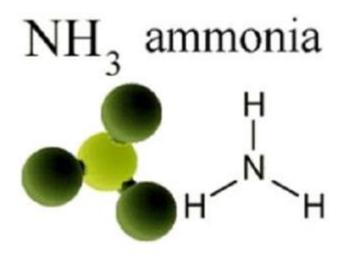
CHEMICAL PROCESS INDUSTRIES UNIVERSITY OF DIYALA CHEMICAL ENGINEERING DEPARTMENT

LECTURE (6)



Ammonia NH₃

Raw material: $H_2 \& N_2$

Feed stocks: 1) Coal lignite/ bituminous coal and coke.

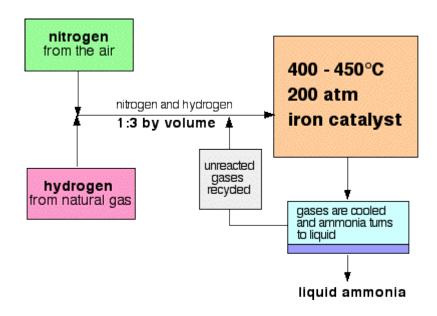
2) Gases, i.e coke oven gas, NG, Refinery gas.

3) Electrolytic H₂

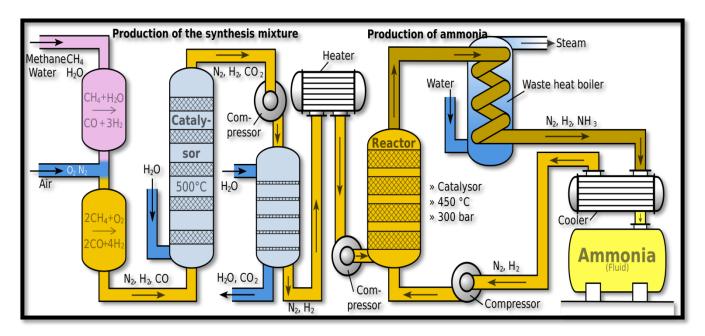
4) petroleum: naphtha, furnace oil, low sulfur heavy stock.

Manufacture of ammonia:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$



Hydrogen(from NG) react in the presence of an iron catalyst to form ammonia. The hydrogen is formed by reacting natural gas and steam at high temperatures and the nitrogen is supplied from the air. Other gases (such as water and carbon dioxide) are removed from the gas stream and the nitrogen and hydrogen passed over an iron catalyst at high temperature and pressure to form the ammonia.



Hydrogen is produced by the reaction of methane with water. However, before this can be carried out, all sulfurous compounds must be removed from the natural gas to prevent catalyst poisoning, These are removed by reacting them with zinc oxide, e.g.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Following this, the gas is sent to the primary reformer for steam reforming, where superheated steam is fed into the reformer with the methane. The gas mixture heated with natural gas and purge gas to 700°C in the presence of catalyst. At this temperature the following equilibrium reactions are driven to the right, converting the methane to hydrogen, carbon dioxide and small quantities of carbon monoxide:

$$CH_4 + H_2O \leftrightarrows 3H_2 + CO$$

 $CH_4 + 2H_2O \leftrightarrows 4H_2 + CO_2$
 $CO + H_2O \leftrightarrows H_2 + CO_2$

This gaseous mixture is known as synthesis gas.

The synthesis gas is cooled slightly. It then flows to the secondary reformer where it is mixed with a calculated amount of air. The highly exothermic reaction between oxygen and methane produces more hydrogen. Important reactions are:

$$CO + H_2O \leftrightarrows CO_2 + H_2$$

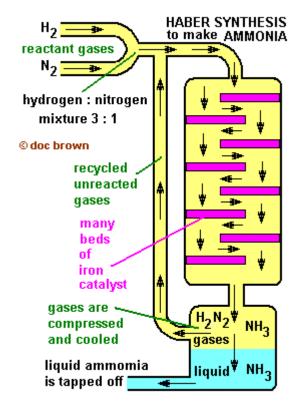
 $O_2 + 2CH_4 \leftrightarrows 2CO + 4H_2$
 $O_2 + CH_4 \leftrightarrows CO_2 + 2H_2$

In addition, the necessary nitrogen is added in the secondary reformer. As the catalyst that is used to form the ammonia is pure iron, water, carbon dioxide and carbon monoxide must be removed from the gas stream to prevent oxidation of the iron catalyst.

The carbon monoxide is converted to carbon dioxide (which is used later in the synthesis of urea) in a reaction known as the **water gas shift reaction**, and the carbon dioxide removed:

$$CO + H_2O \leftrightarrows CO_2 + H_2$$

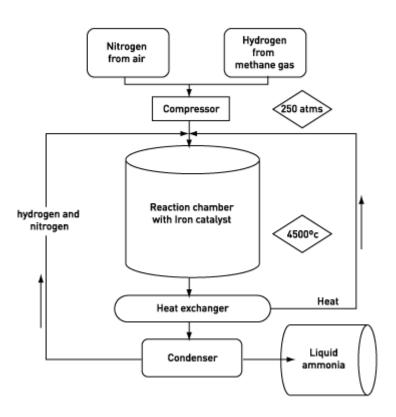
The remaining traces of CO and CO_2 are converted to methane and then the gases cooled until the water becomes liquid and can be easily removed.



The nitrogen and hydrogen are then reacted at high temperature and pressure using an iron catalyst to form ammonia:

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

The Haber Process for Manufacturing Ammonia



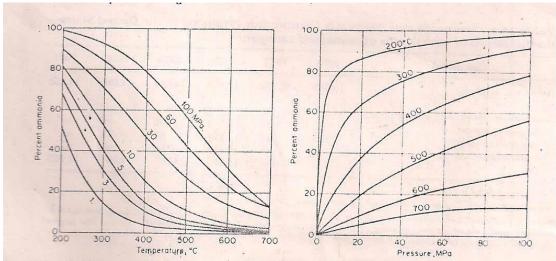


Fig. 18.2. Percentage of ammonia at equilibrium from an initial mixture of 3:1 H₂/N₂ gas at various temperatures and pressures. (Comings, High Pressure Technology, p. 410. Compare Frear and Baber, ECT, 2d ed., vol. 2, 1963, p. 260.)

