could be fixed by calcium carbide to form calcium cyanamide. Calcium cyanamide could be hydrolyzed with water to give ammonia accordingly.

This process ruled over the nitrogen chemical plant during 1900s to 1910s, especially during the First World War which required nitrate for munitions production. But this method became less popular due to high power consumption and expensiveness.

The process adopted and practiced nowadays dates back to 1902 when Fritz Haber, a German chemistry professor at the Karlsruhe Engineering College and Walter Nernst, a physical chemistry professor at the University of Berlin, began their research on formation of ammonia and made a comprehensive study of the $N_2-H_2-NH_3$ equilibrium at temperatures up to $1,800^{\circ}F$.

Catalysts were also studied and used at that time.

In 1909 the ammonia synthesis reached a concentration of 6 per cent with an osmium catalyst. A plant was set up to manufacture synthetic ammonia at the rate of 80 g/hr. Carl Bosch began to develop a cheaper and more available catalyst by using iron catalyst promoted by small amount of potassium magnesium, aluminium and calcium. The first commercial ammonia plant went on in 1913 located at BASF's plant complies with a production rate of 30 t/d. Another plant was built in 1917 producing 36,000 t/y which was expanded to 240,000 tons by the end of the year.

After the war, development was made independently in the USA and this technology was sold to Europe. During the years 1930-1950, several improvements were made. Many organization entered the field, bringing in processes, such as Casale, Fauser, Claude and Mont Cenis. These processes differed from the Haber-Bosch process in various ways, for example, the Casale process operates at a very high temperature on the order of 750 atm. However the technology was not much changed. But production increased rapidly, from 4,000 tons/year in 1914, 100,000 in 1920, 400,000 tons in 1925, 900,000 tons in 1930 to 3.65 million tons in 1950. Still few plants were being built with capacities higher than 100 ton/day. (Slack, 1973)

A rapid expansion of ammonia production took place in 1950s and 1960s particularly in the USA as the period 1965-1970 brought a sudden increase in capacity. The world production doubled from 33.5 million tons in 1965 to 67 million tons in 1973. Figures II-1 and II-2 show

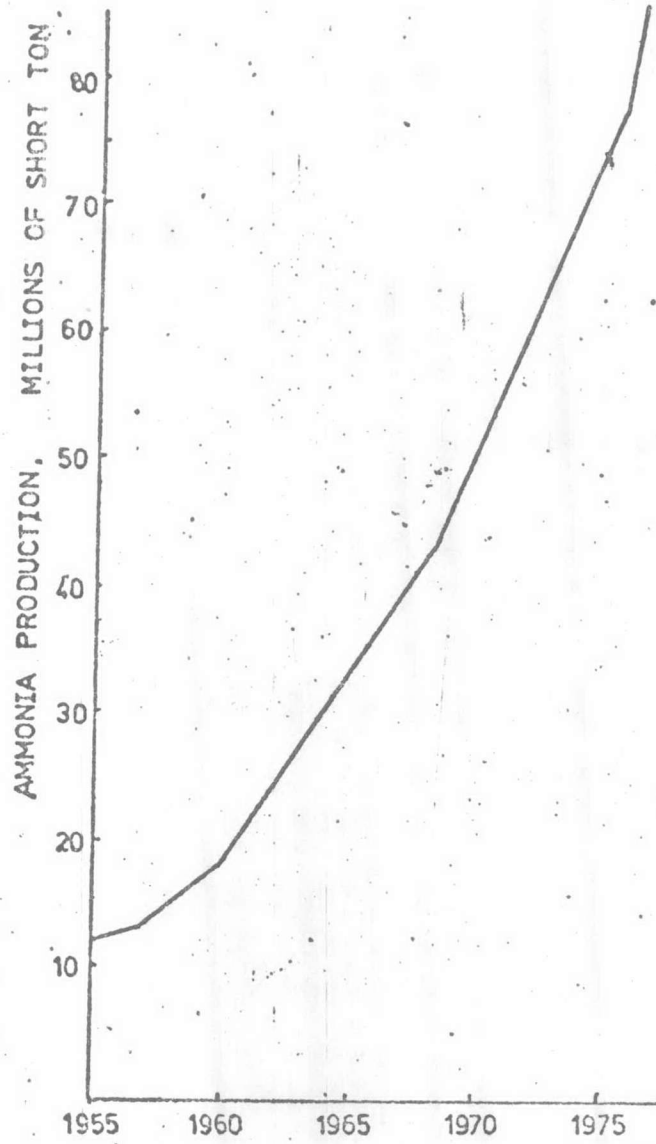


FIGURE II-1 Annual World Ammonia Production

Number of 600 T/D
Ammonia Plant operating

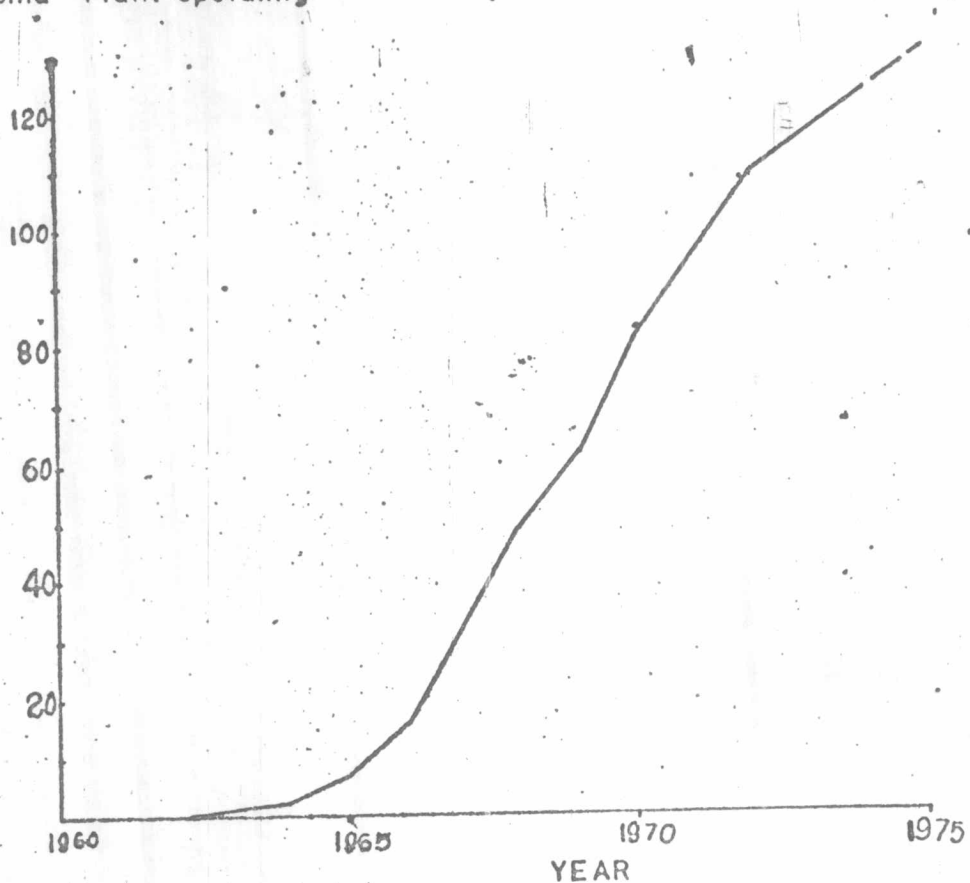


FIGURE II-2 Number of Large Capacity Ammonia Plant

the annual world ammonia production and the number of large capacity ammonia plants over 600 t/d.

New technology began in the early 1950s by the introduction of centrifugal compressors and the other significant developments: integral design of the ammonia plant rather than the assembly of unrelated units, increase in the size of converter as a notable feature of the new practice occurring in mid-1960s. The capacity of the plant increased to 600 t/d and rose up to 1,000-1,500 t/d at 4,000-5,000 psi synthesis loop. New technology includes waste heat recovery throughout the system, high pressure steam to drive compressors and other equipments, higher pressure in the gas preparation section, integrating scheme to reduce energy consumption, energy production, equipment size and catalyst volumes.

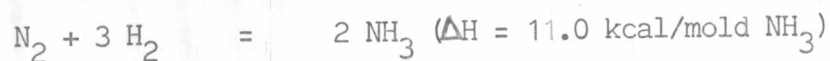
The worldwide shipping of ammonia by ocean freight is also in the beginning phase as it allows high volume, low-cost production from countries that have raw materials but not enough internal demand to make large plants feasible. Transportation through pipelines was also developed during 1965-1970 in Europe, Mexico and the USA. Transportation was also made through tankers.

Future changes in ammonia production technology are to be expected in the future, as low cost natural gas, the main raw material, and oil, another kind of raw material, is gaining higher price. Expected shortage of natural gas is forcing the gas industry to coal gasification as a source of raw materials.

Developments are also being made but no certain predictions can be made as new processes are in the early stage, such as the production of ammonia by the use of organic titanium compound as intermediate or catalyst in order to lower temperature and pressure in the process (Slack, 1973).

2.2 Ammonia Synthesis Process

Ammonia consists of nitrogen and hydrogen, the availability of nitrogen gas and hydrogen gas is important to undergo reaction at the right condition. The essential process of synthesizing ammonia is



This reaction is very slow at normal temperatures in the absence of catalyst. Also the reaction will not go to completion even in the presence of catalyst for an equilibrium is set up according to the Le Chatelier's principle. The concentration of ammonia at equilibrium is increased either by increasing the pressure or by decreasing the temperature. The concentration of ammonia in equilibrium with a 3:1 mixture of hydrogen gas and nitrogen gas is given in Figure II-3.

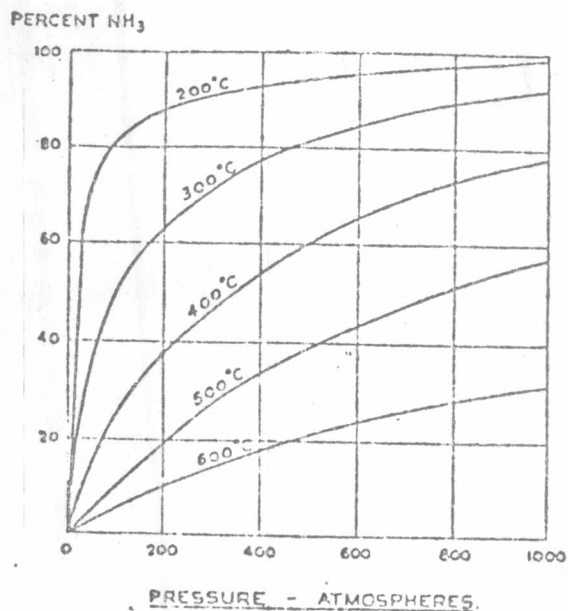


Figure II-3 Percentage ammonia in equilibrium
with $3\text{H}_2 : \text{N}_2$ mixture

The equilibrium concentration of ammonia is considerably increased by lowering the temperature. But in the synthesis process the rate of desired reaction is also as important as the equilibrium concentration. It increases as the temperature is raised in accordance with the Arrhenius equation. A compromise between the demands of a high temperature to give high reaction rate and a low temperature to give a high equilibrium concentration of ammonia exists. By increasing the pressure both the reaction rate and the position of equilibrium can be improved; by using active catalyst the rate can be increased while the

position of equilibrium still being unaffected.

In practice the best temperature and pressure for synthesis process are determined by the combined demands of an advantageous equilibrium and a reasonable rate of reaction which are controlled by the performance of catalyst applied and economic consideration, such as cost of pipeworks, compressors, vessels, etc. Most plants nowadays operate at about pressure of 150-330 atm, 660-1110^oF. At this temperature and pressure the equilibrium concentration of NH₃ lies between 15% to 50%. The reaction gases are not allowed infinite time to attain to this equilibrium, so the concentration of ammonia is even lower. The unreacted gas will be separated from ammonia and recirculated over the same catalyst again as fresh gas is added as fast as ammonia is removed.

The catalysts used are very sensitive to impurities: carbon monoxide, carbon dioxide, oxygen, water and sulfur compounds. Compressed synthesis gas must not contain more than a few ppm of these impurities as the life of the active catalyst will be seriously shortened. The favorable condition applied in the process may make the life of the catalyst last up to 10 years.

The differentiation of ammonia synthesis process: Haber Bosch process, Claude process, Cassale process, etc. have become less important as they differentiate from one another from the pressure and temperature operated and improvements are made from lessons learned from each other. Mostly they are in the region of pressures of 200 to 350 atm, using promoted iron catalyst. Mont Cenis process differs in using a catalyst made from iron cyanide at a pressure of 120 atm. (Harding, 1959)

The more important factors that differentiate processes are the various sources of hydrogen gas and nitrogen gas and methods used to purify them. These can be combined in many ways to provide a complete plant for making synthesis ammonia. The raw materials used for the production of hydrogen gas are:

1. Coal -- Although coal is the major fossil resource, the high investment required for using it as feedstock in an ammonia plant is a major handicap. This situation may change in the future as the cost of other fossil fuel feedstocks continue to rise.

2. Oil -- Use of oil as feedstock requires partial oxidation as the method for producing hydrogen. The cost of air liquefaction to supply oxygen for partial oxidation is a considerable drawback to the extent that very few of the newer plants use oil.

3. Natural gas -- The purity and relatively low cost of natural gas make it the preferred feedstock where available. It can be said that modern ammonia technology is based mainly on natural gas.

4. Naphtha -- Where natural gas is not available, naphtha, a low boiling petroleum fraction, is usually the best choice. It behaves almost like natural gas in hydrogen production.

5. Coke oven gas -- Of the several by-product sources, the hydrogen present in coke oven gas is the most important. Several metallurgical companies in the United States and Europe freeze out the components other than hydrogen in their coke oven gas and use the hydrogen to make ammonia.

The process differences due to raw materials used can then be classified into three categories:

1. The light hydrocarbon process
2. The heavy hydrocarbon process
3. Coal-based ammonia synthesis process

Each process will serve 3 main functions:

1. The production of hydrogen gas
2. The production of nitrogen gas
3. The synthesis of ammonia

The process of hydrogen gas manufacturing is the main unit that differentiates the process while supply of nitrogen gas is mostly from the air.

Under typical conditions the approximate quantities of alternative raw materials required to make 1 ton of ammonia (i.e. about 2,100 m³ of hydrogen gas) are: 1.5 tons coke or coal; 800 m³ natural gas; 3,500 m³ coke oven gas, 2,500 m³ refinery gas or 0.7 ton fuel oil. (Harding, 1959)

2.2.1 Light Hydrocarbon Process

The raw material for this process includes natural gas and naphtha. Most of the world ammonia plants use natural gas and naphtha as raw materials. Natural gas constitutes 72% of raw material for hydrogen gas production in the United States in 1957, 50% of Italian hydrogen production in the same year and approximately 60-65% ammonia production of the world in 1973. (Le Blanc et al, 1979)

Natural gas is an ideal raw material to produce ammonia as it can readily form with water to release hydrogen gas, one of the main reactants to form ammonia, the other reactant is nitrogen. The other

as raw materials. Natural gas constitutes 72% of raw material for hydrogen gas production in the United States in 1957, 50% of Italian hydrogen production in the same year and approximately 60-65% ammonia production of the world in 1973. (Le Blanc et al, 1979).

Natural gas is an ideal raw material to produce ammonia as it can readily form with water to release hydrogen gas, one of the main reactants to form ammonia, the other reactant is nitrogen. The other carbonaceous raw materials has to be cracked to methane first, while natural gas consists mostly of methane. Catalytic reforming of methane was developed since 1822-1829, but the use of methane on a large scale has to wait after the natural gas development, that is the development of transporting the gas from the gasfield to the consumption area.

Hydrogen is formed from methane in the reforming and shift conversion reactions as follows:



Raw methane gas is often quite pure with a little of hydrogen sulphide and carbon dioxide or both. Normally gas delivered by pipelines was treated to the extent that it contains very little of either. The raw gas also contains small amounts of higher hydrocarbon. Table II-1 shows the typical composition of natural gas.

Table II-1 Typical Composition of Natural Gas

Constituents	% at well head	% as delivered by pipes
CH ₄	75.9	93.3
N ₂		2.0
Ar		0.4
CO ₂	7.3	0.01
H ₂ S	8.9	Less than 5 ppm
Hydrocarbons		
C ₂	3.3	3.3
C ₃	1.2	0.9
C ₄	0.8	0.2
C ₅	0.5	0.01
C ₆	2.3	---

In the area lacking natural gas, ammonia producers (notably United Kingdom) tends to use light petroleum distillates, naphtha. This process was developed by the Imperial Chemical Industry in England. Naphtha, has become a major feedstock for ammonia production in United Kingdom, Western Germany, India and Japan. In some areas, when natural gas was available after the introduction of naphtha, the process was shifted over to natural gas as it has been relatively easy to do so.

The process to manufacture ammonia of light hydrocarbon process can be sub-divided into:

1. Desulfurisation
2. Gas Reforming
3. Shift Conversion
4. Carbon Dioxide Removal
5. Final Purification
6. Compression
7. Synthesis Loop and Purges

The whole process is shown briefly in the block diagram in Figure II-4

In brief, natural gas, mainly methane, is passed through sulfur-compound removal equipment to remove hydrogen sulfide and COS. Sulfur compounds should be got rid of before other things as it poisons catalysts used in the process. The treated gas is preheated and mixed with steam to form hydrogen. There are several furnace designs in use, each with

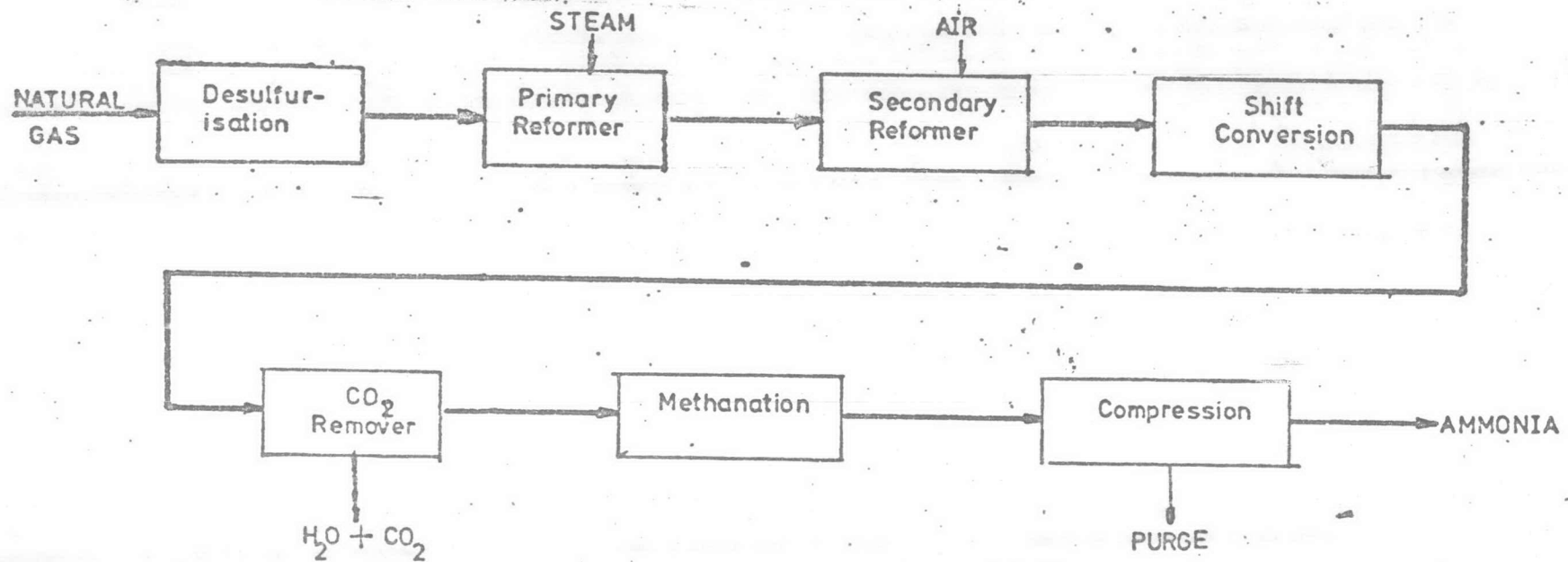


FIGURE II-4 Ammonia Synthesis from Natural Gas



particular advantages and disadvantages. This step is called primary reforming. It is done in the presence of nickel catalyst. Air is mixed in the secondary reforming process to supply nitrogen gas as well as to complete reaction of the feedstock. The hydrogen gas formed is favoured at high temperature, low pressure and excess of steam. As there are still carbon monoxide in the gas mixture, the gas is passed through another reactor called "shift converter" to form hydrogen from water and CO. A different catalyst, mostly iron oxides, is used in this step.

Before the ammonia synthesis, carbon dioxide formed in the gas mixture must be removed. It can be removed by any of several methods that have been developed, most of which involve a wet-scrubbing operation with an aqueous solution of an absorbent. Potassium carbonate, usually with small amounts of 'promoters' or 'activators', is a popular absorbent. Organic absorbents are also used.

A residual oxides and impurities will be harmful to the catalyst in the next reaction stage as it is quite sensitive to poisoning by oxides. The gas is therefore passed over another catalyst where the oxides react with hydrogen to give harmless methane.

Ammonia synthesis requires a higher pressure than for the purification step. The compressors used in the modern large plants are centrifugals, which require less investment than the older reciprocating type. Synthesis pressure is generally in the 2,500 to 3,500 psi range; few was built to operate at high pressure (8,000 psi and above).

Ammonia synthesis is not complete in one pass through the catalyst as equilibrium set up according to the law of le Chatelier. Unreacted gas is recirculated back over the same catalyst again and new fresh gas is added to replace the reacted-gas, ammonia.

Ammonia is removed by condensation. Purging was done to lower down the percentage of methane, argon and other impurities as they will accumulate in the process and decrease the rate of reaction.

Ammonia synthesis requires a large amount of energy in the form of steam and power, but offsetting this is the large release of heat by exothermic reactions involved. The problem is to recover this heat economically and use it in the process.

Each stage of the process will be discussed in details in the following parts.

Desulfurisation

Purity of process streams is of particular importance for steam reforming operations and other reaction process as catalysts may be poisoned by sulfur compounds. Natural gas usually contains from 1 to 15 per cent by volume of hydrogen sulphide, mercaptans $R.SH$, and other sulfur compounds. Catalysts in the ammonia synthesis process, namely, primary reforming catalyst, secondary steam-reforming catalyst, low temperature shift conversion catalyst, methanation (purification) catalyst and the ammonia synthesis catalyst, are all sulfur-sensitive catalysts, and some of these catalysts require complete removal of sulphur compounds, for

example, nickel catalyst is quite susceptible to poisoning by sulfur, even by as little as a few tenths of a ppm. This is also true for low-temperature shift catalysts, where the poisoning is irreversible. Thus practically all ammonia plant operated on natural gas are equipped with gas purification, even if for insurance only.

Processes to remove sulfur compounds are:

1. Adsorption on activated carbon.
2. Removal by chemical reaction with zinc oxide.
3. Hydrogenation to convert organic and sulfur compounds to hydrogen sulphide, followed by absorption of the hydrogen sulfide in zinc oxide, MEA or carbonate solution.
4. Adsorption on molecular sieves.
5. In case of large amounts of H_2S , absorption-stripping operation is used, followed by one of the above process to pick up trace amount of H_2S .

The most commonly used methods of removing sulfur are adsorption by activated carbon at about 60-120°F (Le Blanc et al, 1979). Frequent regeneration of the activated carbon adsorbent is required and is accomplished by heating the bed and stripping with steam or hot gases. High-boiling sulfur compounds, such as mercaptans, are more readily adsorbed than the low boiling compounds like H_2S . In addition, the presence of condensable hydrocarbons can rapidly saturate the adsorbent. Under such circumstances, the use of zinc oxide is advisable. Usually two beds of activated carbon are provided, one being on line while the other being

regenerated by steam.

Zinc oxide removes H_2S , mercaptans, and to some extent chlorine at temperatures of 600-750°F. Usually a zinc oxide bed is designed to adsorb sulfur to the extent of 18-20% of its weight before being discarded (Slack 1973). Activated carbon drums and zinc oxide can be used in series to remove different types of sulfur compounds. At temperatures of 660-750°F, mercaptans decompose to hydrocarbon and H_2S which then reacts with the zinc oxide. Usually a bed is replaced once a year.

For organic sulfur compounds not easily removed by activated carbon or zinc oxide, hydrodesulfurization is recommended. The organic sulfur is converted to H_2S in the presence of hydrogen over a cobalt or nickel molybdate catalyst at about 645-750°F. In addition to the hydrogenating catalyst bed at the top, the hydrodesulfurizer vessel normally contains a bed of zinc oxide at the bottom. If the natural gas contains relatively large quantities of both H_2S and unreactive organic sulfur, the hydrogenating catalyst bed is sand between two zinc oxide beds. More information on hydrogenolysis may be found in Catalyst Handbook (Philipson, 1970).

When natural gas contains large amounts of hydrogen sulfide; the use of any fixed bed desulfurization technique is impractical; hence hydrogen sulfide is removed in an absorption-stripping operation followed by a zinc oxide drum to pick up any residual H_2S .

Molecular sieves are not yet widely used for sulfur removal and operating information on this technique as applied to ammonia plants is scarce.

Detailed discussion of the sulphur removal system used in ammonia synthesis processes is given by Habermehl and Long (1974) and Kjeldgaard (1974).

Steam Reforming

The purified natural gas is compressed in the range of 25-35 atm, temperature elevated within the range of 1435-1560^oF (Slack 1973). Then it is mixed with high pressure steam, steam to carbon ratio being between 3-4. High value of steam to carbon ratio suppresses the deposition of carbon which causes the physical breakdown of catalysts. The mixture is then fed to the primary reformer where methane reacts with steam to form hydrogen and carbon oxide. A part of the hydrocarbon is converted to carbon monoxide which is to be reacted with steam to hydrogen and carbon dioxide in the next stage, the shift reaction.

Reforming step is divided into two stages: primary and secondary. Primary reforming will process the gas partially, having an outlet gas composition of 2-10% residual methane (on dry basis). The effluent gas from the primary reformer is passed to the unheated secondary reformer which usually operates at 165-670 psig and at a temperature of 1780-1830^oF. Air is introduced at a temperature of 1200^oF in an amount to provide an oxygen to molar dry gas ratio of between 0.05 to 0.15, or enough to make

the final hydrogen to nitrogen ratio of 3:1. Exit gas from the secondary reformer will contain about 0.2-0.4 per cent methane, at a temperature range of 1700-1800°F.

Basic reactions for steam reforming are:



Method of calculating the exit gas composition from the reformer is shown in the appendix of the Catalyst Handbook (Bridger & Chin Chen, 1970), rapid calculation of gas yield from steam reforming is given by Stanbridge (1975). The details of design consideration are discussed extensively by Russell (1974). The thermodynamic data of the reforming reaction are given by Atwood & Knight (1973).

The catalyst used in the primary reformer is nickel supported on alumina. In operations at higher pressure and temperature, calcium aluminate has generally replaced calcium aluminum silicate as a support material in order to avoid silica migration.

The nickel content ranges from 12 to 22%. However, other materials are also found practical, but less effective, such as Cobalt, Platinum, Palladium, Iridium, Rhuthenium, Rhenium are more active than nickel on a weight basis, but their costs per unit activity are higher than nickel and make it beyond practice. Nickel present in fresh catalyst is in the form of nickel oxide, NiO, which is reduced to the metal in the reformer immediately before use.

Activity in the secondary reformer is less important than in the primary one. A typical secondary reforming catalyst contains 14% Ni, 15% CaO, and 67% Al_2O_3 .

Nickel catalysts are poisoned by sulphur, arsenic, halogens, phosphorus and lead. A discussion of catalyst poisoning is given by Bridger and Chin Chen (1970).

As air is added in the secondary reformer, part of the residual methane is burnt and its concentration is lowered from about 7% to 0.3%, giving a typical gas composition by volume:

H_2	N_2	CO_2	CO	CH_4	Ar
57	balance	8.0	12	Balance	

Methane concentration must be kept as low as possible because it is not reduced in the gas purification process and will affect the ammonia synthesis system.

Shift Conversion

The oxides of carbon deactivating the ammonia synthesis catalyst must be removed before going to the synthesis loop. Carbon dioxide is more easy to remove than carbon monoxide, so the latter is shifted to the former in another unit process.

In order to maximise yield, shift conversion is divided into two parts, high temperature gas shift and low temperature gas shift. The high temperature gas shift is operated at 660-850°F and pressures up to 30 atm.

The exit gas temperature is then reduced by the use of a heat exchanger to 350-550°F. Most of the remaining CO is shifted to CO₂, leaving the effluent gas of approximately 0.2 mole per cent carbon monoxide.

Catalysts used in the hot temperature shift consists mainly of iron oxide (85%) and chromium oxide. Phosphorus, arsenic, and large amounts of sulfur are poisonous to the catalyst. Small quantities of sulfur are not poisonous but should be avoided.

In the low temperature shift, copper oxide supported on zinc oxide and alumina and consists mainly of 30-45% CuO, 45-50% ZnO and 10-20% alumina, is used as catalyst as copper is a highly active catalyst for the shift conversion of CO as well as effective at lower temperatures. However, this catalyst is extremely sensitive to deactivation and poisoning by sulfur and chlorine.

The detailed consideration of shift converter design, derivation of kinetic rate equations, and plant and equipment description are given by Borgars and Campbell (1974).

A typical composition by volume of this exit gas is

H ₂	N ₂	CO ₂	CO	CH ₄	Ar	
61	balance	18.2	0.3	balance		%

Carbon Dioxide Removal

Effluent gases from the shift converters contains about 17-19% CO₂ and sometimes reaching 30%. This is undesirable because it poisons

the ammonia synthesis catalyst. It must, therefore, be reduced to a few ppm, in 2 steps, first in a bulk removal and then in a final purification step.

Commercial CO₂ removal systems can be broadly classified as reaction, combined reaction-physical, and physical-absorption systems. The processes generally have an absorber-stripper configuration. Table II-2 compares the main features of various CO₂ removal systems. The commonly used systems are:

MEA Process Acid gases may be removed by mono-di-or occasionally triethanolamine. In purifying synthesis gas, scrubbing with an aqueous solution (15-20 wt. %) of monoethanolamine (MEA) is a standard method for removing CO₂.

Excessive temperatures or localized overheating in reboilers cause the MEA to decompose and form corrosive compounds. An inhibitor systems, such as the amine guard system developed by Union Carbide (Quartulli, 1977), is an effective method of corrosion control.

The solution is regenerated by heating as well as by lowering the pressure. The details and design consideration of the process are provided by Jackson (1974) and Strelzoff (1974).

Activated Carbonate Process This process was developed by the US Bureau of Mines in 1950 for a less expensive method. The process comparison of MEA-Carbonate systems is available (Benson 1974). This process is based on absorption of CO₂ by potassium carbonate to give potassium bicarbonate.

Table II-2 Acid Gas Treating Processes

Process	Solvent	Solution Circulation	Acid gas content in treated gas
Reaction Systems			
MEA	20% monoethanolamine	medium	less than 50 ppm
Promoted MEA	25-35% monoethanolamine plus Amine Guard	medium	less than 50 ppm
DGA	60% diglycol amine	medium	less than 100 ppm
Vetrocoke	K ₂ CO ₃ plus As ₂ O ₃ -glycine	high	500-1,000 ppm
Carsol	K ₂ CO ₃ plus additives	high	500-1,000 ppm
Catacarb	25-30% K ₂ CO ₃ plus additives	high	500-1,000 ppm
Benfield	25-30% K ₂ CO ₃ plus diethanolamine and additives	high	500-1,000 ppm
Lurgi	25-30% K ₂ CO ₃ plus additives	high	500-1,000 ppm
Alkazid	potassium salt of 2-(or 3-) methylamino propionic acid	dependent on service	dependent on service
Combination reaction-physical systems			
Sulfinol	sulfolane and 1, 1' -imminobis-2-propanol	medium	less than 100 ppm
TEA-MEA	triethanolamine and monoethanolamine	high (TEA)	less than 50 ppm
Physical absorption systems			
Purisol (NMP)	N-methyl-2-pyrrolidinone	medium	less than 50 ppm
Rectisol	methanol	medium	less than 10 ppm
Fluor solvent	propylene carbonate	dependent on pressure	dependent on pressure
Selexol	dimethyl ether of polyethylene glycol	dependent on pressure	dependent on pressure

Reference: Le Blanc et al, 1979



When the bicarbonate is heated it releases CO_2 , regenerating potassium carbonate. Various additives improve the mass transfer rate and inhibit corrosion. This process generally use less reboiler heat than the MEA process, but its tower is generally bigger than MEA tower. The choice of a specific CO_2 removal system depends on the overall ammonia plant design and on how well a specific process can be integrated with the rest of the plant. The details of various types of this process can be found from Field (1974), Benson (1974), Eichmeyer (1974), and Giammarco (1974). Data on potassium carbonate solution in the process can also be found from Strelzoff (1974).

The details of selection criteria for carbon dioxide removal are given by Thirkell (1974) and Strelzoff (1975).

Final Purification Before ammonia synthesis, residual carbon monoxide and carbon dioxide must be either removed or converted to inert species, since any oxygen or oxygen compounds entering the synthesis loop poisons the catalyst. Carbon dioxide and carbon monoxide must be reduced to a total of less than 15 ppm. Two major processes are practical nowadays.

a. Methanation Process The methanation reactions are the reverse of the reforming reactions. Any oxygen present in the synthesis gas will react with hydrogen to produce steam. The CO and CO_2 content of the treated gas is of the order of a few ppm. A methanator typically operates in the temperature range of $570\text{-}750^\circ\text{F}$. Since these reactions are strongly exothermic, the CO and CO_2 at the inlet should be carefully monitored to avoid

damage to catalyst and vessel.

Most commercial methanator catalysts contain nickel supported on alumina, kaolin, or calcium aluminate cement. Sulfur and arsenic are catalyst poisons. The design and operation of methanators is given by Allen and Yen (1973) and the application of methanation is given by Phillips (1974).

b. Copper Liquor Scrubbing The cuprous diammine ion $\text{Cu}(\text{NH}_3)_2^+$ present in ammoniacal solutions of copper salts has the property of reacting reversibly with carbon monoxide in the presence of more ammonia to form another complex ion:



The scrubbing solvent contains both a cupric and a cuprous ammonical salt of acid, such as formic, acetic or carbonic, plus an excess of ammonia.

The absorption is under high pressure and low temperature (32°F) and the regeneration is done by heating the solvent to about 175°F and at low pressure (0.1-18.5 psig). This process is rather expensive and is energy consuming, but it has the advantages that it removes carbon monoxide from the system rather than converting it to methane as in the methanation process. The details of this process are given by Kohl and Riesenfeld (1960) and Allgood (1974).

Ammonia Synthesis

After hydrogen production, the addition of nitrogen, and the purification of the raw gas, the synthesis gas is ready for compression and ammonia manufacture in a synthesis loop. The modern loops all recycle the unreacted gases because of equilibrium limitations. The loops differ in terms of the pressure used and the point at which ammonia is recovered.

As ammonia synthesis is a high pressure process, the low pressure synthesis gas from the final purification process must be compressed before entering the ammonia synthesis system. Reciprocating compressors are normally used in small capacity plants, i.e., those below 600 tons per day, while centrifugal compressors are more favourable for high capacity plants. The economic consideration is cited by Noyes (1967). In high capacity ammonia plants, the overall capital cost savings when using centrifugal compressors are up to ten per cent as compared to the use of reciprocating compressors.

To some degree, the arrangement of the synthesis loop, the compressor selection, and the coolant used for ammonia recovery are influenced by the pressure chosen. Currently the operating pressure for most modern synthesis loops fall in the range of 2,000-5,000 psi. Plants designed before 1964 tended to favour the region above 4,500 psi whereas new plants favor the lower range. The economics of the more recent large tonnage ammonia plants is more favorable at these pressure because of the reduction in compression power (Le Blanc et al, 1979)

Quartulli, Fleming and Finneran suggest 2,000-2,200 psi as an economically acceptable pressure for plants of 544-907 t/d capacity. Even

for large tonnage plants of the order of 1,361 t/d, based on horsepower alone, 2,200 psi was optimal. The economic advantages, however, between this pressure and 4,750 psi was small and because of other considerations, such as ammonia converter size, the pressure range of 3,000-3,200 was recommended (Le Blanc et al 1979).

The catalyst is contained in large pressure vessels or converters each of which may weight 100 tons or more. A typical converter contains about 100 cub. ft., 7.5 tons of catalyst in pieces about the size of a pea as well as heat exchangers and other equipment. The catalyst itself is normally prepared by mixing oxides of iron with small quantities of promoters (aluminium oxide, potassium hydroxide, etc.) and fusing the mixture at a high temperature.

No synthesis reaction will take place until the catalyst has attained a certain minimum temperature, which depends on its activity but is usually about 660 to 750°F. For this reason, a heater, either electric or gas fired, must be used to heat the synthesis gas when starting up.

The net rate of reaction is the difference between the rate of the forward reaction and the reverse one:



As reverse reaction also occurs at the same time, and as equilibrium of ammonia synthesis tends to the right as temperature is decreased, the catalyst bed (later part) should be cooled down, and most ingenuity has gone into different designs for equipment to make the temperature in

the catalyst bed follow more closely the optimum. Cooling can be done by tubes embedded in it through which cold inlet synthesis gas passes, by direct admission of cold synthesis gas at one or several points through the lengths of the bed, or by cold coil in which water is heated.

The exit gas from the converter containing 10 to 20% ammonia and at 212 to 392°F are cooled down to atmospheric temperature by water cooling whereupon some ammonia condenses and is collected in Catchpots. In some plants the gas, still containing 6% to 7% ammonia, is then recycled to the converter. In others, more ammonia is removed by refrigerating the gas to -4 °F, the recycled gas then contains 1 to 2% ammonia. Alternatively ammonia may be removed in aqueous solution by washing the gas with water.

A part of the uncondensed, unreacted hydrogen and nitrogen stream together with a small amount of inert gases: argon and methane, which are not harmful to the catalyst and take no part in the reaction, is purged or else the impurities will accumulate in the system and the rate of synthesis would fall away to zero. A small amount of ammonia will also be in the purged gas and can be recovered by absorption with water. The design and operation of synthesis loop is given by Finneran (1977).

2.2.2 The Heavy hydrocarbon Process

Heavy hydrocarbons used range from naphtha to fuel oil. Partial oxidation processes are employed as steam-reform feeds are not available or favourable economic conditions demand. It was developed after the World War II.

As this process produces hydrogen by the oxidation of the feedstock, hydrogen is generated less than by steam reforming. Consequently, in the manufacture of hydrogen for ammonia synthesis, partial oxidation process require more feed which leads to larger CO₂ removal facilities. In addition, the raw synthesis gas generated by partial oxidation is much high in CO content than that coming from a steam-reforming operation, which requires larger facilities, both equipment and catalyst, for shift conversion. These factors demand higher investment and operating costs. Partial oxidation processes are therefore normally employed for coal or heavy hydrocarbon feeds, materials which cannot be handled by steam reforming. The production cost of ammonia by this process is about 50% more if based on natural gas and 100% more if based on coal (Lowenheim, 1975).

Two major commercial processes for heavy hydrocarbon are available, Shell and Texaco, accounting for 11-12% of world ammonia production. Operating conditions in the gas generator vary from 1200-1370°C and 465-1215 psi. In general, heavy oils are the hydrocarbon feeds; however, feeds from natural gas to residual oils can be accommodated. In the Shell gasification process preheated hydrocarbon feed and oxygen are mixed with steam and fed to the combustion chamber of the reactor. A non-catalytic flame reaction takes place to produce the raw synthesis gas. The hot reactor effluent is cooled and the raw synthesis gas routed to the carbon removal system. The carbon is removed as a water slurry and carbon-oil pellets are formed in a device called a pelletizer. Figure II-5 shows

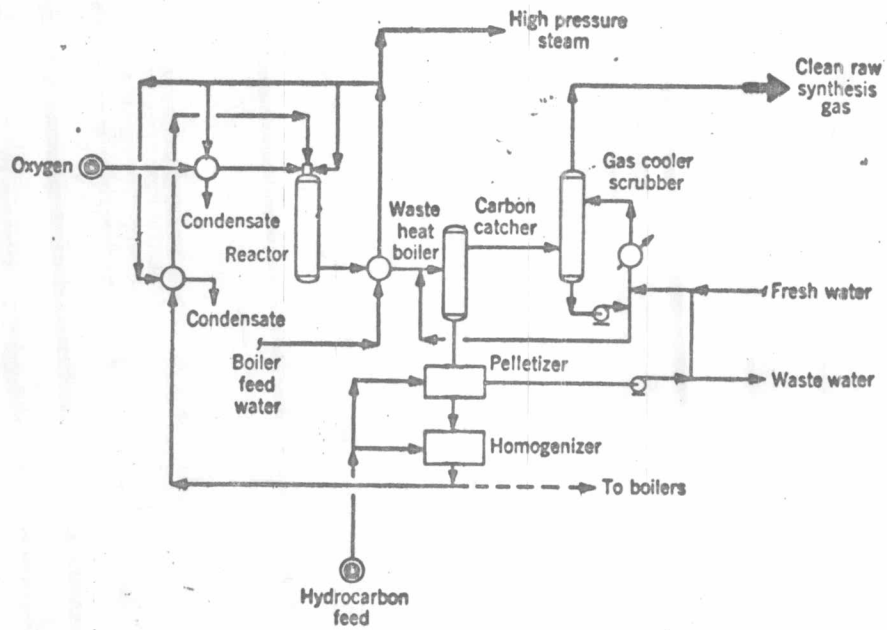


Figure II-5. Shell Gasification Process

the flow of the process.

In the Texaco gasification process preheated hydrocarbon with oxygen and steam are fed to the reactor. The hot raw synthesis gas is quenched with a hot water stream from the scrubber, removing most of the remaining carbon. The water stream containing carbon is mixed with naphtha which preferentially removes the carbon in the naphtha separator. The lighter naphtha-carbon layer is mixed with incoming hydrocarbon feed and the resultant mixture is processed in the naphtha stripper. From the overheads, naphtha is recycled to the carbon extraction step. The bottoms (a hydrocarbon stream containing carbon) is recycled to the reactor. The water from the naphtha separator, after the degassing, is routed back to the scrubber. The clean raw synthesis gas is now available for further processing. The diagram for this process is shown in Figure II-6.

2.2.3 Coal-based Partial Oxidation Process

The heart of a coal-based partial oxidation process is the gasification step. The two important commercial processes are the Lurgi and Koppers-Totzek.

In the Lurgi Process (Quartulli, 1977), coal is gasified in a fixed-bed reactor using oxygen and steam at about 20-30 atm. The ash is removed in a non-slagging operation by the rotary grate. Depending on the feed characteristics, gasification temperatures range from about 1040 to 1150°F. At this temperature and relatively high pressure, the methane and carbon dioxide content of the crude gas is considerably greater than in conventional reforming and partial oxidation processes,

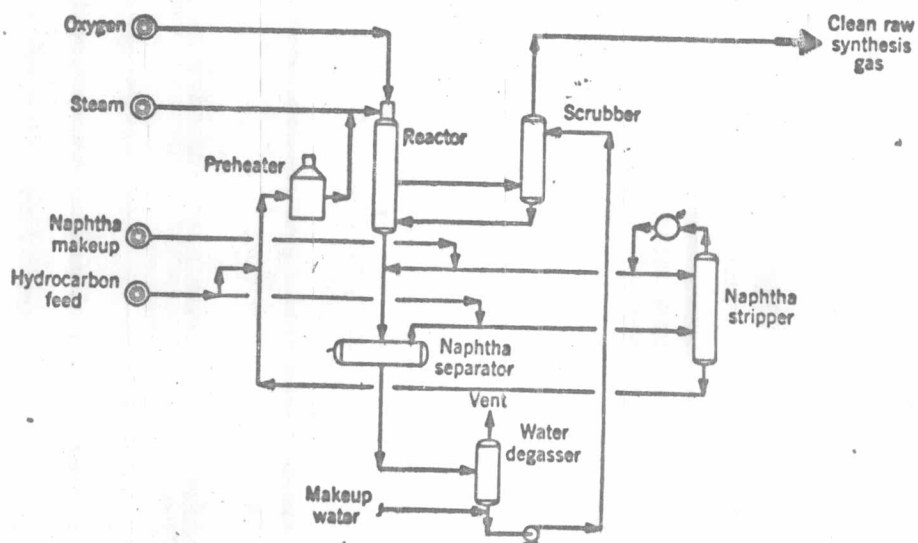


Figure II-6. Texaco Gasification Process

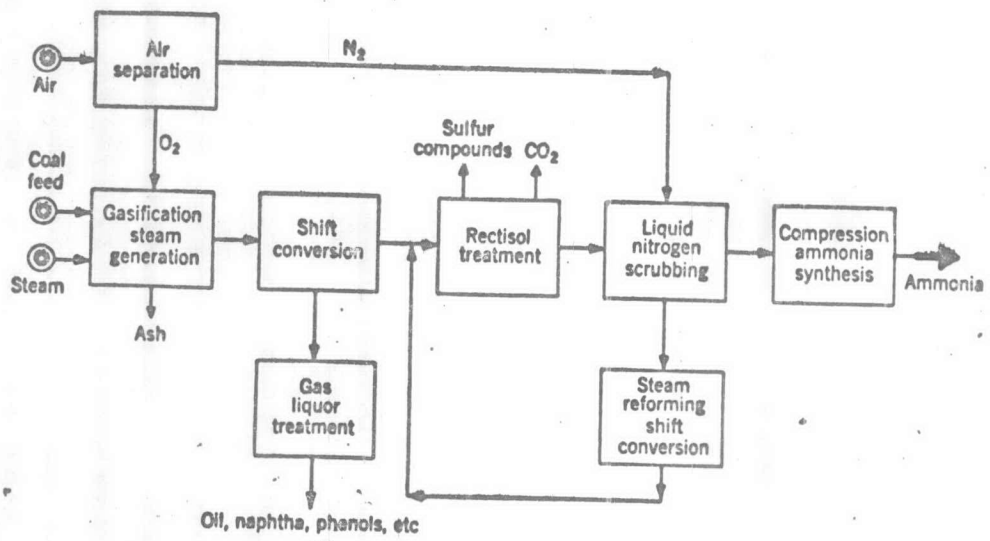


Figure II-7. Ammonia via Lurgi Coal Gasification

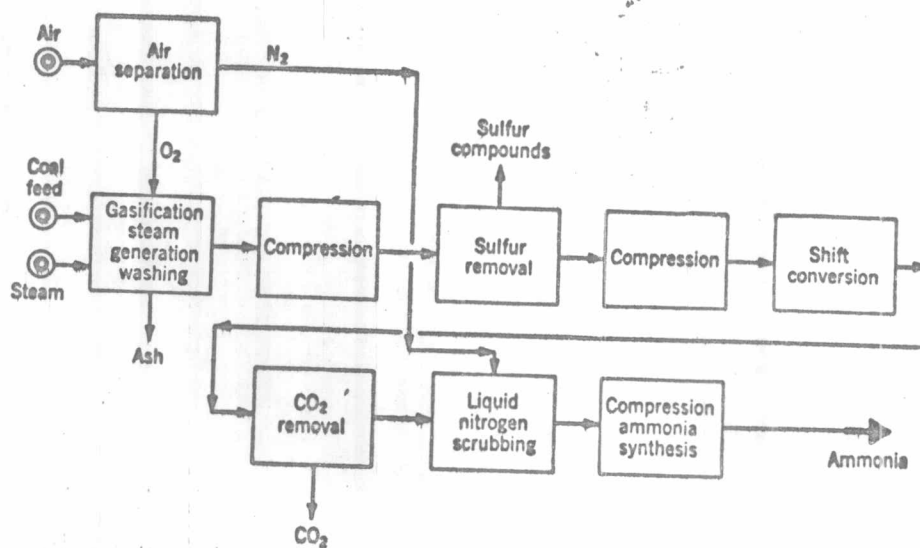


Figure II-8. Ammonia via Koppers-Totzek Coal Gasification

directed toward the manufacture of substitute natural gas rather than synthesis gas. With the current energy problem and the rising costs for both natural gas and light hydrocarbons, the use of coal as an ammonia feedstock is again being considered (Le Blanc et al 1979).

2.3 Future Development

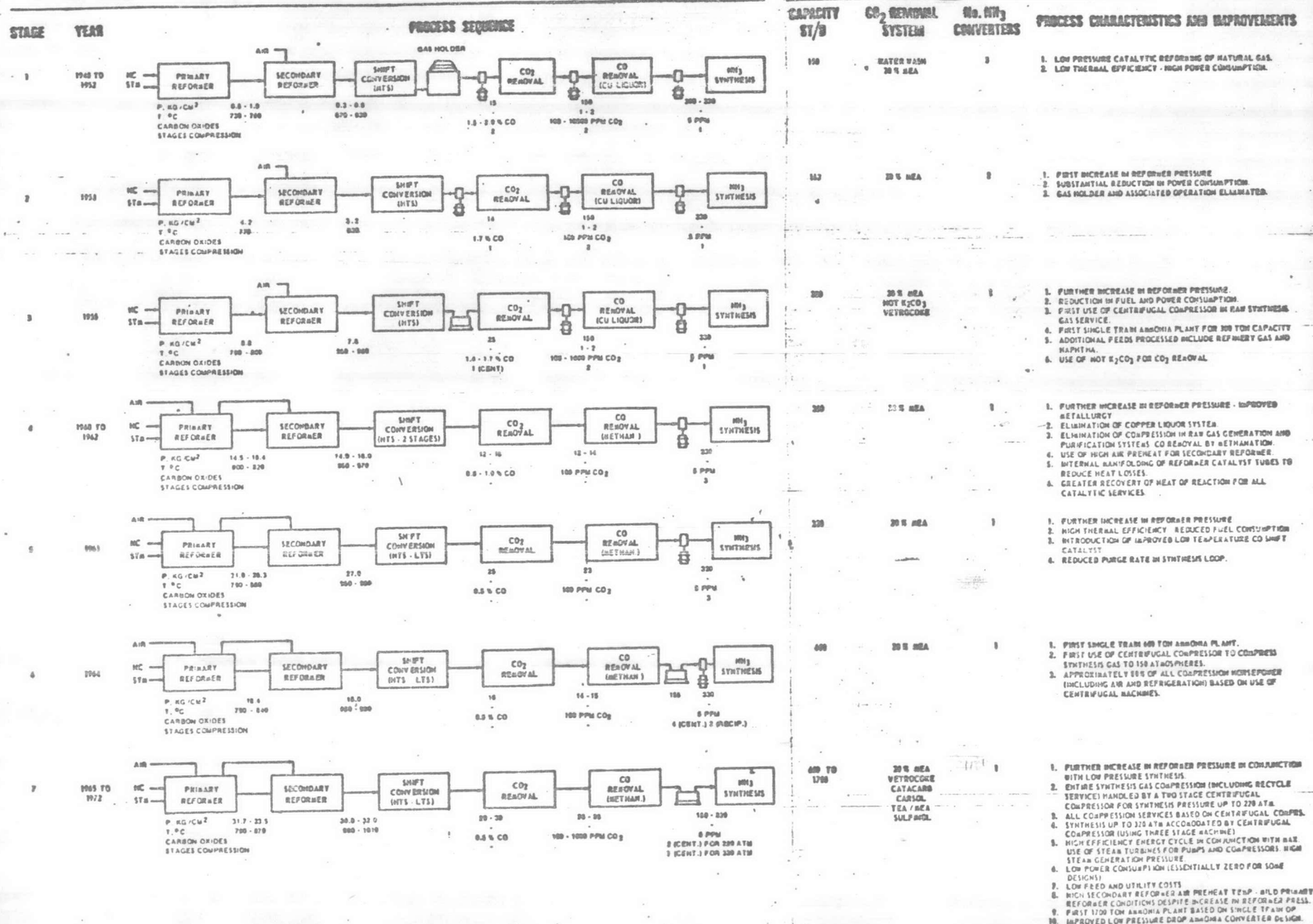
Ammonia production process in single train utilizing natural gas as raw material has developed since 1910 and up to 1965 few plants with 600 t/d capacity was built. But after 1965 plants with capacity of over 600 t/d has increased, and the trend of the capacity is increasing. The trend of increasing capacity is shown in Figure II-2.

The increased capacity gave an advantage in capital and operating cost because of size and better heat recovery. This makes the cost of the ammonia per ton lower. Production cost decreased during the period of the 1960-1970 decade when large plants based on use of centrifugal compressors became common. Typical production cost per short ton of ammonia was about \$33 and in 1970 about \$20 or less (Slack 1973). The stages of development of modern ammonia plant from 1940 to 1972 is in Figure II-9.

The improvement in the design of large-scale ammonia plants is in efficient energy cycle. The basic concepts are to:

1. minimize the thermal requirements for process operation;
2. optimize the process operating conditions;
3. intergrate the process with the energy systems; and
4. select rotating machinery that satisfies power demands and makes the maximum use of available thermal energy.

Figure II-9. Stages in the Development of Modern NH₃ Process.



All the above includes the development and use of a centrifugal compressor, better heat recovery of the energy loop, improved catalyst, better welding, better corrosion inhibitor, which account for a more economical cost.

A good example of minimizing the thermal requirements is the use of a CO₂ removal system requiring a relatively low energy input.

Consideration should also be given to the reforming pressure which in most older ammonia plants was kept below 2.5 psi. Thus makeup synthesis gas was available at a relatively low pressure, requiring large amounts of compression energy to achieve synthesis-loop operating pressures. Increasing the operating pressure of the reforming section leads to a reduction in synthesis gas compression. Most modern large-scale plants operate at a reforming pressure of 415-515 psi. Final design considerations in this regard include air compression requirements, reformer metallurgy, synthesis loop pressure, rotating equipment availability, and plant size, to mention a few.

The design of modern ammonia plants reflects a high degree of intergration between the process and energy systems. Waste process heat is used to provide energy for boiler-feedwater heating and steam generation. Energy recovery in the convection section of the primary reformer includes satisfying similar utility demands of boiler feedwater heating, and steam generation and superheating.

In most ammonia older plants, pumps and compressors were motor

driven. Through the use of high pressure steam generation and the selection of expansion and condensing turbines, it is possible to satisfy driver requirements with little or no imported power.

The mentioned development all account as major factors in lower production cost. They come with the new plant size. The largest size reported so far is 1500 t/d (1973) in a single train, but future plants may produce 3000 t/d or more. Other developments may be expected in higher reforming pressure, better catalysts, and lower cost removal of carbon dioxide.

The prices and supply of hydrocarbon feedstock may, in the future, force the ammonia-production process to other kinds of raw material or processes. For example, the use of waste heat from nuclear installations, the use of thermal energy from the ocean (Le Blanc et al 1979). The details of the production of ammonia through electrolysis are discussed by Mrochek (1973).