

PROCESS IMPLICATIONS OF ELECTRIFYING AMMONIA PRODUCTION

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ABSTRACT

The current ammonia production plants - Steam Methane Reforming (SMR) and Haber-Bosch (HB) - are responsible for 1.2% of global CO₂ emissions. As more sectors are shifting to electrification, so does the NH₃ industry as shown by the amount of studies focusing on electrolyzers and Pressure Swing Adsorbers (PSA) to replace SMR. Haber-Bosch itself is being questioned as a new alternative technology is emerging: Chemical Looping (CL). Such transformations imply changes to the current process. This work assesses such implications by comparing 2 alternative scenarios with the conventional case. In terms of emissions, the electrification is clearly benefic with a cut of 74-95% when using wind energy. The replacement of SMR by electrolyzers and PSA also improves the energy efficiency, as >60% of the energy consumption in conventional plants originates from the compressors and heat integration. Finally, the combination of Alkaline Electrolyzers (AE) and CL is determined as the most suitable for small-scale flexible and economical installations.

Keywords: Ammonia Synthesis, Hydrogen Production, Electrolysis, Electrification, Green Hydrogen

INTRODUCTION

There is no doubt that the climate crisis is the number one issue the world has to tackle. As a consequence, paradigm shifts are happening globally to reduce greenhouse gas emissions, be it on small scales such as in individuals' routines, or on larger scales such as in the transport, building, power and industrial sector. Looking closer at the chemical sector, it was responsible for 1.4 GtCO₂ in 2019, which is equivalent to 4.2% of global CO₂ emissions [1][2]. Within those 4.2%, 1.2% are attributable to ammonia production and its methane-based Haber-Bosch (HB) process, making it one of the largest greenhouse gas emitters within the chemical sector [3][4]. Solutions to reduce its carbon footprint could therefore have quite a significant impact on global emissions. Lately, electrification has been one of the main focuses when assessing decarbonizing solutions for different sectors [5], and the chemical industry is one of them. Several studies have assessed the electrification of NH₃ production by replacing the standard Steam Methane Reforming (SMR) by water electrolysis [3][4][6]. Implementing such a change in technology implies changes in the process. The main objective of this work is to review these implications by comparing three scenarios. Scenario 0 is the current situation of NH₃ production: the combination of SMR and HB. Scenario 1 replaces SMR by a Solid Oxide Electrolyser (SOE). Finally, Scenario 2 replaces SMR by an Alkaline Electrolyser (AE) and HB by Chemical Looping (CL).

SCENARIOS DESCRIPTION

Scenario 0: SMR + HB

Scenario 0 is the reference scenario as it describes the current situation. Ammonia is produced through a Haber-Bosch process which is fed with a H₂/N₂ mix produced by Steam Methane Reforming (Fig. 1a). The combination of SMR and HB currently represents the Best Available Technique (BAT) for NH₃ production as it yields the highest efficiency and lowest carbon emissions while being the most economical route for large scale NH₃ production [3][4].

The SMR is composed of several units. It is first supplied with methane (CH₄) and air which enter a primary and secondary reforming reactor. The reforming is endothermic. Its primary reactor is thus heated by a methane-fed furnace while the secondary reactor is autothermal. The latter generates a gas mixture which comprises N₂, H₂, CO and unreacted steam and CH₄. It enters a water-gas shift reactor (WGS) where the CO reacts with steam to produce H₂. This reaction is exothermic, and heat should be removed to decrease the CO equilibrium concentration. The mixture at the output, stripped from most of the CO, successively goes through an acid gas removal unit and a methanator to respectively strip the remaining CO₂ and CO. The product mixture is sent to the HB loop. It is first compressed and pre-heated before entering the HB catalytic reactor. The resulting feed is then condensed to separate the NH₃ from the remaining reactants and inerts. The latter are partially purged and recycled to the reactants feed. Overall, this system works at high temperatures and pressures (550°C and 250 bar). [4][6]

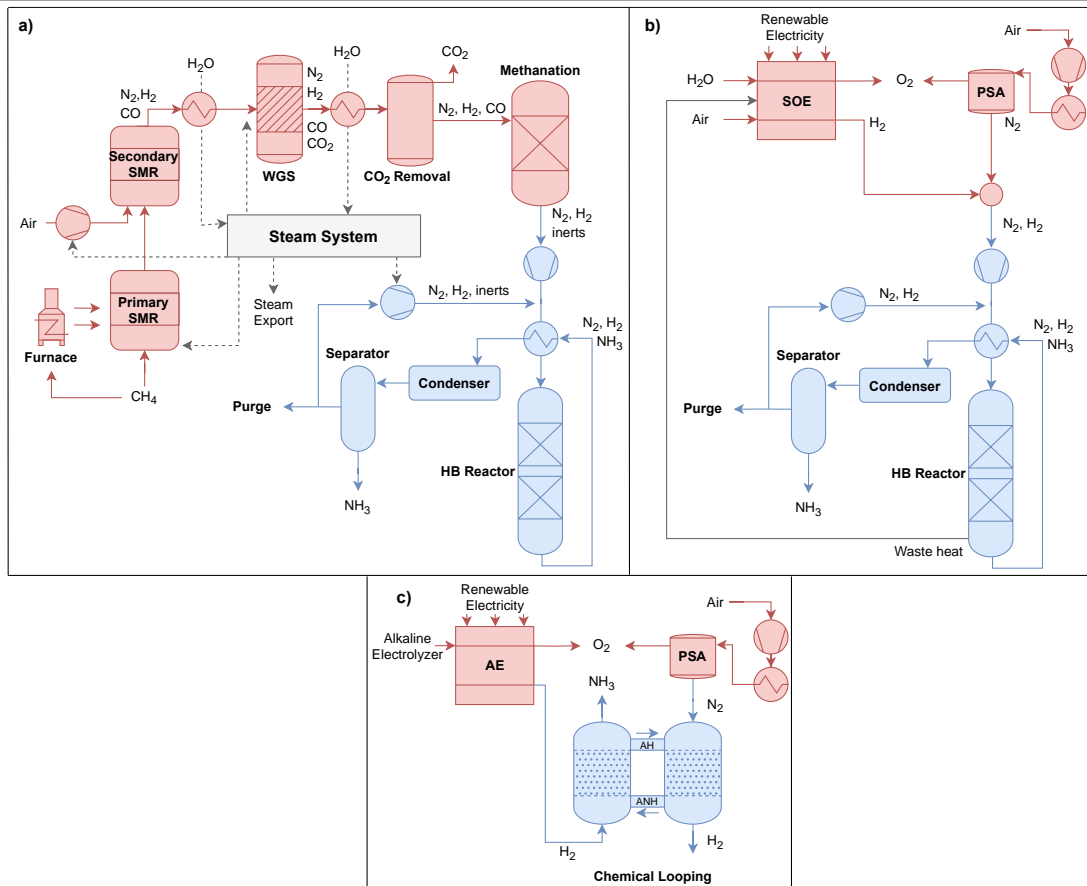


Fig. 1. Process diagrams of Scenario 0 (a), 1 (b) and 2 (c). Each has a H₂/N₂ production unit (red) and a NH₃ production unit (blue)

Scenario 1: SOE + HB

The first alternative scenario involves a change of technology by implementing a Solid Oxide Electrolyzer (SOE) to replace the SMR process while keeping the HB loop (Fig. 1b). As the SOE only produces H₂, the N₂ feed is produced via Pressure Swing Adsorption (PSA). Both technologies are powered electrically. Assuming that the electricity comes from renewable sources, the hydrogen produced here can be qualified as Green H₂ [7]. The SOE unit can be represented as a single block, as opposed to the SMR process which is a succession of numerous units. It is fed with air and water and generates H₂. At the output, the H₂ is separated from the unreacted water and mixed with the N₂, which is produced through the PSA unit fed with air. The resulting mixture is then compressed and heated before being sent to the conventional HB loop. In terms of operating conditions, the SOE must operate at high temperature and pressure to match the HB conditions (650°C and 550 bar) and the HB reactor waste heat can therefore be recycled to the SOE. [6]

Scenario 2: AE + CL

The second alternative scenario implies a change in both hydrogen and ammonia production units. The SMR is replaced by an Alkaline Electrolyzer (AE) for the H₂ production and a PSA for the N₂. The HB loop is replaced by a Chemical Looping (CL) unit (Fig. 1c). Just as in the first alternative scenario, the electrolyzer is represented by a single block. This time, it is only fed with an alkaline electrolyte. In this scenario, however, the H₂ output is not mixed with the N₂ output. In fact, both are sent to two distinct entries in the CL reactor. The latter technology relies on a decoupling of the conventional catalytic reaction that normally takes place in a single HB reactor. The CL reactor is here composed of 2 separate reactors connected in a cycle and in which two sub-reactions are conducted. The CL process of interest in this case is the one proposed by Gao et al. which uses alkaline earth metal hydrides (AH) and imides (ANH). During the first step, N₂ is fed into the first reactor and reduced by the H in the AH catalysts, producing ANH intermediates. The latter are sent to the second reactor and undergo a hydrogenation by the H₂ feed. This last step produces the NH₃ but also regenerates the metal hydride which is recycled back to the first step. In terms of operating conditions, both AE and CL run at a relatively low temperature (~100°C) and pressure (1 bar) compared to the previous scenarios. [9]

COMPARISON AND DISCUSSION

To compare the three scenarios, four characteristics are examined: emissions, energy losses, scalability and flexibility. In terms of emission, it appears that the conventional process described in Scenario 0 is the most polluting. Specifically, it emits in average 2.0-2.5 ton CO_{2,eq} per ton NH₃, and these numbers would be higher for smaller plants. In comparison, only 0.12-0.53 ton CO_{2,eq} are emitted for a wind powered plant in Scenario 1 and 2, which is 74 to 95% smaller [4][10].

This trend is comparable regarding energy intensity. In fact, the steam compressors alone account for 60% of the energy consumption in Scenario 0. In addition, the heat integration system and the HB purge also take part in decreasing the energy efficiency [4]. Considering the steam system would not be present anymore in both Scenario 1 and 2, this is a sensible optimisation in energy efficiency. The losses due to the purge in those scenarios are also negligible as almost no inerts are present in the feeds [6]. Furthermore, Chemical Looping in Scenario 2 allows an in-situ separation of the NH₃, which allows more energy savings as the separation system in HB is very energy-intensive [11].

The scalability aspect is directly linked to the latter observations. First, due to the absence of any steam management units (compressors and steam turbines) when using electrolysers, and due to the latter's compactness, both electrified scenarios are suitable for small-scale installations. Then, regarding pressure, the NH₃ production cost being affected by the operating pressure, Scenario 1 and its high-pressure conditions make it less favorable to be scaled down [12]. This makes Scenario 2 the best to build small and agile production plants at low capital costs and flexible operation to cope with the intermittent nature of renewable energy.

CONCLUSIONS

- The carbon intensity in the current NH₃ production can be cut by 70-95% by electrifying the process.
- Replacing the SMR by electrolysers and PSA allows energy savings of at least 60% and avoid the need of a purge.
- It also allows more compact and straightforward installations.
- Replacing HB by CL avoid the use of an energy intensive separation unit.
- Combining AE and CL allows ambient operating pressure, making it favorable for small-scale agile plants.

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