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Towards the Decarbonization of a Conventional Ammonia Plant by the Gradual Incorporation of Green Hydrogen

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ABSTRACT

As initiatives to decarbonize societies increase, industry is also being considered for policies to encourage its sustainability. Ammonia (NH_3) industry relies entirely on Haber-Bosch (HB) process, consuming fossil fuels for hydrogen production and energy purposes, accounting for more than 1 % of anthropogenic carbon dioxide (CO_2) emissions. Emerging technologies such as the electrochemical synthesis of NH_3 promise sustainable production from water, air, and renewable energies, but low TRLs are still reported. The electrification of the HB process opens a more viable path for sustainable NH_3 production in the near future, where hydrogen (H_2) is produced by electrolysis of water, powered from renewable energy sources. Many studies have focused on the production of 100 % green NH_3 using only electric HB. In this work, a different approach is presented, which consists of studying the gradual incorporation of green H_2 into a conventional NH_3 plant. An *Aspen Plus® V14* model of the methane-fed HB process was developed, and the limitations of the process were identified by sequentially incorporating 0 to 10 % green H_2. To avoid overheating the equipment in the natural gas reforming stage, a new configuration is suggested for this step. With this modification, the study is extended to incorporating higher percentages of green H_2, up to a limit of around 61 %. Finally, the impact of the reforming temperature tolerance on the green H_2 incorporation limits for the suggested configuration was studied.

Keywords: Ammonia, Haber-Bosch Process, Green Hydrogen

INTRODUCTION

At the beginning of the 20th century, the agricultural sector was under pressure to find a source of nitrogen allowing the increase of food production in response to the growing population. Until then, nitrogen, one of the most critical needs for crop development, relied on limited natural sources (such as guano). In 1909, Fritz Haber succeeded in fixing atmospheric nitrogen (N_2) by synthesizing ammonia (NH_3) through its reaction with hydrogen (H_2), using an iron-based catalyst (Equation (1)). In 1913, Carl Bosch adapted the process for industrial scale, which is known to this day as the Haber-Bosch Process (HB), considered one of the most important technological developments of humankind [1].

$$N_2 + 3\,H_2 \leftrightarrow 2\,NH_3 \tag{1}$$

Ammonia is currently the second most produced chemical worldwide, with around 85 % of its production used in the nitrogen fertilizer industry (urea, ammonium nitrate, among others). It is estimated that half of the world's current population depends directly on the application of these fertilizers in the agricultural sector. In addition, ammonia also finds uses in the pharmaceutical industry, textiles, explosives production and $deNO_x$ technologies [2].

The global relevance and scale of the HB process makes it responsible for the consumption of 2 % of the final energy consumed and the emission of 1 to 2 % of the world's carbon dioxide (CO_2) emissions. This is justified by its high dependence on fossil fuels, not only for process heat, but also as a feedstock for hydrogen production. Around 75 % of NH_3 is produced from light hydrocarbons such as natural gas and naphtha. In Europe, almost all plants operate with natural gas consumption, producing H_2 by Steam Methane Reforming (SMR), which is considered the Best Available Technology for its high energy efficiencies and lower emissions. The remaining 25 % is produced using coal and heavy fuel oil, which are consumed mainly by Asian ammonia industry [2,3].

Driven by carbon neutrality and energy independence policies, the ammonia industry is striving for decarbonization. In the European Union, the Renewable Energy Directive III requires that, by 2030, 42 % of the hydrogen consumed in industrial processes should come from renewable sources [4]. The decarbonization of the sector has driven the development of technologies that allow NH_3 production to move away from the HB process, which is more decentralized, less carbon and energy intensive, more flexible and with the possibility of fully incorporating renewable energies These include electrochemical, electrocatalytic and plasma synthesis, among others. However, these technologies are still at a low Technology Readiness Level (TRL). The most mature green NH_3 production technology relies on the electrification of the HB process, where the SMR process is replaced by water electrolysis – powered via renewables – as the source of hydrogen [1,2].

However, the flexibility of the HB synthesis has yet to be proven, specifically, under the fluctuating supply of H_2 when coupled with a renewable power source, which poses major challenges in managing its operation. Many papers have been published on the production of fully green NH_3, especially on energy management to ensure the continuous operation of the HB process. The effectiveness of this management is, in most of these works, only achieved by storing hydrogen in tanks or by storing energy in batteries [4]. As the paradigm of NH_3 manufacture is changing towards green production, this creates a challenge for the ammonia industry, largely relying on fossil fuels. Namely, this raises questions about how plants will adapt to remain competitive and make the most of the capital invested in the current infrastructure.

The European ammonia industry is starting to adapt and try to position itself in the new reality. Fertiberia, in Spain, and Yara, in Norway, are examples of companies with a long-established position in the ammonia market that have recently begun to introduce green hydrogen into their conventional plants, albeit in small quantities [4]. A single study related to this practice is found in the literature [5], with a maximum green H_2 incorporation of around 20 %, limited, among other factors, by overheating of equipment. Inspired by the operating procedures at one real-life plant, this work addresses the challenges of gradually incorporating green H_2 into a conventional ammonia production plant and presents a new configuration to achieve higher incorporations.

GREY TO GREEN AMMONIA

To simulate a conventional methane-fed HB process, an Aspen Plus® V14 model was developed. This model can be divided into two different sections: the SMR section and the HB synthesis section, as shown in Figure 1.

SMR Section

The SMR section produces hydrogen from natural gas (~CH_4), which is initially purified by hydrodesulphurization. The removal of sulphur compounds prevents catalysts' poisoning in multiple process units. This stream is heated, mixed with steam, and fed into a reforming section made up of two separate reactors. In the first reformer, Ref-I, H2 is produced by steam consumption, according to Equations (2) and (3). Steam is supplied in excess to minimize carbon formation reactions and shift the equilibrium towards the products.

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

The effluent gas mixture from Ref-I is mixed with compressed hot air and fed into the second reformer, Ref-II, where the conversion of unreacted CH_4 is completed (CH_4 molar fraction below 0.005). The air stream flowrate (N_2 ~0.78, O_2 ~0.21, Ar ~0.01 molar fractions) supplied to Ref-II is adjusted to achieve the desired H_2/N_2 ratio in the NH_3 synthesis section, although simultaneously the oxygen (O_2) feed must be fully consumed in this unit according to Equation (4). Argon (Ar) is introduced in this stage and remains as a chemical inert in all process units.

$$CH_4 + 0.5\,O_2 \leftrightarrow CO + 2\,H_2 \tag{4}$$

From Ref-II, the gas mixture is cooled and the carbon monoxide (CO) formed in the reforming stages is converted. This conversion is described by Equation (3) and takes place in two different stages: high-temperature shift (HT) followed by low-temperature shift (LT).

Carbon dioxide is then removed by scrubbing the mixture with an ammonia solution. The removal of CO_2 from the syngas stream, as well as all oxygen compounds, is critical to the HB synthesis operation, since these compounds act as poisons to the iron-based catalysts in this stage. The unconverted CO fraction and the uncaptured CO_2 undergo a methanation step, consuming a small amount of H_2 and generating CH_4 and water (H_2O), Equations (5) and (6).

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \tag{5}$$

$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + H_2O \tag{6}$$

Like Ar, CH_4 is an inert chemical in the HB section and water is separated by molecular sieve adsorbers, ensuring that no oxides are admitted to the HB section. The gas mixture obtained is therefore mostly composed of H_2 and N_2 in a 3:1 molar ratio, with small amounts of CH_4 and

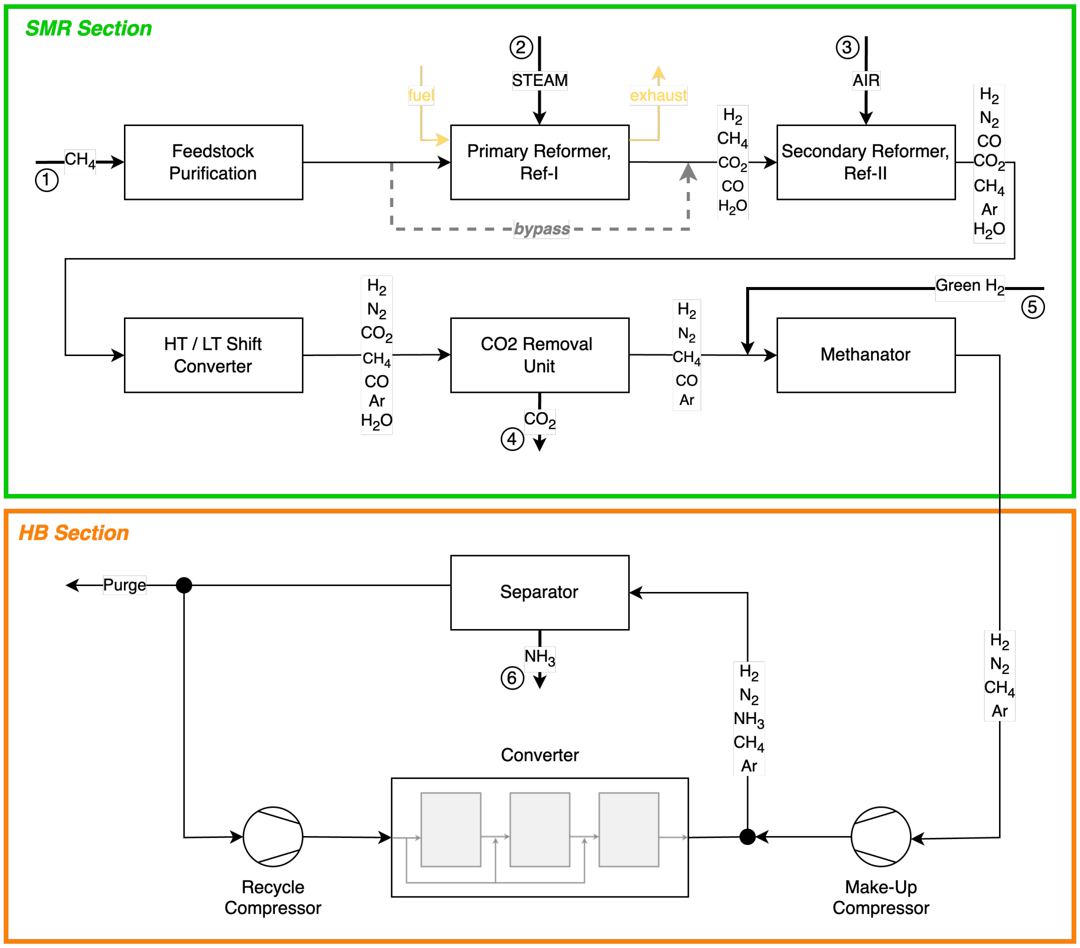

Figure 1: Simplified schematics of the model developed, divided into SMR and HB section (adapted from [4]). The first part of this work studies the incorporation of green H2 (stream ⑤) with manipulation of the flow rate of the natural gas stream (stream ①). The second part studies a new configuration of the reforming section, with bypass to primary reforming (as illustrated in dashed line).

Ar. Some metrics of the SMR section are listed in Table 1.

Table 1: Main consumptions in the SMR section for hydrogen production of 3 000 kmol/hr, based on the model developed.

① Natural Gas Consumption [ton/hr]	15.7
② Steam Consumption [ton/hr]	51.1
③ Air Consumption [ton/hr]	41.2

HB Section

The formation of NH_3, according to Equation (1), is highly exothermic and thermodynamically favored by high pressures and low temperatures. However, low temperatures favor low reaction rates. To achieve higher rates, the industry synthesizes NH_3 at pressures between 150 and 300 bar and temperatures ranging from 400 to 450 °C [4].

Due to the high exothermicity of the synthesis reaction, the reactor is usually divided into three catalytic beds, which promotes a more efficient strategy for effluents' temperature control. This is achieved by splitting the feed stream and introducing it in stages at the entrance to each of the catalytic beds as shown in the HB Section in Figure 1 (Converter).

The conversions achieved per pass are typically low (less than 25 %) and require the recycling of unconverted nitrogen and hydrogen, which must be separated from the NH_3 produced to achieve economic viability. Several configurations on the arrangement of reactor beds, stream splits and process units have been reported; the model developed in this work is fully consistent with the process diagram shown in Figure 1.

After leaving the third catalytic bed, the effluent is cooled in a heat exchanger network where the syngas feed is pre-heated and steam is generated (not visible in the diagram). This stream is then mixed with the compressed syngas makeup from the SMR section. Cooling in the separator stage allows ammonia to be separated from this mixture in the liquid phase, and the gaseous phase is purged to avoid the accumulation of CH_4 and Ar. The remaining gas stream is slightly compressed to compensate for the pressure drop, heated, split and admitted to the reaction beds, closing the ammonia synthesis loop. Some indicators of the HB section can be found in Table 2.

Table 2: Production and yield achieved in HB section.

Ammonia Production [kton/year]	~200
Ammonia Yield [%]	93.4

Green Hydrogen Incorporation

The introduction of green H_2 into the process was considered immediately upstream of the methanation step (in the SMR section, stream ⑤) and its intake leads to two different operating strategies: S-I and S-II. The S-I reduces the production of grey H_2 by reducing natural gas and process steam in the SMR section. The intake of green H_2 allows NH_3 production to remain fixed. In strategy S-II, grey H_2 production remains unchanged, resulting in higher H_2 feed to the HB section. By taking in larger quantities of process air, higher NH_3 production can be achieved in HB section. Table 3 summarizes the main changes to the process according to the operating strategy considered.

Table 3: Effect on the quantities of air, natural gas and steam consumed and on the quantity of NH_3 produced with the incorporation of green H_2, for S-I and S-II.

	Natural Gas ①	Steam ②	Air ③	NH_3 Prod. ⑥
S-I	↓	↓	=	=
S-II	=	=	↑	↑

Although both strategies lead to a certain degree of decarbonization of NH_3 production, it was the authors' decision to focus on the S-I study in this work as it better represents the industrial reality of reaching a certain product capacity to be sold on the market, as well as the effective replacement of grey H_2 with green H_2. For this study, the input of green H_2 by a pure stream ($xH_2 = 1$) was assumed, without modelling the upstream electrolysis process; and full availability of green H_2 was considered, with no limit on its supply to the process. The incorporation of green H_2 was defined as a function of the total amount of H2 (green + grey) that is supplied to the HB section. To maintain this total amount of H_2 unchanged, the natural gas flow (stream ①) is manipulated as the amount of green H_2 introduced increases (stream ⑤). To keep the carbon/steam ratio at Ref-I, the steam flow rate (stream ②) is also adjusted.

RESULTS

Standard SMR

The incorporation of H_2 was considered from 0 to 10 % and the results obtained (Figure 2) show a very similar relationship between the incorporation of green H_2 and the reduction in natural gas consumption, as well as with the decarbonization of the process (only the CO_2 emissions directly generated by the production of H_2 are taken into account, which are those obtained in the CO_2 removal unit – stream ④, without the emissions associated with burning natural gas for energy purposes).

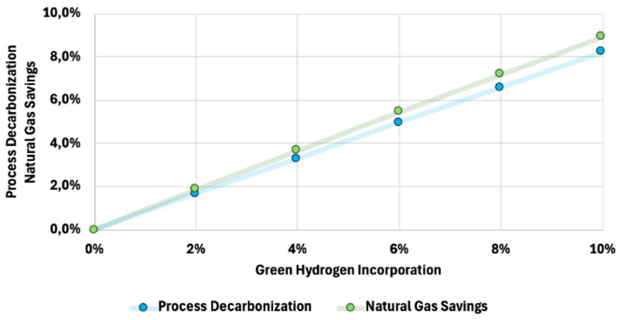

Figure 2: Process decarbonization and natural gas savings for an incorporation of green H_2 of 0 to 10 %.

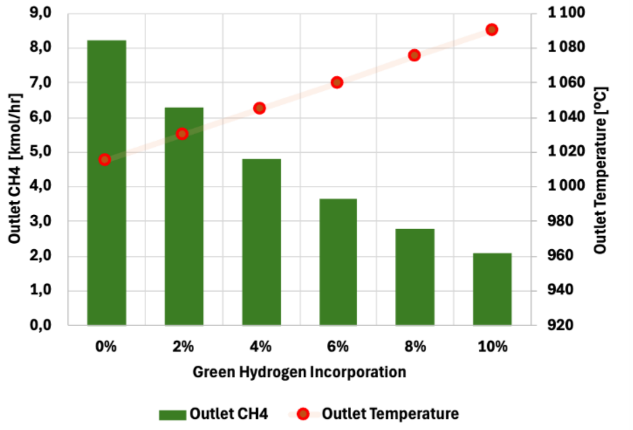

Figure 3: CH_4 flowrate and effluent temperature of the second reformer for an incorporation of green H_2 between 0 to 10 %.

Although the reduction in CH_4 consumption has an influence on all the stages of the SMR section, the main effects are found in the reforming step, more specifically in Ref-II. Figure 3 shows the results obtained for the CH_4 flowrate and the temperature of the Ref-II outlet. These variables are highlighted because they can constrain higher values of green H_2 incorporation, due to the possible incomplete consumption of O_2 and overheating of the equipment, as explained below.The reduction in the flowrate of CH_4 exiting Ref-II is justified by the reduction in natural gas and the requirement to consume the same amount of atmospheric O_2. Recalling the importance of this O_2 consumption, the declining trend in the amount of CH4 in the effluent may result in incomplete O_2 consumption for greater incorporations of green H_2. This can lead to O_2 being carried over to the HB section and impact on the lifespan of the catalyst used in NH_3 synthesis.

The temperature of the effluent is influenced by the exothermicity of the reaction and the heat release is dissipated by a smaller volumetric flow of effluent, due to a lower supply of natural gas. The increase in temperature (around 75 °C for a green H_2 incorporation of 10 %) over the already high temperatures of the base case (~1000 °C, 0 % green H_2) can lead to equipment overheating, not only of the Ref-II but also downstream. The same results were obtained in a similar study [5], although the variation in temperature obtained by those authors was less sharp than that obtained by the current simulation. The authors also stress the importance of temperature in determining the incorporation of green H_2 and limited its variation to a maximum of 100 °C, which resulted in an incorporation of between 15 and 20 % of green H_2. Applying the same criteria to this work would result in a maximum limit close to 12 %.

Adapted SMR

The challenge of introducing green H_2, while producing the remaining grey H_2, and ensuring the necessary N_2 input, total O_2 consumption and controlling the temperature of Ref-II is a challenge that could unlock greater incorporations of green H_2 and more extensive decarbonization of NH_3 production. This can be achieved by a different balance of the fraction of natural gas that is processed in Ref-I and Ref-II. The diverting of CH_4 from Ref-I to Ref-II can avoid the obligatory consumption of CH_4 per pass in Ref-I, guaranteeing the amount of CH_4 necessary for total O_2 consumption and grey H_2 production and, eventually, temperature control in Ref-II.

To study this possibility, a new configuration was considered for the reforming stage, highlighted by the dashed lines in Figure 4. This new configuration includes a bypass to Ref-I, which gives the model the flexibility it needs to manage CH_4 consumption between Ref-I and Ref-II. In this study, the outlet temperature of Ref-II effluent is kept constant and equal to the base case (~1015 °C, 0 % green H_2), by adjusting the bypass fraction accordingly.

For an incorporation of green H_2 from 0 to 10 %, Figure 5 shows a similar relationship between the decarbonization of the process and the reduction of natural gas. The same figure shows the results obtained for the bypass fraction, which suggest a linear behavior with the increasing incorporation of H_2. For example, introducing 10 % of green H_2 means that only around 80 % of the flow is fed to Ref-I. The flow reduction in Ref-I is, however, even more pronounced compared to the base case, since the natural gas flow is already reduced to allow only 90 % of the total hydrogen to be produced.

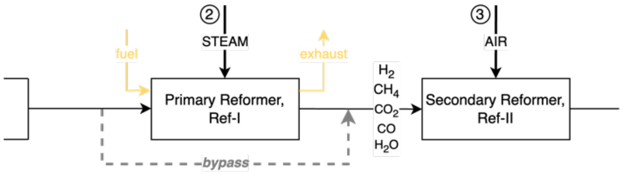

Figure 4: New proposed configuration, with Ref-I bypass (detail from **Figure 1**).

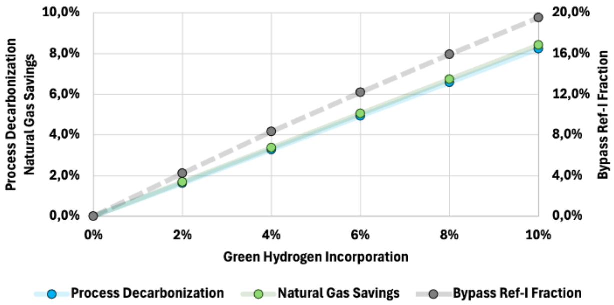

Figure 5: Process decarbonization, natural gas savings and bypass fraction for an incorporation of green H_2 of 0 to 10 % (adapted SMR with Ref-I bypass).

By analyzing the effluent from Ref-II, whose temperature and molar flow of CH_4 are shown in Figure 6, it is possible to identify that temperature control also allows the reduction of CH_4 in this stream to be less dependent on green H_2 incorporation, possibly leading to a less sudden and delayed depletion of this compound.

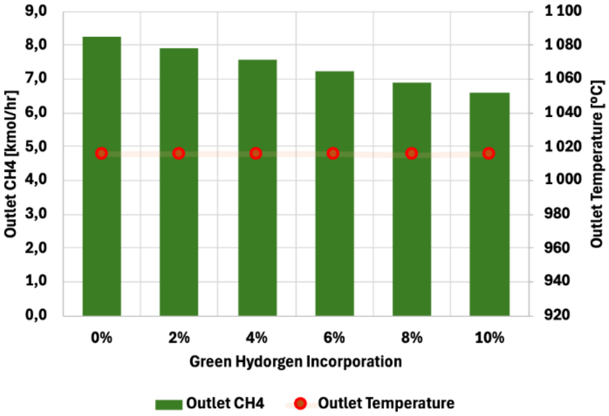

Figure 6: CH_4 flow rate and effluent temperature of the second reformer for an incorporation of green H_2 of 0 to 10 % (adapted SMR with Ref-I bypass).

Once control of the effluent temperature and the presence of enough CH_4 to consume O_2 were ensured by

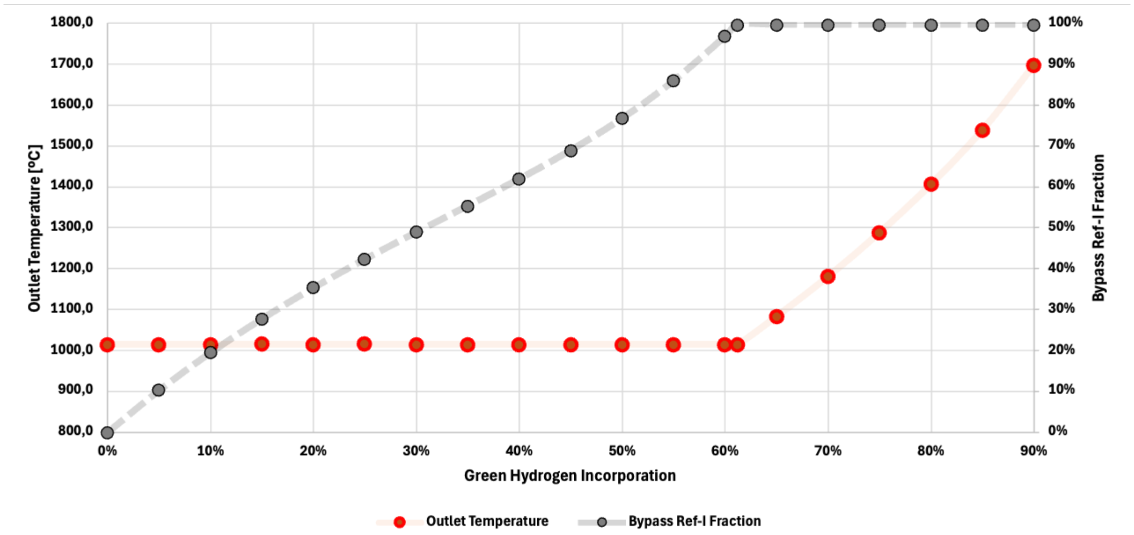

Figure 7: Effluent temperature of the second reformer, Ref-II, and bypass fraction for an incorporation of green H_2 of 0 to 90 % (adapted SMR with Ref-I bypass).

the new Ref-I bypass configuration, further incorporation of green H_2 was studied. Figure 7 shows the behavior of the effluent temperature and the evolution of the bypass fraction for incorporations of 0 to 90 % green H_2. Adjustment of the bypass fraction allows the temperature to be controlled up to around 61 % of green H_2 intake, at which point the bypass fraction is total, meaning the Ref-I is no longer in operation. This is one of the important points of this analysis, from which the introduction of green H_2 is limited by the inability to control the temperature of Ref-II. However, operating at values close to this point implies operating Ref-I with very small flow rates that are far from its nominal capacity.

At this stage, no minimum limit on the volume of gas fed to Ref-I and Ref-II (or any other equipment) has been considered, which could be useful in a future study where the effect of their minimum operating capacities should be addressed. Nevertheless, it is to be expected that the assumption of a minimum capacity value for Ref-I will inevitably result in a limitation of the maximum bypass fraction and, as a result, this limit point will be reached for a smaller incorporation of green H_2.

Another important point will be the start of the bypass operation. In this study, the start of operation of the bypass coincides exactly with the start of the green H_2 intake because no tolerance to the temperature of the base case (~1015 °C) was considered. Moreover, if it is possible to increase the Ref-II outlet temperature, its effect is found as the % of green H_2 incorporated. Assuming a tolerance in that temperature of + 50 and + 100 °C, the start of the bypass becomes increasingly distinct from the start of the incorporation of green H_2, and the temperature can be controlled for increasingly higher incorporations. Table 4 summarizes the results obtained.

Table 4: Influence of the Ref-II outlet temperature tolerance (ΔT) on the operation of the Ref-I bypass.

ΔT [°C]	T_{out} [°C]	% Bypass >0 [% Green H_2]	% Bypass ~100 [% Green H_2]
+ 0	1015	0	61
+ 50	1065	7	64
+ 100	1115	13	67

CONCLUSIONS

The incorporation of green H_2 into a conventional NH3 plant was investigated using a model developed in Aspen Plus® V14. The incorporation of green H_2 reduces natural gas consumption and CO_2 emissions. It was found that the increase in the temperature of the second reformer could limit extensive incorporation of green H_2. A new configuration of the reforming section has been proposed, consisting of a bypass to Ref-I, which allows 61 % of green H_2 to be incorporated while maintaining the temperature recorded in conventional operation at 0 %. By studying the influence of the tolerance of this temperature, according to the proposed configuration, it was concluded that greater tolerances make it possible to extend the incorporation of green H_2 even further and thus decarbonise the plant to a greater extent.

DEDICATION

The authors would like to dedicate this article to the memory of Professor Pedro Castro, who was involved in the discussion of this work. His guidance, knowledge and friendship will be greatly missed.

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