Production of Ammonia

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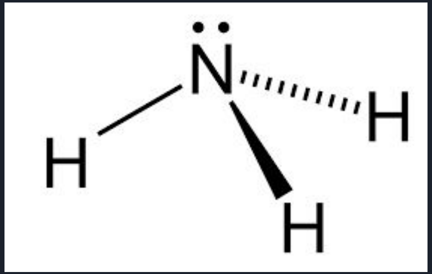
Introduction to Ammonia

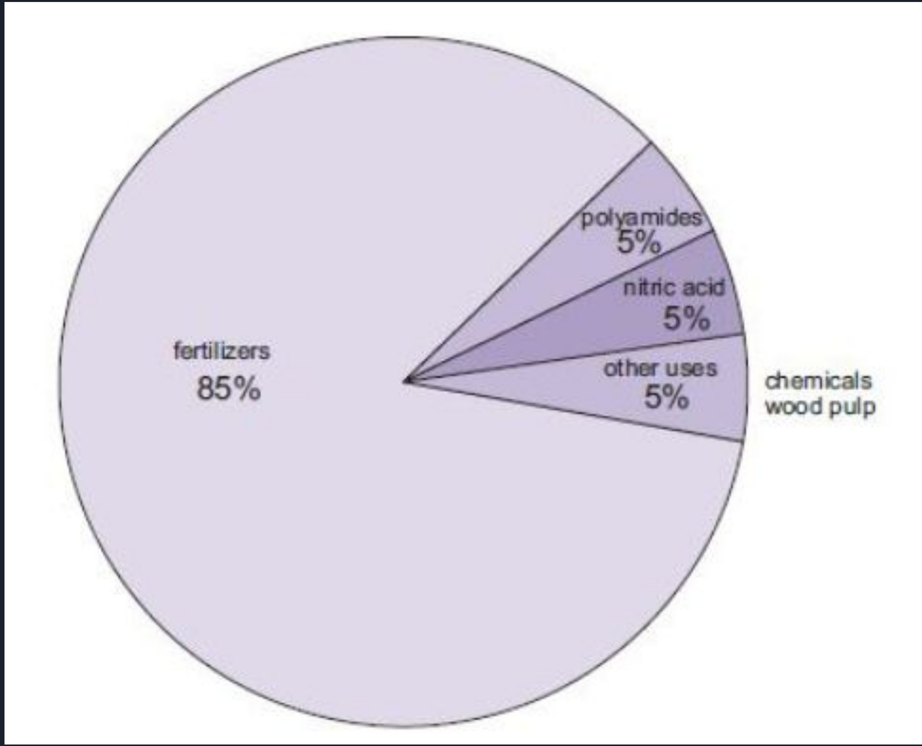


- Ammonia is **a colorless, poisonous gas with a familiar noxious odor**.
- Ammonia is one of the most highly produced inorganic chemicals.
- Ammonia has high volumetric hydrogen density, low storage pressure, high stability for long-term storage, high auto-ignition temperature, low condensation pressure, and lower gas density than air.

Chemical/Physical properties of Ammonia

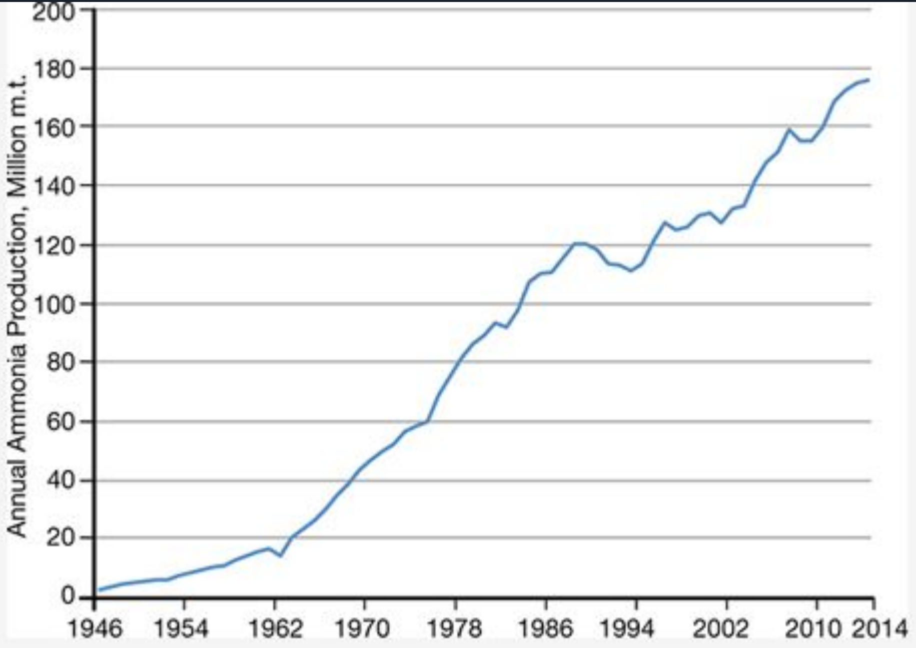
- At room temperature, ammonia is a colorless, highly irritating gas with a pungent, suffocating odor.
- In pure form, it is known as anhydrous ammonia and is hygroscopic (readily absorbs moisture).
- Alkaline properties and corrosive.
- Ammonia gas dissolves easily in water to form ammonium hydroxide, a caustic solution and weak base.
- easily compressed and forms a clear liquid under pressure.
- shipped as a compressed liquid in steel containers.
- not highly flammable

Uses of Ammonia



- Ammonia in Industries
- Agriculture
- Household Products
- For Manufacturing Various Compounds(nitric acid, Hydrogen cyanide, and a lot of other)
- Metal Treating(furnace brazing, atomic hydrogen welding)

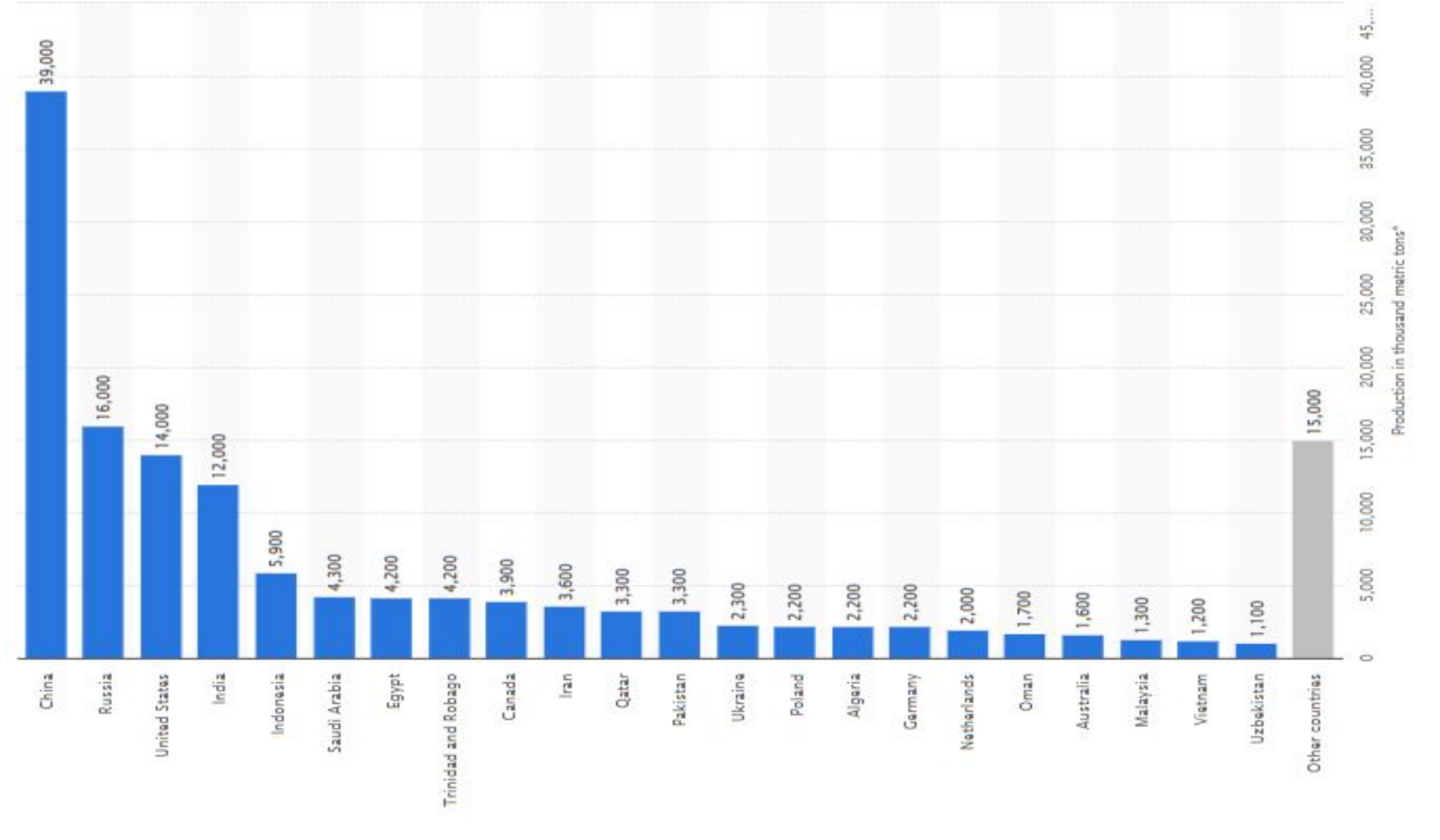
Production Rate of Ammonia



2. Worldwide ammonia production has steadily increased from 1946 to 2014.

- Ammonia plants worldwide, producing a grand total of 175 million tonnes of ammonia in 2016. It increased to 235 million tonnes of ammonia in 2021.
- China produced about 32.6% of the global production in 2014, while Russia, India, and the U.S. produced 8.1%, 7.6%, and 6.4%, respectively

Ammonia production worldwide in 2021



Design Basis :

- Location
- Amount

Design Basis : Location

States include in regional market :

1. Gujrat
2. Rajasthan
3. Maharashtra
4. others

Location : Gujrat

Table: State-wise Natural Gas Production Trends (MMSCM)						
State/Source	2014-15	2015-16	2016-17	2017-18	2018-19	2019-20 (upto Dec'19)
Onshore						
Andhra Pradesh	541	619	868	959.16	1081.31	688.84
Arunachal Pradesh	34	30	28	29.51	27.81	31.75
Assam	2958	3025	3128	3219.02	3289.06	2462.51
Gujarat	1527	1490	1580	1606.66	1402.22	1011.78
Rajasthan	1178	1338	1277	1441.93	1483.25	1343.80
Tamil Nadu	1192	1011	983	1207.22	1207.85	824.18
Tripura	1140	1332	1430	1440.37	1554.30	1173.64
CBM-WB, MP, Jharkhand	228	392	564	734.80	710.46	485.07

Source: *https://www.expertmarketresearch.com/reports/indian-ammonia-market*

Process Design

Different Processes:

1) Haber -Bosch Process
2) Electrochemical Processing
3) Thermochemical Synthesis

Haber - Bosch Process

The currently adopted ammonia production process basically employs the system invented by Fritz Haber and Carl Bosch about 100 years ago . Therefore, this system is well known as Haber–Bosch process. About 85% of total production of ammonia worldwide is produced by this process.

$$3\,H_2 + N_2 \rightarrow 2\,NH_3 \quad \Delta H°27\,°C = -46.35\ kJ/mol$$

- Ammonia synthesis is an exothermic reaction, and it occurs spontaneously at low temperatures .
- To effectively synthesize ammonia , the reaction should be performed at a relatively high temperature and pressure of 400–500 °C and 10–30 MPa, respectively, with the assistance of an iron-based catalyst.

Haber - Bosch Process

Staring with natural gas(CH_4) feedstock

- ➔ Remove sulfur compounds from the feedstock

$$H_2 + RSH \rightarrow RH + H_2S_{(gas)}$$

- ➔ Hydrogen sulfide is then adsorbed and removed

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

- ➔ Catalytic steam reforming of the sulfur-free feedstock

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

- ➔ Catalytic shift conversion to convert the carbon monoxide to carbon dioxide

$$CO + H_2O \rightarrow CO_2 + H_2$$

Haber - Bosch Process

- The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA).
- Catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide.

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

- Hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia.

$$3\,H_2 + N_2 \rightarrow 2\,NH_3$$

Pros and Cons

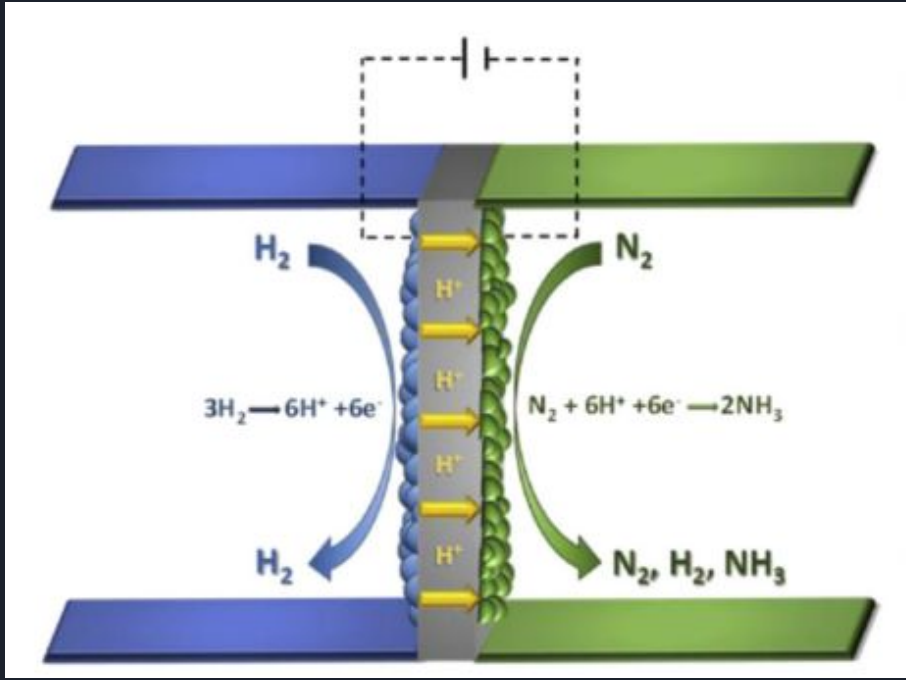
Pros:

- The process made ammonia fertilizer widely available.
- It helping cause a world population boom as yields from agriculture increased rapidly in a short time.

Cons:

- The Haber Bosch Process Leads to Eutrophication and Biodiversity Loss
- High Energy Consumption Levels Are Used in the Haber Bosch Process
- high GHG emissions

Electrochemical Processing



- The energy consumed by this process is about 20% lower than the Haber–Bosch process.
- Its application is considered to potentially reduce system configuration and control complexity.
- The investment cost can be lower compared to currently adopted ammonia synthesis systems.

Electrochemical Processing

- The reactions at both cathode and anode in proton conducting cells are shown below:

$$N_2 + 6\,H+ + 6\,e- \rightleftharpoons 2\,NH_3$$

$$3\,H_2 \rightleftharpoons 6\,H+ + 6\,e-$$

- The reactions at each cathode and anode are basically reversible.
- Four different types of electrolytes are currently available: (a) liquid electrolytes, (b) molten salt, (c) composite membranes and (d) solid state electrolytes

Pros and Cons

Pros:

- At mild operating conditions, zero emission of carbon dioxide
- capability to store renewable electricity in chemical bonds
- possibilities for distributed ammonia production.

Cons:

- electricity demand increases dramatically because of the high energy requirements of electrolysis

Thermochemical Cycle of Ammonia Production

In this Process The system consists of two circulated processes: reduction (nitrogen activation) and steam-hydrolysis (ammonia formation).

$$Al_2O_3 + 3C + N_2 \rightarrow 2\,AlN + 3\,CO \qquad \Delta H°25\,°C = 708.1\ kJ/mol$$

$$2AlN + 3\,H_2O \rightarrow Al_2O_3 + 2\,NH_3 \qquad \Delta H°25\,°C = -274.1\ kJ/mol$$

- ❑ Unlike the Haber–Bosch process, this thermochemical cycle can be carried out at atmospheric pressure and without a catalyst.
- ❑ The process allows independent reaction control for nitrogen activation and ammonia formation
- ❑ In their system, the heat required for reduction is basically covered by heat generated by the combustion of fuel gases produced during ammonia production.

Pros and Cons

Pros:

- Possibility of independent control of nitrogen activation and ammonia formation.
- Direct hydrogenation of nitrogen with water,implies separate hydrogen production tep is not required.

Cons:

- High temperature required for reduction of metal oxides.
- Use of CO.