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Towards the Decarbonization of a Conventional Ammonia Plant by the Gradual Incorporation of Green Hydrogen and Air-Separated Nitrogen

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ABSTRACT

As economies advance towards decarbonization, industry follows suit. The ammonia (NH_3) sector heavily relies on the energy- and carbon-intensive Haber-Bosch (HB) process, which accounts for nearly 2% of global CO_2 emissions due to its reliance on fossil fuels. Emerging technologies are paving the way for fully renewable NH_3 production, although the most mature green process still relies on the HB process, entirely replacing fossil fuels with electrolytic green hydrogen (H_2). This work introduces the first developments towards the gradual incorporation of green H_2 and air-separated nitrogen (N_2) into a conventional NH_3 production plant. Using *Aspen Plus® V14* for modelling and simulation of Steam Methane Reforming (SMR), different scenarios incorporating 0 to 40 % of these alternative feedstocks were analyzed. An economic objective function is used in each scenario's optimization. To improve green H_2 incorporation and ensure operational constraints were met, the simulations used an adapted SMR section proposed in previous work. Preliminary results in the development of this methodology indicate that at 40 % green H_2 and 40 % air-separated N_2 incorporations, a 29.4 % reduction in carbon emissions was achieved, along with 30.1 % natural gas savings and a 35 % decreased in conventional operational costs (without green H_2 and air-separated N_2 costs) compared to the base case, where no alternative feedstocks were used. At current market prices, in the same scenario, incorporating alternative feedstocks can increase total operational costs by 52 %.

Keywords: Ammonia, Steam Methane Reforming, Green Hydrogen, Aspen Plus

INTRODUCTION

At the beginning of the 20th century, agriculture faced increasing pressure to secure a reliable source of nitrogen to enable higher food production for a rapidly growing population. Nitrogen is an essential nutrient for crop growth, and until then, it was obtained mainly from limited natural sources. In 1909, Fritz Haber achieved the fixation of atmospheric nitrogen (N_2) by synthesizing ammonia (NH_3) through its reaction with hydrogen (H_2) using an iron-based catalyst, Equation (1). Years later, in 1913, Carl Bosch successfully scaled up ammonia synthesis for industrial application, giving rise to what is now known as the Haber-Bosch (HB) process. This breakthrough is widely regarded as one of the most important technological developments in human history. [1]

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad (1)$$

Ammonia is the second-most-produced chemical globally, with 85 % of its output used in the nitrogen-based fertilizer industry, including urea and ammonium nitrate. It is estimated that almost half of the world's population relies directly on these fertilizers for food production. Besides agriculture, ammonia has diverse uses, including pharmaceuticals, textiles, explosives manufacturing, and deNOx technologies. [2, 3]

Given its global significance and extensive production scale, the Haber-Bosch (HB) process accounts for approximately 2 % of the world's total energy consumption and contributes between 1 % and 2 % to worldwide carbon dioxide (CO_2) emissions. [1] This considerable environmental footprint primarily stems from its substantial

reliance on fossil fuels, which serve as feedstocks for hydrogen production and process heat. Currently, around 75 % of global ammonia synthesis is derived from light hydrocarbons such as natural gas and naphtha, whereas the remaining 25 % originates from heavy hydrocarbons, including coal and Heavy Fuel Oil (HFO). In the European context, nearly all ammonia manufacturing facilities operate exclusively on natural gas, producing hydrogen via Steam Methane Reforming (SMR). [2, 3] This manufacturing route is regarded as the Best Available Technology, owing to its superior energy efficiencies, reduced emissions, and lower capital investment.

Driven by policies aimed at achieving carbon neutrality and energy independence, the ammonia industry is increasingly exploring decarbonization pathways. In the European Union (EU), the Renewable Energy Directive III stipulates that by 2030, 42 % of the hydrogen used in industrial processes must be derived from renewable sources. To align with these regulations and targets, the ammonia sector has intensified efforts to develop alternative synthesis technologies that transcend the conventional HB process, striving for a more decentralized, flexible, and energy-efficient production. The emerging routes under investigation are designed to facilitate the complete integration of renewable energy sources and encompass electrochemical, electrocatalytic, and photocatalytic methods for ammonia synthesis. Nevertheless, most of these technological approaches remain at early stages of development and are distant from commercial deployment. [4]

Currently, the most mature technology for green NH_3 production is based on electrifying the HB process, in which SMR is replaced by water electrolysis as the hydrogen source and an Air Separation Unit as the nitrogen source. By supplying renewable electricity to the process, green NH_3 can be produced. However, operating the HB process within the inherent variability of renewable energy sources, particularly solar and wind, remains a significant challenge. Numerous studies have addressed the issues related to fluctuating energy supply and, consequently, hydrogen production. Under such conditions, the operation of the HB process often requires hydrogen storage in buffer tanks and/or the use of energy storage systems such as batteries. Therefore, producing fully green NH_3 remains costly due to expensive infrastructure, high energy prices, and logistical challenges stemming from the underdeveloped electrolyser market. [4]

The NH_3 industry is consequently striving to balance economic competitiveness with the attainment of decarbonization targets, ideally leveraging existing capital investments in current infrastructure. As examples, Fertiberia and Yara are major players in the European ammonia industry, which has begun incorporating green hydrogen into its conventional plants. Inspired by the operating procedures at a real-life plant, a previous work addressed the incorporation of green hydrogen into a conventional, methane-fed NH_3 plant. [5] The authors pointed out that overheating in some equipment limits green H_2 integration and proposed a new SMR configuration to prevent it. With an adapted SMR, a maximum green hydrogen incorporation of 60 % can be achieved, although lower fractions may lead to issues with equipment load reduction. [5]

Building on the previous study, this work explores the simultaneous use of green H_2 and air-separated N_2 as alternative feedstocks in the SMR section of a conventional ammonia plant.

METHODOLOGY

As part of a conventional ammonia plant with an annual capacity of around 200 kton, an SMR section was modeled in *Aspen Plus® V14*, as shown in **Figure 1**.

SMR Section

The SMR section relies on natural gas, steam, and atmospheric air consumption to produce a synthesis gas mixture of H_2 and N_2. The process natural gas is first purified by hydrodesulfurization to remove sulphur compounds and prevent catalyst poisoning. This stream is then heated, mixed with process steam, and fed into a pre-reforming section, where the heavier hydrocarbons in natural gas are converted into methane (CH_4). Following this step, the reforming process begins in the primary reformer, Ref-I, where CH_4 reacts with steam to produce H_2, carbon monoxide (CO), and CO_2, Equations (2) and (3).

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2 \quad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3)$$

The gas mixture is mixed with compressed hot atmospheric air and fed into a secondary reformer, Ref-II, where CH_4 conversion is completed. The atmospheric air supplied in this unit must ensure the right amount of N_2 for ammonia synthesis, as well as the oxygen (O_2) needed for CH_4 partial and total oxidation, Equations (4) and (5).

$$CH_4 + 0.5\ O_2 \rightleftharpoons CO + 2\ H_2 \quad (4)$$

$$CH_4 + 2\ O_2 \rightleftharpoons CO_2 + 2\ H_2O \quad (5)$$

The mixture is then cooled, and CO is converted in a two-stage process: a high-temperature shift (HT) followed by a low-temperature shift (LT) according to the stoichiometry in Equation (3). CO_2 is removed from the process stream by scrubbing the mixture with an ammonia solution. To ensure that the syngas mixture produced does not contain oxygen-containing compounds, the unconverted CO fraction and the final traces of CO_2 are subjected to a methanation step, in which CH_4 and water

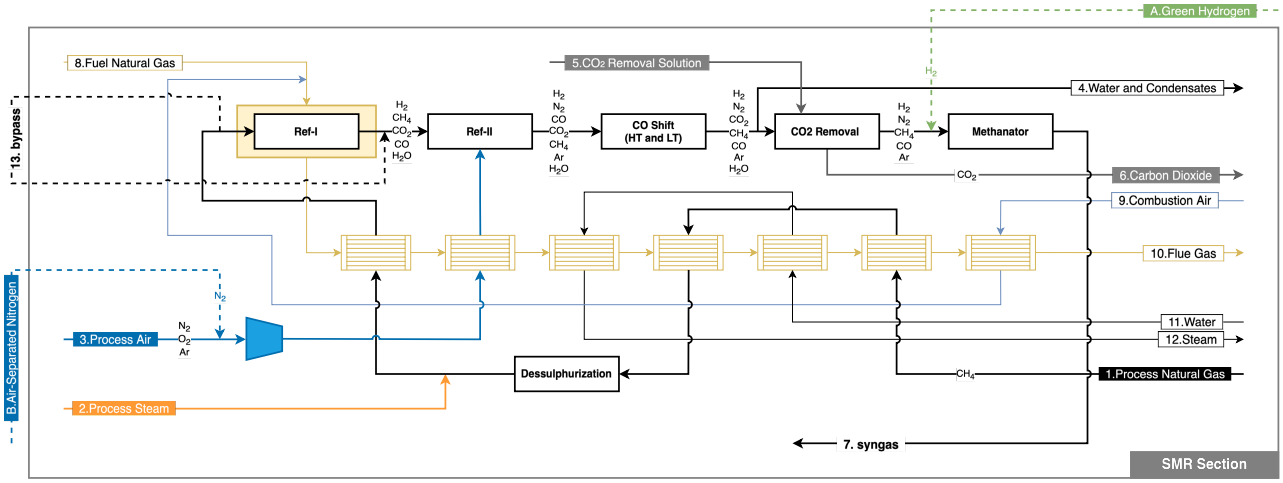

Figure 1: Simplified schematics of the SMR section model developed. The grey box contains the conventional SMR configuration; outside the box are represented the adapted SMR configuration (stream 13, a Ref-I Bypass proposed in [5,6]), stream A (green hydrogen incorporation), and stream B (air-separated nitrogen incorporation).

are produced.

The water is ultimately eliminated using molecular sieve adsorbers, allowing CH_4 and the Argon (Ar) introduced with atmospheric air to proceed to NH_3 synthesis as inert chemicals. The gas mixture obtained is then composed of H_2 and N_2 in a 3:1 molar ratio, with traces of CH_4 and Ar.

In addition to the main process line, the SMR section encompasses an auxiliary line that utilizes natural gas as fuel through combustion with air. The heat generated from this combustion process is employed to supply energy for reforming reactions (as described in Ref-I), to pre-heat various streams such as process natural gas and combustion air, and to generate steam.

Since the integration of alternative feedstocks is considered within the SMR section and the objective remains to produce equivalent flow rates of H_2 and N_2, the NH_3 synthesis process is not addressed in this analysis. Ultimately, incorporating green H_2 and air-separated N_2 could reduce the inert chemical fraction in the syngas stream, thereby decreasing inert component accumulation in the NH_3 synthesis loop and reducing purge fractions. Those additional advantages at NH_3 synthesis are not addressed in this work.

Green Hydrogen Incorporation

The incorporation of green H_2 was modeled as a pure stream (xH_2 = 1). The injection point into the process was positioned immediately prior to the methanation step, where the production of gry hydrogen (from CH_4 reforming) is completed. The study did not include modeling of the water electrolysis process used for green hydrogen production.

Green H_2 incorporation reduces grey H_2 production, thereby decreasing CH_4 reforming and helping achieve potential decarbonization. The extent of this alternative feedstock's incorporation is quantified by the Green Hydrogen Incorporation fraction (GHI), defined as the ratio of green H_2 in the total H_2 supply to NH3 synthesis (grey + green).

Air-Separated Nitrogen Incorporation

The incorporation of air-separated N_2 was treated similarly to green H_2, considering it as a pure stream (xN_2 = 1). This stream was intended to simulate the nitrogen-rich output typically produced by a well-established Air Separation Unit (ASU) technology, although the process itself was not explicitly modeled.

Air-separated N_2 incorporation decreases the requirement for atmospheric air, as the N_2 flow rate in syngas must stay constant to maintain consistent NH_3 production. The extent of incorporation of this alternative feedstock was quantified using the Air-Separated Nitrogen Incorporation fraction (SNI), which is defined as the ratio of N_2 incorporated relative to the total N_2 supplied for NH_3 synthesis (including both direct air supply and air separation).

Economic Optimization

Taking the green H_2 and air-separated N_2 incorporations as independent parameters in this framework, the main goal of this work is to explore how the SMR process can be operated to accommodate multiple combinations of these two key parameters. Building a thorough understanding of how SMR operation can be adapted in this context is vital to map the transition from the classic HB process towards partly or fully green NH_3 manufacture, while achieving the best economic performance. This

transition will only be considered in future work.

To achieve the first goal above, the process flowsheet model was configured and optimized as a function of green H_2 and air-separated N_2 incorporations using the Optimization tool in *Aspen Plus® V14* software. The optimization considers a set of manipulated variables listed in **Table 1**. These variables translate into different stream flow rates that may be adjusted by valves and their respective control, ensuring the optimal operation under different fractions of alternative feedstock incorporation.

Table 1: List of manipulated variables considered.

Variable	Lower Bound	Upper Bound	[Unit]
Process Natural Gas	0	19	ton/hr
Process Steam	0	60	ton/hr
Process Air	0	2 000	kmol/hr
Fuel Natural Gas	0	5	ton/hr
Combustion Air	0	140	ton/hr
CO_2 Removal Solution	0	150	ton/hr
Ref-I Bypass Fraction	0	1	-

Table 2: List of constraints considered.

Equality Constraint	Value	[Unit]
Steam/Carbon in Ref-I	3	mol/mol
H2 in Syngas Stream	3 000	kmol/hr
Combustion Air to Fuel	20	ton/ton
H2 to N2 at Syngas Stream	3	mol/mol
Inequality Constraint	**Value**	**[Unit]**
CO2 Content after Removal	≤ 0.01	%mol
Q (Ref-I) + Q (Fired-Box)	≤ 0	MW
Ref-II Outlet Temperature	≤ 921	ºC

In earlier works [5, 6], the authors introduced a Ref-I Bypass to enable the redistribution of CH_4 reforming reactions between primary and secondary reformers. They found that operating with the Ref-I Bypass can increase the fraction of green H_2 while keeping the Ref-II outlet temperature stable. The overheating problem in the Ref-II unit was identified in the same study when the Ref-I Bypass was not used and was observed to worsen as the GHI fraction rises. Due to its demonstrated effectiveness, the Ref-I Bypass Fraction is listed as a variable in **Table 1**.

The optimal solution must also satisfy the operational constraints listed in **Table 2**. A constraint is included to avoid overheating of Ref-IIThe problem is subsequently formulated to minimize the operational costs associated with the SMR section. For that purpose, a set of economic parameters (**Table 3**) is employed to estimate the costs of raw material streams (including alternative feedstocks), electricity consumption, thermal energy use and production, as well as taxes related to CO_2 emissions.

Table 3: Main economic parameters considered.

Economic Parameter	Value	[Unit]
Natural Gas	490	$/ton
Process Steam	37	$/ton
Electricity	77	$/MWh
CO_2 Emission Tax	83	$/ton
Green H_2	5 000	$/ton
Air-Separated N_2	50	$/ton

The objective function integrates all economic factors to minimize the Operational Net Cost (ONC), Equation (6).

$$\text{minimize } f(x) = \text{ONC} \quad (6)$$

The optimization problem was then solved, incorporating both alternative feedstocks from 0 to 40 % (0 < GHI < 40% and 0 < SNI < 40%) in intervals of 10%.

RESULTS

The Base Case

The base case is defined as the SMR operation with no alternative feedstock incorporated. This simulates a conventional NH_3 plant that operates entirely on natural gas and atmospheric air (GHI = SNI = 0%), with a non-adapted configuration (Ref-I Bypass Fraction = 0). **Table 4** lists some important consumption rates and indicators obtained for the base case.

Table 4: Results obtained for the base case (GHI = SNI = 0 %).

	Value	[Unit]
Natural Gas Consumption	20.8	ton/hr
Atmospheric Air Consumption	39.2	ton/hr
Ref-II Outlet Temperature	920	ºC
CO_2 Emissions	54.5	ton/hr
ONC	14.5	k$/hr
CO_2 Emission per kg of H_2	9.1	kg/kg
ONC per kg of H_2	2.4	$/kg

Alternative Feedstock Incorporation

From the base case, the incorporation of alternative feedstock was considered. Specifically, the incorporation of green H_2 raises concerns about overheating in the Ref-II unit [6]. **Figure 2** shows the outlet stream temperature

of this unit, demonstrating compliance with its constraint.

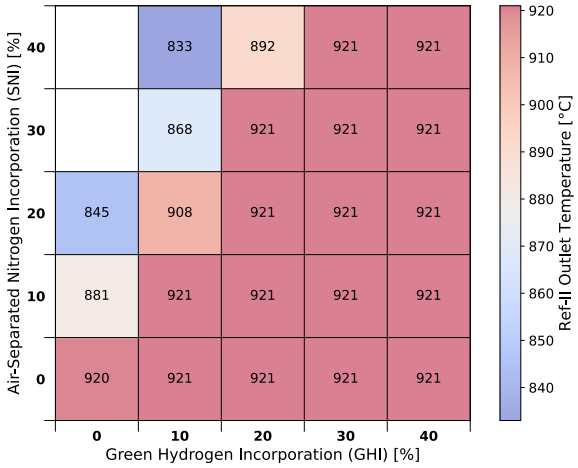

Figure 2: Matrix of Ref-II Outlet Temperature as a function of GHI and SNI (0 - 40 %; blank cells indicate no feasible solution was found).

As air-separated nitrogen incorporation increases, the results show that it has the opposite effect on Ref-II outlet temperature than hydrogen incorporation. This is especially evident when no green H_2 is considered (GHI = 0 %) and suggests that its incorporation may help control this temperature, thereby enabling higher green H_2 incorporation than previously reported [6]. Although the incorporation of green H_2 tends to increase the Ref-II outlet temperature, this temperature is kept constant at the base case value by activating the Ref-I Bypass. Therefore, the effect of increasing green H_2 is reflected not in overheating of this unit but in an increasing Ref-I Bypass fraction. **Figure 3** shows the Ref-I Bypass fraction required to comply with that limit.

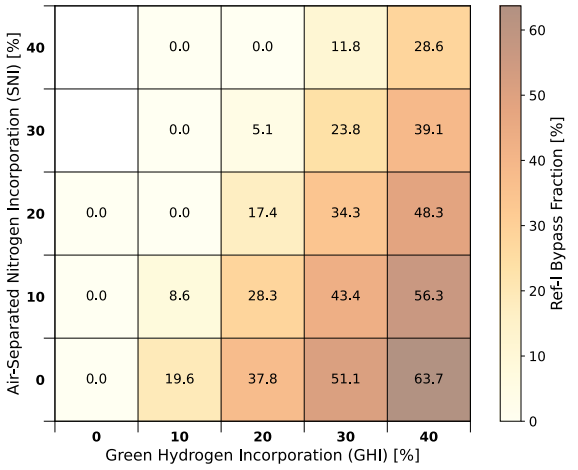

Figure 3: Matrix of Ref-I Bypass Fraction as a function of GHI and SNI (0 - 40 %; blank cells indicate no feasible solution was found).

Although the Ref-I Bypass operation is an important step toward greater green H_2 incorporation, it naturally reduces Ref-I load, as part of it is diverted by the bypass. A previous study considered a limit of 60 % on the reduction of Ref-I nominal capacity. Applying the same criteria in this work would make it impossible to achieve GHI values of 30 % and 40 % if no air-separated N_2 is considered. As SNI increases, the required Ref-I Bypass fraction is lower, which means not reporting such a sharp reduction in Ref-I load. This way, GHI of 30 % and 40 % are possible when SNI of 10 % and 40 %, respectively, are applied. Therefore, the results show that simultaneous incorporation of both alternative feedstocks can, in fact, enable higher green H_2 incorporation, contributing to greater decarbonization and deeper natural gas savings.

Figure 4 illustrates the Total Decarbonization extent achieved through both alternative feedstock incorporation. This indicator represents the relative difference in CO_2 emissions for each case compared to the previous base case. Included in CO_2 emissions are those captured in the CO_2 Removal Section, as well as emissions from flue gas generated by burning natural gas for energy production.

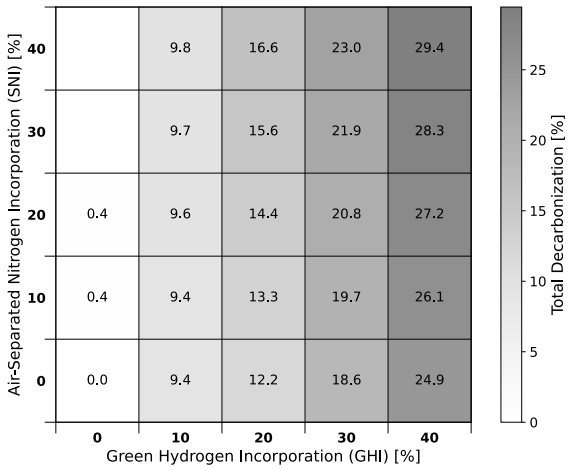

Figure 4: Matrix of Total Decarbonization as a function of GHI and SNI (0 - 40 %; blank cells indicate no feasible solution was found).

The decarbonization values achieved are notably significant, especially when green hydrogen is incorporated. These values arise from the reduced use of grey H_2 and the corresponding decrease in CH_4 required for both reforming and combustion, thereby substantiating the reported decarbonization levels. With respect to air-separated nitrogen, its influence is minor at low green hydrogen incorporation fractions (GHI < 10%), but it can contribute substantially to additional decarbonization at higher GHI values.

The reduction in natural consumption is quantified through Natural Gas Savings, which measures the

savings in natural gas (both as feedstock and fuel) reported relative to the base case. The results are presented in **Figure 5**.

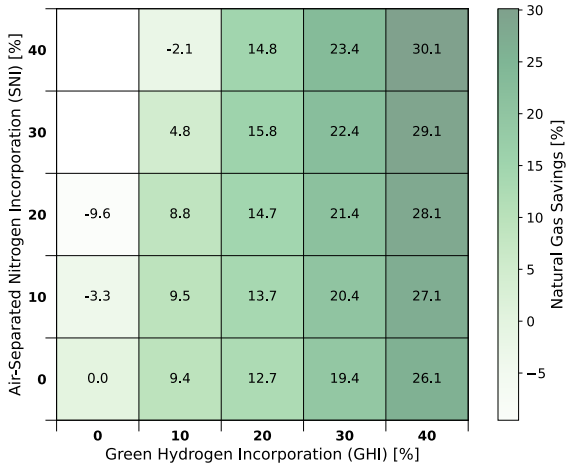

Figure 5: Matrix of Natural Gas Savings as a function of GHI and SNI (0 - 40 %; blank cells indicate no feasible solution was found).

Reducing natural gas consumption is a crucial consideration for the plant's economics, particularly given that, in the base case, natural gas costs account for approximately 70 % of total operational expenses. The economics obtained are reported in **Figure 6**.

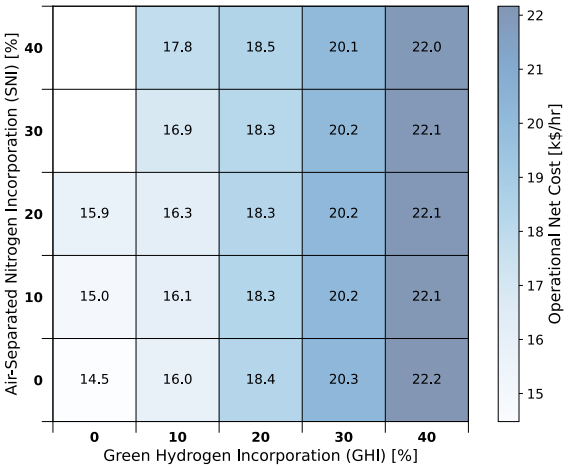

Figure 6: Matrix of ONC as a function of GHI and SNI (0 - 40 %; blank cells indicate no feasible solution was found).

Combining the effects of natural gas savings and the reduction in CO_2 emission taxes enabled by the extent of decarbonization, it would be expected that a cheaper operation would result as alternative feedstock incorporation is considered. Nevertheless, significant increases in operational costs are reported due to the cost of alternative feedstock considered. This is especially noted for green H_2, whose price is way higher than that of air-separated N_2. For instance, in the most decarbonized scenario, with GHI and SNI at 40 %, green H_2 expenses account for more than 50 % of total operating costs, while air-separation accounts for less than 3 %. Green H_2 may only be economically attractive once its production cost falls to around 2.4 $ per kilogram, at which point it becomes competitive with grey H_2 production.

CONCLUSIONS AND FUTURE WORK

The incorporation of green H_2 and air-separated N_2 into a conventional NH_3 plant was investigated using a model developed in *Aspen Plus® V14*. Incorporating green H_2 makes a greater contribution to natural gas savings and to the extent of SMR process decarbonization. Although its contribution is limited, air-separated N_2 can be significant in enabling broader control of the Ref-II outlet temperature.

Building on the previously proposed Ref-I Bypass operation, it was shown that higher GHI fractions can be achieved by considering a minimum fraction of air-separated N_2.

Despite technical viability, incorporating both alternative feedstocks (H_2 and N_2) increases SMR operational costs, mainly due to the cost of green H_2 considered. The threshold could be reached with a green H_2 cost of around 2.4 $ per kilogram, at which point it becomes competitive with grey H_2 production.

As these are preliminary results, future research may include exploring alternative feedstock compositions, varying injection points, or modifying the flowsheet to facilitate more flexible operation of the SMR process under the proposed conditions and to achieve greater decarbonization. Given the substantial costs involved, subsequent studies might also incorporate an economic analysis of green H_2 production costs to assess their impact on the economics of retrofitted NH_3 plants.

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