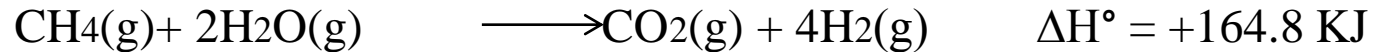


Lecture Eight

The main steam reforming reactions are:



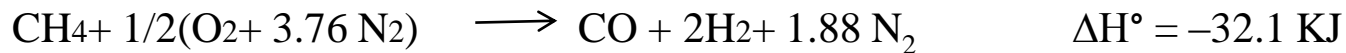
$$\Delta H^\circ_{800^\circ\text{C}} = +226 \text{ KJ}$$



For the production of methanol, this mixture could be used directly with no further treatment except adjusting the $\text{H}_2/(\text{CO} + \text{CO}_2)$ ratio to approximately 2:1.

For producing hydrogen for ammonia synthesis, however, further treatment steps are needed. First, the required amount of nitrogen for ammonia must be obtained from atmospheric air. This is done by partially oxidizing unreacted methane in the exit gas mixture from the first reactor in another reactor (secondary reforming).

The main reaction occurring in the secondary reformer is the partial oxidation of methane with a limited amount of air. The product is a mixture of hydrogen, carbon dioxide, carbon monoxide, plus nitrogen, which does not react under these conditions. The reaction is represented as follows:



The reactor temperature can reach over 900°C in the secondary reformer due to the exothermic reaction heat. Typical analysis of the exit gas from the primary and the secondary reformers is shown in Table 5-1.

The second step after secondary reforming is removing carbon monoxide, which poisons the catalyst used for ammonia synthesis. This is done in three further steps, shift conversion, carbon dioxide removal, and methanation of the remaining CO and CO₂.

Table 5-1

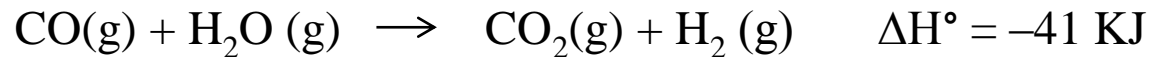
Typical analysis of effluent from primary and secondary reformers

Constituent	Primary reformer	Secondary reformer
H ₂	47	39.0
CO	10.2	12.2
CO ₂	6.3	4.2
CH ₄	7.0	0.6
H ₂ O	29.4	27.0
N ₂	0.02	17.0

Shift Conversion

The product gas mixture from the secondary reformer is cooled then subjected to shift conversion.

In the shift converter, carbon monoxide is reacted with steam to give carbon dioxide and hydrogen. The reaction is exothermic and independent of pressure:



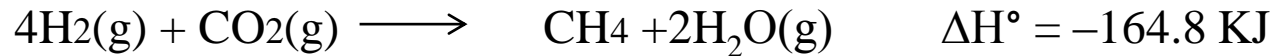
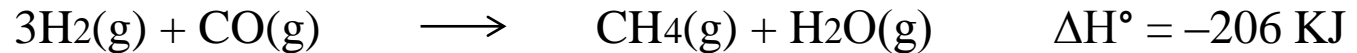
The feed to the shift converter contains large amounts of carbon monoxide which should be oxidized. An iron catalyst promoted with chromium oxide is used at a temperature range of 425–500°C to enhance the oxidation.

Exit gases from the shift conversion are treated to remove carbon dioxide. This may be done by absorbing carbon dioxide in a physical or chemical absorption solvent or by adsorbing it using a special type of molecular sieves. Carbon dioxide, recovered from the treatment agent as a byproduct, is mainly used with ammonia to produce urea. The product is a pure hydrogen gas containing small amounts of carbon monoxide and carbon dioxide, which are further removed by methanation.

Methanation

Catalytic methanation is the reverse of the steam reforming reaction.

Hydrogen reacts with carbon monoxide and carbon dioxide, converting them to methane. Methanation reactions are exothermic, and methane yield is favored at lower temperatures:



The forward reactions are also favored at higher pressures. However, the space velocity becomes high with increased pressures, and contact time becomes shorter, decreasing the yield. The actual process conditions of pressure, temperature, and space velocity are practically a compromise of several factors. Rany nickel is the preferred catalyst. Typical methanation reactor operating conditions are 200–300°C and approximately 10 atmospheres. The product is a gas mixture of hydrogen and nitrogen having an approximate ratio of 3:1 for ammonia production. Figure 5-2 shows the ICI process for the production of synthesis gas for the manufacture of ammonia.

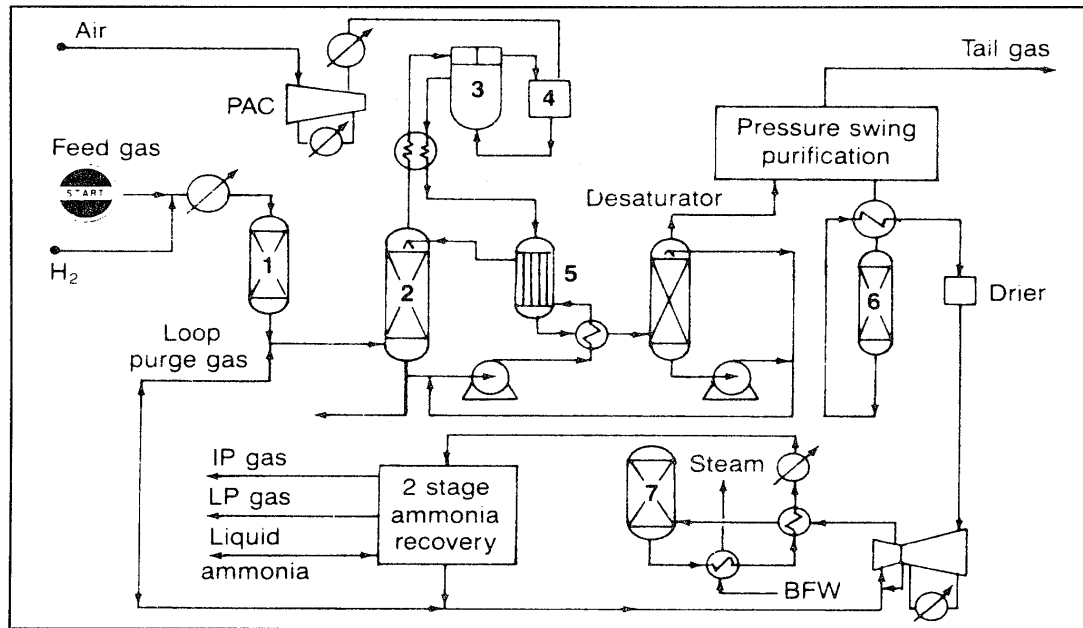


Figure 5-2. The ICI process for producing synthesis gas and ammonia:(1) desulfurization,(2) feed gas saturator,(3) primary reformer(4) secondary reformer, (5)shiftconverter,(6) methanator,(7) ammonia reactor.

CHEMICALS BASED ON SYNTHESIS GAS

Many chemicals are produced from synthesis gas. This is a consequence of the high reactivity associated with hydrogen and carbon monoxide gases, the two constituents of synthesis gas. The reactivity of this mixture was demonstrated during World War II, when it was used to produce alternative hydrocarbon fuels using Fischer Tropsch technology. The synthesis gas mixture was produced then by gasifying coal.

Synthesis gas is also an important building block for aldehydes from olefins. The catalytic hydroformylation reaction (Oxo reaction) is used with many olefins to produce aldehydes and alcohols of commercial importance.

The two major chemicals based on synthesis gas are ammonia and methanol. Each compound is a precursor for many other chemicals. From ammonia, urea, nitric acid, hydrazine, acrylonitrile, methylamines and many other minor chemicals are produced (see Figure 5-1). Each of these chemicals is also a precursor of more chemicals.

Methanol, the second major product from synthesis gas, is a unique compound of high chemical reactivity as well as good fuel properties. It is a building block for many reactive compounds such as formaldehyde, acetic acid, and methylamine. It also offers an alternative way to produce hydrocarbons in the gasoline range (Mobil to gasoline MTG process). It may prove to be a competitive source for producing light olefins in the future.

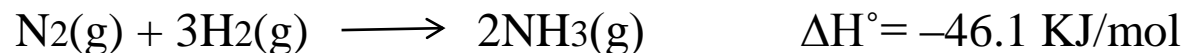
AMMONIA (NH₃)

Ammonia is one of the most important inorganic chemicals, exceeded only by sulfuric acid and lime. This colorless gas has an irritating odor, and is very soluble in water, forming a weakly basic solution. Ammonia could be easily liquefied under pressure (liquid ammonia), and it is an important refrigerant. Anhydrous ammonia is a fertilizer by direct application to the soil. Ammonia is obtained by the reaction of hydrogen and atmospheric nitrogen, the synthesis gas for ammonia. The 1994 U.S. ammonia production was approximately 40 billion pounds (sixth highest volume chemical).

Ammonia Production (Haber Process)

The production of ammonia is of historical interest because it represents the first important application of thermodynamics to an industrial process. Considering the synthesis reaction of ammonia from its elements, the calculated reaction heat (ΔH) and free energy change (ΔG) at room temperature are approximately -46 and -16.5 KJ/mol, respectively.

Although the calculated equilibrium constant $K_c = 3.6 \times 10^8$ at room temperature is substantially high, no reaction occurs under these conditions, and the rate is practically zero. The ammonia synthesis reaction could be represented as follows:



Increasing the temperature increases the reaction rate, but decreases the equilibrium ($K_c @ 500^\circ\text{C} = 0.08$). According to LeChatlier's principle, the equilibrium is favored at high pressures and at lower temperatures. Much of Haber's research was to find a catalyst that favored the formation of ammonia at a reasonable rate at lower temperatures. Iron oxide promoted with other oxides such as potassium and aluminum oxides is currently used to produce ammonia in good yield at relatively low temperatures.

In a commercial process, a mixture of hydrogen and nitrogen (exit gas from the methanator) in a ratio of 3:1 is compressed to the desired pressure (150–1,000 atmospheres). The compressed mixture is then preheated by heat exchange with the product stream before entering the ammonia reactor. The reaction occurs over the catalyst bed at about 450°C . The exit gas containing ammonia is passed through a cooling chamber where ammonia is condensed to a liquid, while unreacted hydrogen and nitrogen are recycled (see Figure 5-2). Usually, a conversion of approximately 15% per pass is obtained under these conditions.

Uses of Ammonia

The major end use of ammonia is the fertilizer field for the production of urea, ammonium nitrate and ammonium phosphate, and sulfate.

Anhydrous ammonia could be directly applied to the soil as a fertilizer.

Urea is gaining wide acceptance as a slow-acting fertilizer.

Ammonia is the precursor for many other chemicals such as nitric acid, hydrazine, acrylonitrile, and hexamethylenediamine. Ammonia, having three hydrogen atoms per molecule, may be viewed as an energy source. It has been proposed that anhydrous liquid ammonia may be used as a clean fuel for the automotive industry. Compared with hydrogen, anhydrous ammonia is more manageable. It is stored in iron or steel containers and could be transported commercially via pipeline, railroad tanker cars, and highway tanker trucks.

The oxidation reaction could be represented as:

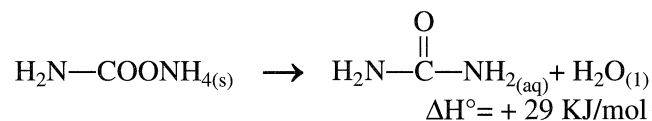


Only nitrogen and water are produced. However, many factors must be considered such as the coproduction of nitrogen oxides, the economics related to retrofitting of auto engines, etc. The following describes the important chemicals based on ammonia.



The highest fixed nitrogen-containing fertilizer 46.7 wt %, urea is a white solid that is soluble in water and alcohol. It is usually sold in the form of crystals, prills, flakes, or granules. Urea is an active compound that reacts with many reagents. It forms adducts and clathrates with many substances such as phenol and salicylic acid. By reacting with formaldehyde, it produces an important commercial polymer (urea formaldehyde resins) that is used as glue for particle board and plywood.

Production. The technical production of urea is based on the reaction of ammonia with carbon dioxide:



The reaction occurs in two steps: ammonium carbamate is formed first, followed by a decomposition step of the carbamate to urea and water. The first reaction is exothermic, and the equilibrium is favored at lower temperatures and higher pressures. Higher operating pressures are also desirable for the separation absorption step that results in a higher carbamate solution concentration. A higher ammonia ratio than stoichiometric is used to compensate for the ammonia that dissolves in the melt. The reactor temperature ranges between 170–220°C at a pressure of about 200 atmospheres.

The second reaction represents the decomposition of the carbamate. The reaction conditions are 200°C and 30 atmospheres. Decomposition in presence of excess ammonia limits corrosion problems and inhibits the decomposition of the carbamate to ammonia and carbon dioxide. The urea solution leaving the carbamate decomposer is expanded by heating at low pressures and ammonia recycled. The resultant solution is further concentrated to a melt, which is then prilled by passing it through special sprays in an air stream. Figure 5-3 shows the Snamprogetti process for urea production.

Uses of Urea. The major use of urea is the fertilizer field, which accounts for approximately 80% of its production (about 16.2 billion pounds were produced during 1994 in U.S.). About 10% of urea is used for the production of adhesives and plastics (urea formaldehyde and melamine formaldehyde resins). Animal feed accounts for about 5% of the urea produced.

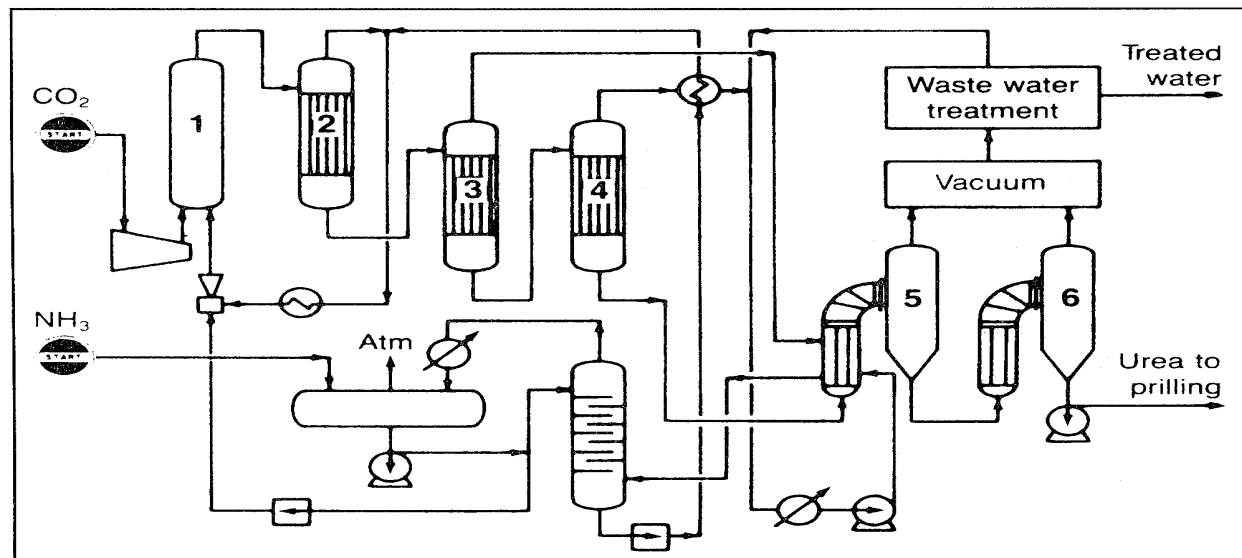


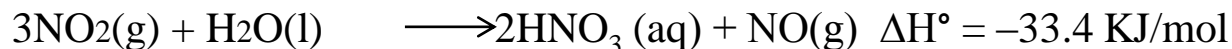
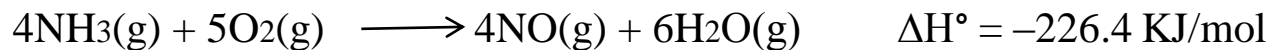
Figure 5-3. The Snamprogetti process for producing urea: (1) reactor, (2,3,4) carbamate decomposers, (5,6) crystallizing and prilling.

Urea possesses a unique property of forming adducts with n-paraffins. This is used in separating C₁₂ – C₁₄ n-paraffins from kerosines for detergent production .

Nitric Acid (HNO₃)

Nitric acid is one of the most used chemicals. The 1994 U.S. production was approximately 17.65 billion pounds. It is a colorless to a yellow liquid, which is very corrosive. It is a strong oxidizing acid that can attack almost any metal. The most important use of nitric acid is to produce ammonium nitrate fertilizer.

Nitric acid is commercially produced by oxidizing ammonia with air over a platinum-rhodium wire gauze. The following sequence represents the reactions occurring over the heterogeneous catalyst:



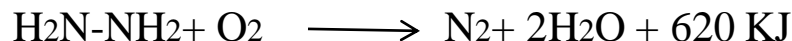
The three reactions are exothermic, and the equilibrium constants for the first two reactions fall rapidly with increase of temperature. Increasing pressure favors the second reaction but adversely affects the first reaction.

For this reason, operation around atmospheric pressures is typical. Space velocity should be high to avoid the reaction of ammonia with oxygen on the reactor walls, which produces nitrogen and water, and results in lower conversions. The concentration of ammonia must be kept below the inflammability limit of the feed gas mixture to avoid explosion. Optimum nitric acid production was found to be obtained at approximately 900°C and atmospheric pressure.

Uses of Nitric Acid. The primary use of nitric acid is for the production of ammonium nitrate for fertilizers. A second major use of nitric acid is in the field of explosives. It is also a nitrating agent for aromatic and paraffinic compounds, which are useful intermediates in the dye and explosive industries. It is also used in steel refining and in uranium extraction.

Hydrazine (H₂N-NH₂)

A colorless, fuming liquid miscible with water, hydrazine (diazine) is a weak base but a strong reducing agent. Hydrazine is used as a rocket fuel because its combustion is highly exothermic and produces 620 KJ/mol:

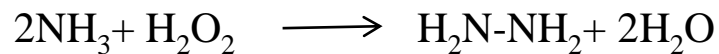


Hydrazine is produced by the oxidation of ammonia using the Raschig process. Sodium hypochlorite is the oxidizing agent and yields chloramine NH₂Cl as an intermediate. Chloramine further reacts with ammonia producing hydrazine:



Hydrazine is then evaporated from the sodium chloride solution.

Hydrazine can also be produced by the Puck process. The oxidizing agent is hydrogen peroxide:



Uses of Hydrazine. In addition to rocket fuel, hydrazine is used as a blowing agent and in the pharmaceutical and fertilizer industries. Due to the weak N-N bond, it is used as a polymerization initiator. As a reducing agent, hydrazine is used as an oxygen scavenger for steam boilers. It is also a selective reducing agent for nitro compounds. Hydrazine is a good building block for many chemicals, especially agricultural products which dominates its use.