Ammonia Production

HIGHLIGHTS

Ammonia - Ammonia is critical in the manufacturing of fertilizers, and is one of the largest-volume synthetic inorganic chemicals produced worldwide. Moreover, ammonia is an ideal carbon-free energy carrier and storage material [1].

Processes and technology status – The main industrial procedure for the production of ammonia is Haber–Bosch process. In this process, nitrogen (N_2) reacts with hydrogen (H_2) under high pressures of 150 to 200 bar and temperature 500 °C. The overall reaction is $N_2 + 3H_2O \rightarrow 2NH_3 + 3/2O_2$. Feedstock for the Haber process are air and natural gas to supply N_2 and H_2 respectively. The other raw materials are coal and naphtha [2]. Novel electric assisted technologies such as direct electrochemical ammonia synthesis and solid oxide electrolyzers are, also, under development [3].

Cost - Capital investment for conventional Haber–Bosch facilities are essentially equivalent at 276.11[1] M€$_{2017}$ for 2000-tpd capacity. Grundt et al. estimated capital expenses of 176.99 M€$_{2017}$ for a 1000 tpd ammonia facility [4].

Potential and barriers – Ammonia has the potential of being a carbon-free energy carrier. As the barrier, ammonia production requires high pressures and temperatures utilizing a large amount of energy and generating significant CO_2 emissions [5].

Process overview - Today, most large scale ammonia is produced by the Haber–Bosch process which is an artificial nitrogen fixation process as shown in figure 1. In this process, N_2 and H_2 gases are allowed to react at pressures of 200 bar and temperatures around 500 °C [2]. The stoichiometric value of feedstocks are 1:3 of N_2:H_2 [6]. The conventional Haber Bosch plants produce ammonia using natural gas (50%), oil (31%) or coal (19%) as feedstock [7]. Natural gas is the preferred feedstock for ammonia production due to its low price

[1] Converted from Dollars to Euros,1 € $_{2017}$ = 1.13 \$ $_{2017}$

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and wide availability. Moreover, other feedstocks such as coal and naphtha, release more than double GHGs amount, making them less attractive [8].

Reforming – Following the first step of natural gas feed desulphurization, the natural gas is reacted with steam to produce an equilibrium mixture of H_2, CO, CO_2, and CH_4. This reaction is endothermic, so it is carried out in tubular reactors placed in a heated furnace in order to supply the heat for the reaction and to maximize the equilibrium content of the desired products H_2 and CO.

N_2 from air - Following steam reforming, air is added to supply the N_2 required for ammonia production, while the O_2 from the air converts the remaining CH_4 in an exothermic reaction that increases the temperature and the H_2 and CO content further. Since all oxygen-containing molecules poison the ammonia synthesis catalyst, CO_2 is subsequently removed by absorption and a final CO/CO_2 cleanup is carried out.

Compression and the main reaction – The dried synthesis gas is compressed then is entered into the ammonia reactor. Ammonia synthesis is an equilibrium-limited exothermic reaction, and the ammonia product is favored by low temperature and high pressure. Most of the N_2 and H_2 passes unreacted through the reactor, and must be recycled in the loop after being cleaned for ammonia [9].

Investment and production costs -

The price of ammonia is closely related to the price of the feedstock. Haber–Bosch production cost is equal to 80.36 $€_{2019}$[2]/t for natural gas feed and 199.11 $€_{2019}$/t for hydrogen by water electrolysis [10]. Capital investment for conventional Haber–Bosch facilities are essentially equivalent at 276.11[3] $M€_{2017}$ for 2000-tpd capacity [4]. Grundt et al. estimated capital expenses of 176.99 $M€_{2017}$ for a 1000 tpd ammonia facility [4].

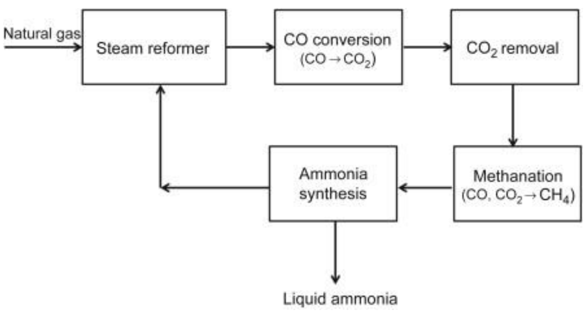

Figure 1. Conventional ammonia production process

[2] Converted from Dollars to Euros,1 $€_{2019}$ = 1.12 $$_{2019}$ [15]

[3] Converted from Dollars to Euros,1 $€_{2017}$ = 1.13 $$_{2017}$

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Carbon capture and storage (CCS) in ammonia production - Ammonia mainly used in the fertilizer industry and that is responsible for around 2–3 % of the world greenhouse gas emissions [11]. A modern, optimized and highly efficient methane-fed Haber-Bosch process emits 1.5–1.6 t_{CO2-eq}/t_{NH3} making the global manufacturing of ammonia accounting for 1.2% of anthropogenic CO_2 emissions. The CO_2 emissions stream released from the primary reformer have high purity of approximately 99% CO_2. CO_2 emissions are regularly captured at ammonia facilities to produce urea and is not contributed to environmental emissions nor available for CO_2 capture and storage (CCS). Hence, CCS can be investigated for the combustion emissions from the primary reformer [12]. For the natural gas fed process yielding an energy efficiency around 65 %, the overall life cycle emissions can be reduced to 0.79 kg_{CO2}/kg_{NH3} with CO_2 capture compared to 1.6 kg_{CO2}/kg_{NH3} without capture [11].

Energy requirements of ammonia production - Approximately 2/3 of consumed natural gas is used as a feedstock, while around 1/3 is used for energy purposes [13]. The conventional highly optimized Haber–Bosch process uses about 7.9 kWh of energy derived from fossil fuels per kg NH_3 at the scale of 1,000 t/day, where 2.0 kWh/kg is used for pressurization, heating, pumping and so on. This number will be higher at a smaller scale due to the increased heat losses [10]. The minimum energy requirement for the Haber-Bosch process, defined as the heat of combustion of ammonia, is 18.6 GJ/t_{NH3} based on the lower heating value of ammonia (LHV). For the methane fed process, the theoretical minimum energy input is 22.2 GJ/t_{NH3} broken down as 17.7 GJ/t_{NH3} associated to the methane feedstock and 4.5 GJ/t_{NH3} associated to methane fuel to fire the steam methane reforming (SMR) reactor [7]. For comparison purposes, the energy requirement for the direct electrochemical synthesis of NH_3 from liquid water and nitrogen at 25 °C and 1 bar is 19.9 GJ/t_{NH3} (1.17 volts) [7].

Ammonia as an energy storage molecule - Ammonia is an ideal carbon-free energy storage molecule due to its high energy density (4.32 kWh/L), high weight fraction of hydrogen (17.65%) and ease of liquefaction under mild conditions [1]. Energy storage in the ammonia chemical bonds would enable a much greater uptake of intermittent renewable power sources

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helping to balance the seasonal energy demands in a carbon-free society [7]. Furthermore, green ammonia has emerged as a promising fuel option especially for long-distance shipping because of its low carbon footprint [3].

Electrification of ammonia production - One promising solution to decarbonization of ammonia production is to generate hydrogen from water electrolysis using electricity originated from solar or wind sources [14]. Figure 2 depicts the difference between conventional methane-fed and electrified Haber-Bosch process for ammonia production. Switching the hydrogen production method from methane to hydropower-electrolysis reduces the CO_2 emissions from 1.5 to 0.38 $t_{CO2\text{-}eq}/t_{NH3}$ (75% decrease). Assuming that the electrically-driven Haber-Bosch process requires a 38.2 GJ/t_{NH3}, a wind powered ammonia process will have a carbon intensity of 0.12–0.53 $t_{CO2\text{-}eq}/t_{NH3}$ [7].

Novel ammonia production processes – Ligno-cellulosic biomass can be used as a source of hydrogen for ammonia production [8]. The other option is the development of alternative methods of production such as plasma reactions and electrochemical processes. Moreover, using semiconductors with sunlight to drive photocatalytic reactions in a Solar Ammonia Refinery is another approach being pursued to realize environmentally friendly ammonia synthesis [14].

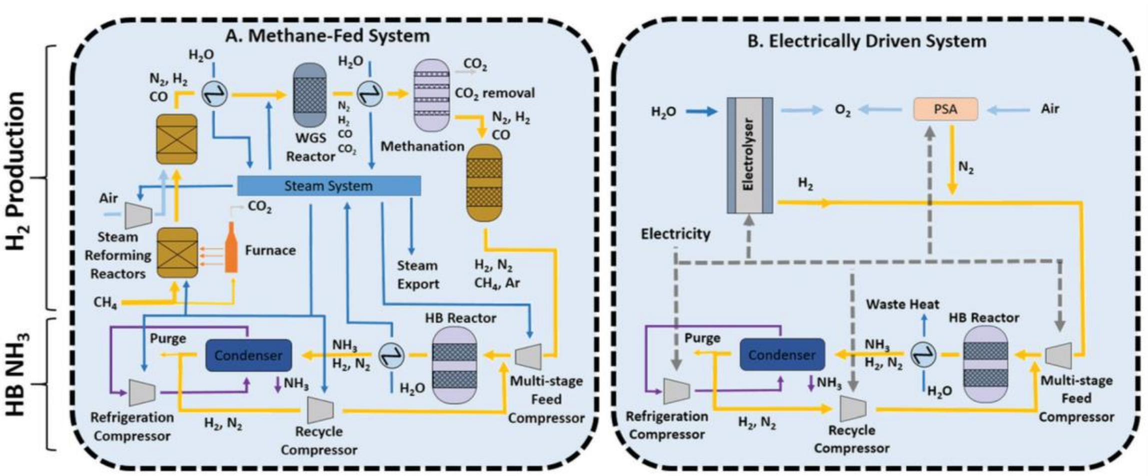

Figure 2. Schematic difference between conventional methane-fed (A) and electrified (B) Haber Bosch process for ammonia production [7].

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Table1. Summary Table: Key ammonia production data

Technical Performance	Desulphurization of the natural gas	Reforming
Energy type inputs	Natural gas, coal and naphtha	Natural gas, coal and naphtha
Output products	Desulphurized natural gas feed	H_2, CO, CO_2, and CH_4
Environmental Impact		
Emitted CO_2 For the natural gas fed process ($kgCO_2/kgNH_3$)		0.79 with CO_2 capture 1.6 without capture
Costs		
Plant size of 2000 tpd*		276.11 $M€_{2017}$
Plant size of 1000 tpd		176.99 $M€_{2017}$
Energy requirements		**Total heat**
For the methane fed		22.2 GJ/t_{NH3}
For the direct electrochemical synthesis of NH_3		19.9 GJ/t_{NH3}

***** ton per day

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