

Recalibration of Carbon-Free NH_3/H_2 Fuel Blend Process: Qatar's Roadmap for blue ammonia

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ABSTRACT: Due to growing concerns about carbon emissions, using zero-carbon fuels has become an interesting alternative to overcome this problem. The $\text{NH}_3(70\%)\text{-H}_2(30\%)$ fuel blend is an innovative fuel example that has the potential to replace conventional hydrocarbon fuels. Studies on the $\text{NH}_3(70\%)\text{-H}_2(30\%)$ fuel blend have shown its superior combustion performance and its effect on enhancing cycle efficiency compared to other compositions of the $\text{NH}_3\text{-H}_2$ blends. However, without calibrating ammonia plants and simply mixing portions of the produced pure ammonia to hydrogen at the desired molar fraction essentially requires coupling ammonia plants with other hydrogen-producing plants, leading to potential difficulties in commercializing the unused (as fuel in the $\text{NH}_3\text{-H}_2/\text{air}$ gas turbines) hydrogen portions from the hydrogen-producing plan. Therefore, in this paper, as an attempt to utilize the existing ammonia production infrastructure and facility without acquiring major changes that could lead to resisting the adoption of the $\text{NH}_3(70\%)\text{-H}_2(30\%)$ fuel blend, the independent parameters of a conventional ammonia plant have been calibrated, and the reactors have been sized to provide a continuous supply of the $\text{NH}_3(70\%)\text{-H}_2(30\%)$ fuel blend with the exact molar fraction to run a power plant. Calibrating of the ammonia plant has been performed using an ASPEN PLUS model.

KEYWORDS: Ammonia Production; Plant calibration; Alternative Zero-Carbon Fuel; Power Generation, Fuel blending.

1. INTRODUCTION

Over 76% of all nitrogen-based products use ammonia (NH_3), which is a crucial production component and the least expensive chemical that combines nitrogen with other gases (Table 1) [1]. The reaction of N_2 and H_2 occurs at high temperatures and under compression, while properly catalyzed, is the primary way that NH_3 is created. Furthermore, NH_3 is also produced as a byproduct of coal coking; however, the byproduct of natural ammonia is produced in much smaller quantities limiting its availability [2]. The Haber-Bosch method is the most widely used around the globe, but is inherently expensive due to the high levels of pressure that are required to achieve ammonia production on a commercial scale. The Haber-Bosch process was the first industrial chemical reaction to use high pressure. It combines airborne nitrogen and hydrogen directly under extremely high pressures and moderate temperatures [2-3]. A catalyst composed primarily of iron allows the reaction to be conducted at a lower temperature than would otherwise be possible, and the removal of ammonia from the batch as soon as it is formed maintains an equilibrium favoring product formation [2-3]. The greater the proportion of ammonia produced in a mixture, the lower the temperature and the higher the pressure [2-3]. Another way of producing ammonia is through using the convertible facilities of CH_3OH production, which share similar ammonia-production subprocesses such as reforming and CO_2 removal [4]. Table 1 shows, urea ammonium nitrate (UAN), diammonium phosphate (DAP), and monoammonium phosphate (MAP) fertilizers are the main products produced from NH_3 .

Table 1. Ammonia Applications.

Application	Percentage
Direct Application	3%
Non-Fertilizer Uses	15%
Urea	42%
Other Compound	5%
Ammonium Bicarbonate	6%
UAN	5%
DAP	4%
MAP	2%
Ammonium Nitrate	8%
Ammonium Sulphate	3%
Calcium Ammonium Nitrate	3%
Other	4%

Most importantly, NH_3 is used as a zero-carbon fuel in power plants as an energy vector [4–10]. Due to a shortage of natural energy resources, Japan has been searching for renewable alternatives to meet its energy consumption needs during the past few decades [5]. Hydrogen has been proposed as an enticing alternative that may satisfy their energy needs while reducing greenhouse gas emissions. However, Japan has recognized the potential of ammonia to act as a hydrogen-carrying energy vector, and a 22-member consortium led by Tokyo Gas has been established to curate "Green Ammonia" sponsored by Japan's Cross-Ministerial Strategic Innovation Program (SIP) [5]. In the United States, the Advanced Research Project Agency-Energy (ARPA-E), a subsidiary of the Department of Energy, has recently introduced its "Renewable Energy to Fuels through Utilisation of Energy-Dense Liquids" (REFUEL) program, whose goal is to create scalable techniques for producing electric energy derived from alternative sources of energy into energy-dense carbon-neutral liquid fuels (CNLFs) and back into electricity or hydrogen on demand [6].

ARPA-E revealed that funding totaling \$32.7 million will be given to 16 REFUEL initiatives, 13 of which are ammonia-focused. From small-scale ammonia synthesis using stranded wind energy to the improvement of the Haber–Bosch process, this initiative involves both reputable academic institutions and major industrial corporations [7].

In pursuit of a carbon-free economy, fuels with low or zero carbon footprint account for only 1% of global final energy demand, but this is expected to rise to 20% by 2050 [8]. Ammonia dominates the worldwide low-carbon alternative fuel transportation and storage industry. Ammonia is a carbon-free, renewable hydrogen carrier with high energy density and well-established production and distribution infrastructure. However, ammonia's low burning velocity and narrow flammability limit are significant challenges. Blending ammonia with hydrogen improves ignition, flammability, and hydrogen safety, enhancing ammonia combustion. Omar I. Awad et al. [8] reported that decarbonizing the energy sector with ammonia-hydrogen combustion systems is feasible. Omar I. Awad et al. [8] reviewed influential studies and ongoing research on ammonia/hydrogen blended fuels. The review conducted by Omar I. Awad et al. [8] covered ammonia's role in hydrogen safety, ammonia / hydrogen combustion characterization, and low- NO_x ammonia /hydrogen combustion.

As nations seek to cut greenhouse gas (GHG) emissions in difficult-to-abate sectors, interest in hydrogen as an energy source is increasing. Prior studies have concentrated on hydrogen production, well-to-wheel fuel cell vehicle analyses, and the costs and emissions of vehicle refueling [9]. These studies base

their analyses of the techno-economic and GHG emissions on high-level projections for hydrogen transportation systems. The unit prices and emissions footprints (direct and indirect) of 32 hydrogen transportation systems were evaluated and compared by G. Di Lullo et al. [9]. Process-based models were used in the work of G. Di Lullo et al. [9] to evaluate the transportation of pure hydrogen, hydrogen-natural gas blends, ammonia, and liquid organic hydrogen carriers via pipeline, rail, and truck transport of gaseous and liquified hydrogen. Sensitivity and uncertainty analyses were utilized by G. Di Lullo et al. [9] to identify the variables influencing the cost and emission estimations. At 1000 km, the pure hydrogen pipes have a levelized cost of \$0.66/kg hydrogen and a GHG footprint of 595gCO₂eq/kg hydrogen, according to G. Di Lullo et al. [9]. Pure hydrogen pipeline transport and ammonia transport have equal GHG emission footprints, but all other transport systems have emissions that are more than twice as high. These findings might be instructive for worldwide policy-making bodies on clean hydrogen.

Hydrogen is crucial to ensuring reliable and effective renewable electricity penetration. Building a sustainable Hydrogen Economy has many value chain problems. Large-scale manufacturing and storage remain unsolved. Power-to-Ammonia storage of renewable hydrogen is promising. Camel Makhoulfi al. [10] investigates a large-scale ammonia-hydrogen recovery method. Camel Makhoulfi et al. [10] showed that large-scale ammonia-to-hydrogen synthesis is feasible. Ammonia-to-hydrogen plants create 200 MTPD pure hydrogen at 250 bar with 68.5% thermal efficiency. Camel Makhoulfi al. [10] also calculated the Levelized Cost of Hydrogen (LCOH) using green ammonia. Green ammonia cost, which changes with renewable electricity cost, determines LCOH.

Due to faster transcontinental shipping, international trade has increased. Yet, fossil fuel usage and environmental effect rise. Shaimaa Seyam al. [10] proposes a gas Brayton cycle, solid oxide fuel cell, and two organic Rankine cycles marine engines to replace two-stroke internal combustion engines. Green fuels include hydrogen, methane, dimethyl ether, ethanol, and methanol. Liquified natural gas also cools. Aspen Plus thermodynamically analyzes this integrated hybridized marine engine's energetic and exergetic performance. The engine's overall power is increased by 33% to 15758 kW with average energetic and exergetic efficiencies of 38% and 46%. All sustainable fuel mixes reach 16087 kW with 83% carbon emission reduction and minimal specific fuel usage [11]. Traditional engines are less efficient and polluting than the proposed engine. Due to faster transcontinental shipping, international trade has increased.

In addition, even in natural-gas rich countries, a growing trend to convert natural gas into ammonia a carbon-free fuel is emerging to meet their global commitments to reduce greenhouse gas emissions. For example, Qatar Petroleum, a state-owned petroleum company of Qatar has announced its roadmap to implement effective measures to produce cleaner energy using the latest proven emissions reduction technologies. The three primary milestones of the announced roadmap are; (1) to develop a centralized carbon capture and sequestration hub in Qatar; (2) to utilize hydrogen as a carbon-free fuel and (3) to explore the potential of utilizing ammonia as fuel in gas turbines, Figure 1 [12].

Therefore, to approach these announced milestones, Alrebei et al [14] studied the potential of utilizing NH₃-H₂ blends as alternative fuels. Amongst many tested NH₃-H₂ blends with a variety of molar fractions, the NH₃ (70%)-H₂ (30%) blend was recommended by Alrebei et al. [14] due to its preferable combustion characteristics (combustion stability and minimal NO_x emissions compared to other NH₃-H₂ blends) which show the potential of replacing conventional hydrocarbon fuels, while eliminating carbon emissions. Alrebei et al. [14] investigated the possibility of employing NH₃ (70%)-H₂ (30%) as fuel in a simple-cycle gas turbine and discovered that, under lean combustion circumstances, cycle efficiency could be enhanced in comparison to methane-powered gas turbines (i.e., at an equivalence ratio of 0.75).

The roadmap targets:

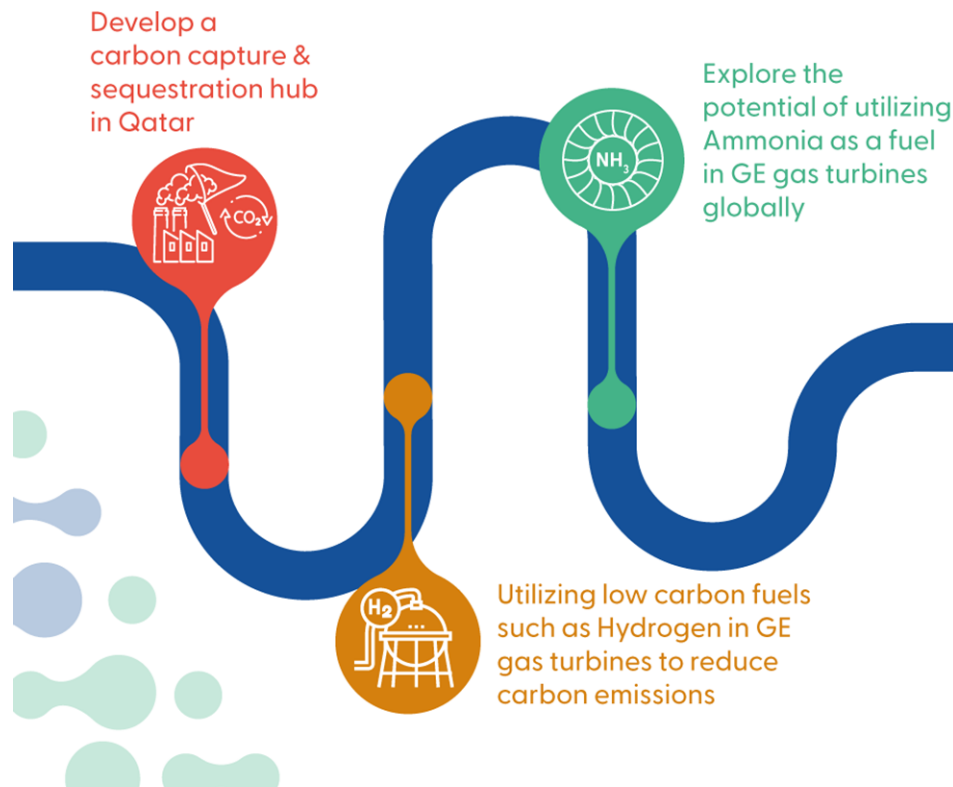


Figure 1. The roadmap to decarbonize hydrocarbon fuels (Announced by Qatar Petroleum).

By highlighting their efficiency and sustainability, ammonia-hydrogen gas turbines have the potential to be promoted to the power generating sector. Alrebei et al [15] performed a numerical investigation of a first-stage stator turbine blade subjected to $\text{NH}_3\text{-H}_2$ /air combustion flue gas. The results of the analysis agreed that the equivalence ratio of 0.75 is the optimal equivalence ratio to ensure the highest gas dynamic performance over the turbine blade compared to other equivalence ratios (i.e., stoichiometric ($\phi = 1.00$) and rich ($\phi = 1.25$)).

However, it is recommended by Alrebei et al. [15] to develop a process that is calibrated to provide a continuous supply of the 70% NH_3 -30% H_2 (vol%) fuel blend. Such processes could be developed and evaluated in process simulation programs (such as ASPEN PLUS). ASPEN PLUS is a process simulation software that is adopted as an industry standard to design and numerically calibrate a chemical process through mathematical subunits [16]. The iterative analysis approach available in ASPEN enables developers to optimize and calibrate the performance of a process by predicting energy consumptions and technoeconomic feasibility [17]. A similar ASPEN-based numerical calibration of the setup of existing plants is presented by Alrebei et al [16]. Alrebei et al. represented an ASPEN-based numerical calibration for an existing plant that involves an air separation unit (ASU), a steam methane reformer (SMR), water gas shift (WGS) reactors, pressure swing adsorption (PSA) units, and heat exchanged gas turbines (HXGT) with a CCS unit. The calibration performed by Alrebei et al [16] was achieved after defining the system's sensitivities, which have led to defining operating conditions of the ASU-SMR-WGS-PSA-CCS-HXGT

plant that ensure a continuous supply of the desired molar fractions of CO₂-Argon-Steam Oxy-Fuel (CARSOXY) blend recommended by the references [17-19].

Therefore, as proposed by Alrebei et al [15], which identified the gap of knowledge in the 70% NH₃-30% H₂ (vol%) fuel blend, this paper provides a calibration for existing plants to produce the desired molar fractions. In addition, following the calibration approach adopted by Alrebei et al [16], however, for ammonia plants, the sensitivities of the system have been identified using ASPEN PLUS to enable calibrating the ammonia plant to produce a continuous supply of the 70% NH₃-30% H₂ (vol%) fuel blend. Without the proposed calibration in this paper and simply mixing portions of the produced pure ammonia to hydrogen at the desired molar fraction, essentially require coupling ammonia plants with other hydrogen-producing plants, leading to potential difficulties in commercializing the unused (as fuel in the NH₃-H₂/air gas turbines) hydrogen portions from the hydrogen-producing plants. Moreover, without the proposed calibration in this paper, the existing ammonia plants produce ammonia at a high level of purity, which essentially requires extensive postprocessing after the synthesis loop (refrigeration and separation) [20-21], which is unnecessary in the case of the 70% NH₃-30% H₂ (vol%) fuel blend. In fact, without the proposed calibration in this paper, mixing "or unpurifying" ammonia would be needed to reverse the effect of the purifying postprocessing to achieve the desired 70%-30% molar fractions, thus; wasting the energy involved in the ammonia purifying postprocessing. Therefore, after identifying the system's sensitivities, this paper also suggests a reduction in the existing ammonia plant process.

The proposed calibration concept in this paper also aims to utilize the carbon capture facility in the ammonia plant as a centralized carbon capturing hub (i.e., the first milestone of the hydrocarbon fuel decarbonization roadmap, announced by Qatar Petroleum [12]) while distributing the decarbonized fuel to power plants in wider geographic scope. The feasibility of integrating each power plant with its own carbon capturing unit heavily depends on the geographic location of a power plant, in which the geological structure limits the carbon storage and sequestration capacities. Therefore, distributing carbon-free fuel through the proposed calibration concept enables the geographically wide-ranging power plants to generate carbon-free power without the necessity of coupling each power plant with a carbon capturing unit, overcoming any geological limitation of carbon storage and sequestration.

2. METHODOLOGY

2.1 Process description of the conventional ammonia plants

Water, air, energy and hydrocarbons as a source of H₂ are used to create ammonia. In most cases, the energy source is hydrocarbons, from which produce hydrogen. The most effective method is steam reforming of light hydrocarbons, with natural gas accounting for around 77% of the world's ammonia production capacity. The process comprises the following subprocesses, Figure 2:

- Gas desulfurization;
- Gas and steam reforming (as a source of H₂);
- Combustion;
- CO conversion to CO₂ via high temperature gas shift conversion and low temperature gas shift reaction;
- CO₂ removal process;
- Methanization
- Ammonia synthesis

The subprocesses of the analyzed ammonia plant have been linked to each other through streamlines, ensuring the process sequence described by the reference [22]. The fully integrated model (Figure 2) has been developed using ASPEN PLUS software. Tables 2, 3, 4, 5, and 6 provide descriptions of the subprocesses, including the primary reactions, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, pressure drop expression, and ASPEN-plus reactor types. Each unit in Figure 2 had been set up on initial values, which have been modified after the sensitivity analysis to achieve the desired 70% NH₃-30% H₂ molar fractions. The initial input values had been adopted for the furnace, reforming unit, CO-shift conversion unit, carbon dioxide removal unit, methanation unit, and synthesis

units from the references [22-34]. The role of each unit within the process is described in the following parts of this section.

Table 2. The initial (uncalibrated) and final (calibrated after the sensitivity analysis) values of the Furnace unit

Parameter	Initial Value (uncalibrated)	Final Value (calibrated)
ASPEN Reactor Type	RSTOIC	
Furnace Fuel 1:		
• Temperature	• 47°C	• 47°C
• Pressure	• 1.325 kg/sqcm	• 1.325 kg/sqcm
• Total mole flow rate	• 454.36 kmol/h	• 454.36 kmol/h
• Molar fractions	• [N ₂ : 0.7%], [CH ₄ :80%],[O ₂ : 0.2%], [C ₂ H ₆ :17.7%],[C ₃ H ₈ :0.9%], [C ₄ H ₁₀ :0.06%], [C ₅ H ₁₂ : 0.187%], [C ₆ H ₁₄ :0.0595%]	• [N ₂ : 0.7%], [CH ₄ :80%],[O ₂ : 0.2%], [C ₂ H ₆ :17.7%],[C ₃ H ₈ :0.9%], [C ₄ H ₁₀ :0.06%], [C ₅ H ₁₂ : 0.187%], [C ₆ H ₁₄ :0.0595%]
Furnace Fuel 2:		
• Temperature	• 25°C	• 25°C
• Pressure	• 1.325 kg/sqcm	• 1.325 kg/sqcm
• Total mole flow rate	• 484.3 kmol/h	• 484.3 kmol/h
• Molar fractions	• [H ₂ : 60%], [N ₂ : 22%], [CH ₄ : 12%], [Ar: 4%], [NH ₃ : 2%]	• [H ₂ : 60%],[N ₂ : 22%], [CH ₄ : 12%],[Ar: 4%], [NH ₃ : 2%]
Furnace heated air:		
• Temperature	• 271°C	• 271°C
• Pressure	• 1.05 kg/sqcm	• 1.05 kg/sqcm
• Total mole flow rate	• 6903.3 kmol/h	• 6903.3 kmol/h
• Molar fractions	• Air	• Air
Reactions	<ul style="list-style-type: none"> • $2\text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$ • $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ • $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ • $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ • $\text{C}_2\text{H}_6 + 3.5\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$ • $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$ 	<ul style="list-style-type: none"> • $\text{C}_4\text{H}_{10} + 6.5\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$ • $\text{C}_5\text{H}_{12} + 8\text{O}_2 \rightarrow 5\text{CO}_2 + 6\text{H}_2\text{O}$ • $\text{C}_6\text{H}_{14} + 9.5\text{O}_2 \rightarrow 6\text{CO}_2 + 7\text{H}_2\text{O}$ • $\text{C}_7\text{H}_{16} + 11\text{O}_2 \rightarrow 7\text{CO}_2 + 8\text{H}_2\text{O}$
Reference	Integration of the reactors, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, and pressure drop expression are as per the references [22-25].	

The catalyst in the natural gas desulfurization process is damaged by sulfur, which is present in the natural gas up to a maximum of 40 ppm by weight when supplied as dry gas [23-24]. By hydrogenating the sulfur to hydrocarbons and hydrogen sulfide and then absorbing the hydrogen sulfide in zinc oxides, the desulfurization unit lowers the sulfur concentration to approximately 5 ppm [23-24]. There are two parts to the reforming unit: primary reforming and secondary reforming. In addition to being reformed with hot air in the secondary reformer, the desulfurized hydrocarbon feed is reformed with steam in the primary reformer at 3:1 or higher steam gas ratio (S/G) depends on natural gas composition, and the purpose of this step is to produce hydrogen and carbon oxides as well as to protect the catalyst. The amount of CH₄ in the reformed gas is roughly 0.3 vol%; this amount is usually used to monitor the catalyst performance over time. The reactions involved in the reforming process have been modeled based on the reaction description by Moe and Gerhard (1965) [23] and Hyman (1967) [24]. The reformer is supplied with the necessary heat from a furnace. Tables 2 and 3 show the specifications of the furnace reforming units, respectively.

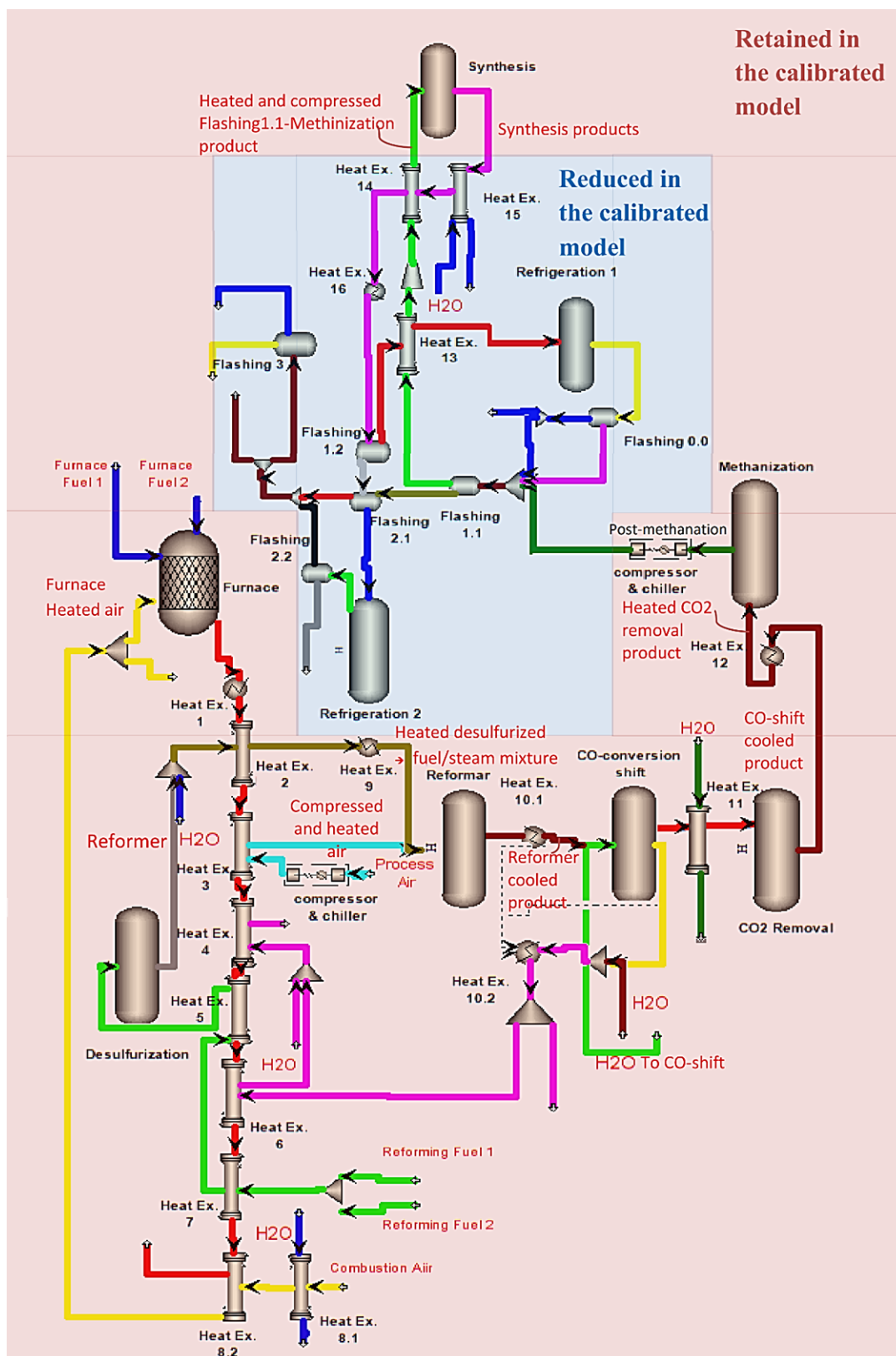


Figure 2. The ASPEN-PLUS model of the conventional ammonia plant (same stream colors within the same unit, however, not necessarily in the other units, are used for the same stream composition).

Table 3. The initial (uncalibrated) and final (Calibrated after the sensitivity analysis) values of the reformer unit.

Parameter	Initial Value (uncalibrated)	Final Value (calibrated)
ASPEN Reactor types	RSTOIC and RPLUG as per the references [22-25].	
Compressed and heated air:		
• Temperature	• 462.4°C	• 462.4°C
• Pressure	• 33 kg/sqcm	• 33 kg/sqcm
• Total mole flow rate	• 2364.6 kmol/h	• 2464.6 kmol/h
• Molar fractions	• Air	• Air
Untreated reformer air supply “process air”		
• Temperature	• 30°C	• 30°C
• Pressure	• 39 kg/sqcm	• 39 kg/sqcm
• Total mole flow rate	• 2364.6 kmol/h	• 2464.6 kmol/h
• Molar fractions	Air	Air
Heated desulfurized fuel/steam mixture:		
• Temperature	• 502.55°C	• 502.55°C
• Pressure	• 36 kg/sqcm	• 36 kg/sqcm
• Total mole flow rate	• 7176.57 kmol/h	• 7176.57 kmol/h
• Molar fractions	• [H ₂ :0.876%], [N ₂ :0.45%], [CH ₄ : 15.93%], [H ₂ O:78.93%], [O ₂ :0.04%], [C ₂ H ₆ :3.52%], [C ₃ H ₈ :0.187%], [C ₄ H ₁₀ :0.012%], [C ₅ H ₁₂ :0.037%], [C ₆ H ₁₄ :0.01184%]	• [H ₂ :0.876%], [N ₂ :0.45%], [CH ₄ : 15.93%], [H ₂ O:78.93%], [O ₂ :0.04%], [C ₂ H ₆ :3.52%], [C ₃ H ₈ :0.187%], [C ₄ H ₁₀ :0.012%], [C ₅ H ₁₂ :0.037%], [C ₆ H ₁₄ :0.01184%]
Reformer H ₂ O supply:		
• Temperature	• 360°C	• 360°C
• Pressure	• 36 kg/sqcm	• 36 kg/sqcm
• Total mole flow rate	• 5664.14 kmol/h	• 5664.14
• Molar fractions	• H ₂ O	• H ₂ O
Reformer fuel 1:		
• Temperature	• 116°C	• 116°C
• Pressure	• 39 kg/sqcm	• 39 kg/sqcm
• Total mole flow rate	• 84.77 kmol/h	• 84.77 kmol/h
• Molar fractions	• [H ₂ : 74.17%], [N ₂ : 24.8%], [CH ₄ : 0.74%] [Ar: 0.2961%]	• [H ₂ : 74.17%], [N ₂ : 24.8%], [CH ₄ : 0.74%][Ar: 0.2961%]
Reformer fuel 2:		
• Temperature	• 45°C	• 45°C
• Pressure	• 39 kg/sqcm	• 39 kg/sqcm
• Total mole flow rate	• 1427.7 kmol/h	• 1427.7 kmol/h
• Molar fractions	• [N ₂ :0.79%], [CH ₄ :80.05%], [O ₂ :0.2%], [C ₂ H ₆ :17.72%], [C ₃ H ₈ :0.94%], [C ₄ H ₁₀ :0.06%], [C ₅ H ₁₂ : 0.187%][C ₆ H ₁₄ :0.06%]	• [N ₂ : 0.79%], [CH ₄ : 80.05%], [O ₂ : 0.2%], [C ₂ H ₆ :17.72%], [C ₃ H ₈ :0.94%], [C ₄ H ₁₀ :0.06%], [C ₅ H ₁₂ : 0.187%][C ₆ H ₁₄ : 0.06%]
Reactions	<ul style="list-style-type: none"> • CH₄ + H₂O → CO + 3H₂ • 3C₂H₆ + H₂O → 5CH₄ + CO • 3n - C₄H₁₀ + 3H₂O → 9CH₄ + 3CO • 3C₆H₁₄ + 5H₂O → 13CH₄ + 5CO 	<ul style="list-style-type: none"> • CO + H₂O → CO₂ + H₂ • 3C₃H₈ + 2H₂O → 7CH₄ + 2CO • 3C₅H₁₂ + 4H₂O → 11CH₄ + 4CO • 3C₇H₁₆ + 6H₂O → 15CH₄ + 6CO
Reference	Integration of the reactors, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, and pressure drop expression are as per the references [22-25].	

In the CO-shift conversion, a major part of the CO contained in the reformed gas is catalytically converted to CO₂ in two catalytic stages, the first at high temperature and the second at low temperature. The low-temperature shift reactor is modeled as a plug flow reactor, RPlug. The reactions involved in the CO-shift conversion process have been modeled based on the reaction description by (Slack, 1974) [26]. Table 4 shows the specifications of the CO-shift conversion unit.

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Table 4. The initial (uncalibrated) and final (Calibrated) values of the CO-shift conversion unit.

Parameter	Initial Value (uncalibrated)	Final Value (calibrated)
ASPEN Reactors Type	RPLUG, FSPLIT, and HEATER as per the references [22, 26].	
Reformer cooled product:		
• Temperature	• 380°C	• 380°C
• Pressure	• 29.3 kg/sqcm	• 29.3 kg/sqcm
• Total mole flow rate	• 12372.9 kmol/h	• 12462.843 kmol/h
• Molar fractions	• [CO ₂ : 5.07%], [CO: 8.4%], [H ₂ : 35.5%], [N ₂ : 15.174%], [CH ₄ : 0.37%], [Ar: 0.184%], [H ₂ O: 35.32%]	• [CO ₂ : 4.959%], [CO: 8.41%], [H ₂ : 34.98%], [N ₂ : 15.7%], [CH ₄ : 0.32%], [Ar: 0.19%], [H ₂ O: 35.40%]
H ₂ O to CO-shift stream:		
• Temperature	• 130°C	• 130°C
• Pressure	• 130 kg/sqcm	• 130 kg/sqcm
• Total mole flow rate	• 3570.3 kmol/h	• 3570.3 kmol/h
• Molar fractions	• H ₂ O	• H ₂ O
Reactions	CO + H ₂ O → CO ₂ + H ₂	
Reference	Integration of the reactors, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, and pressure drop expression are as per the references [22, 26].	

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In the carbon dioxide removal unit, CO₂ is captured by potassium carbonate, and it will generate ammonium hydrogen carbonate as a byproduct. The purified gas with about 0.1 vol% CO₂ is called synthesis gas. The reactions involved in the carbon dioxide removal process have been modeled based on the reaction description by Miles et al. (1975) [27]. Table 5 shows the specifications of the CO₂ removal unit.

Table 5. The initial (uncalibrated) and final (Calibrated) values of the CO₂ removal unit.

Parameter	Initial Value (uncalibrated)	Final Value (calibrated)
ASPEN Reactor types	Flash2, as per the references [22, 27].	
CO-shift cooled product:		
• Temperature	• 40 °C	• 40 °C
• Pressure	• 27.04 kg/sqcm	• 27.04 kg/sqcm
• Total mole flow rate	• 12372.9 kmol/h	• 12463
• Molar fractions	• [CO ₂ :13.25%],[CO:0.22%], [H ₂ :43.66%],[N ₂ :15.17%], [CH ₄ :0.37%],[Ar:0.1836%], [H ₂ O: 27.15%]	• [CO ₂ :13.19%],[CO:0.216%], [H ₂ :43.18%],[N ₂ :15.7%], [CH ₄ : 0.32%],[Ar: 0.1898%] [H ₂ O: 27.19%]
Reactions	<ul style="list-style-type: none"> • 2H₂O ↔ H₃O⁺ + OH⁻ • HCO₃⁻ + H₂O ↔ H₃O⁺ + CO₃²⁻ • H₂NCOO⁻ + H₂O ↔ NH₃ + HCO₃⁻ • H₄HCO₃ → NH₄⁺ + HCO₃⁻ • 2H₂O ↔ H₃O⁺ + OH⁻ • OH⁻ + CO₂ → HCO₃⁻ • NH₃ + CO₂ + H₂O → H₂NCOO⁻ + H₃O⁺ • H₂NCOO⁻ + H₃O⁺ → NH₃ + H₂O + CO₂ 	<ul style="list-style-type: none"> • CO₂ + 2H₂O ↔ H₃O⁺ + HCO₃⁻ • NH₃ + H₂O ↔ NH₄⁺ + OH⁻ • NH₄HCO₃(S) ↔ NH₃ + HCO₃⁻ • NH₃ + H₂O ↔ NH₄⁺ + OH⁻ • HCO₃⁻ + H₂O ↔ H₃O⁺ + CO₃²⁻ • HCO₃⁻ → CO₂ + OH⁻ • NH₄HCO₃(S) ↔ NH₄⁺ + HCO₃⁻
Reference	Integration of the reactors, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, and pressure drop expression are as per the references [22, 27].	

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In the methanation process, even small quantities of CO (0.1 vol%) and CO₂ (0.3 vol%) act as poisons for the ammonia synthesis catalyst; which is very sensitive to CO and CO₂, therefore this gas stream passes over a nickel catalyst to form a methane gas via methanation, and the methane gas can be purged as tail gas. The residual content of CO + CO₂ is less than 10 ppm. The reactions involved in the methanation process have been modeled based on the reaction description by Yadav and Rinker [28].

Hydrogen and nitrogen at 300 bar are catalytically converted to ammonia. The reactions involved in the methanation process have been modeled based on the reaction description by (Nielsen, 1968) [29]. The ammonia in the purge gas from the ammonia unit is recovered in the tail gas scrubbing unit and fed to a refrigeration unit. The treated purge gas is used as fuel for the primary reformer. Table 6 shows the specifications of the methanization and synthesis units.

269 **Table 6.** The initial (uncalibrated) and final (calibrated) values of the methanization and synthesis units.

Table 6: The Initial (uncalibrated) and final (calibrated) values of the methanization and synthesis units.		
Parameter	Initial Value (uncalibrated)	Final Value (calibrated)
Methanization		
ASPEN Reactor types	RPLUG and SEP2, as per the references [22, 28].	
Heated CO ₂ removal products: <ul style="list-style-type: none">• Temperature• Pressure• Total mole flow rate• Molar fractions	<ul style="list-style-type: none">• 280 °C• 27.04 kg/sqcm• 7263.361 kmol/h• [CO₂:0.256%],[CO:0.345%], [H₂:74.37%],[N₂:24.18%], [CH₄:0.40%],[Ar:0.27%] [H₂O:0.164%]	<ul style="list-style-type: none">• 280 °C• 27.04 kg/sqcm• 7039 kmol/h• [CO₂:0%],[CO:0%], [H₂:72.97%],[N₂:25.73%], [CH₄:0.10%],[Ar:0.28%], [H₂O:0 %]
Reactions	• CO + 3H ₂ → CH ₄ + H ₂ O	• CO ₂ + 3H ₂ → CH ₄ + 2H ₂ O
Post-methanization compressor & chiller: <ul style="list-style-type: none">• Discharge pressure• Outlet Temperature	<ul style="list-style-type: none">• 280.4 kg/sqcm• 5 °C	<ul style="list-style-type: none">• 500 kg/sqcm• -160 °C
The heat exchanger prior to the methanization unit (labeled as “Heat Ex. 12”, Figure 2): <ul style="list-style-type: none">• Hot stream outlet temperature	<ul style="list-style-type: none">• 280 °C	280 °C
Reference	Integration of the reactors, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, and pressure drop expression are as per the references [22, 28].	
Synthesis		
ASPEN Reactor types	RPLUG, FSPLIT, and HEATER, as per the references [22, 29].	
Heated and compressed Flashing 1.1-Methinization product: <ul style="list-style-type: none">• Temperature• Pressure• Total mole flow rate• Molar fractions	<ul style="list-style-type: none">• 180 °C• 297.75 kg/sqcm• 20719.41 kmol/h• [H₂: 62.53%], [N₂: 23.1%], [CH₄: 7.5%], [Ar: 2.4%], [NH₃: 4.5%]	--
Reactions	N ₂ + 3H ₂ → 2NH ₃	
Reference	Integration of the reactors, kinetic expressions, chemical equilibrium, catalyst activity, partial pressure expressions, and pressure drop expression are as per the references [22, 28].	

2.2. Process description of the calibrated ammonia plants

Ammonia with a high level of purity (~100 % mol. of NH₃) is produced after postprocessing the products from the synthesis unit through a set of separation units (labeled as flashing 0.0, 1.1, 1.2, 2.1, 2.2, and 3, Figure 2) and refrigeration units (labeled as Refrigeration 1 and 2, Figure 2). However, as discussed in section 1, producing ammonia is neither desired at a high level of purity nor at a low level of temperature when a continuous supply of the 70% NH₃-30% H₂ (vol%) fuel blend is needed for a gas turbine cycle. Therefore, the calibrated model has reduced the separation and refrigeration units (flashing 0.0, 1.1, 1.2, 2.1, 2.2, 3, as Refrigeration 1 and 2, highlighted in light blue in Figure 2) and retained the units highlighted in light red in Figure 2 and integrated as shown in Figure 3. In the calibrated model (Figure 3), the methanization product stream is compressed and fed directly to the synthesis unit, Figure 3. The integration of the retained units remained unchanged and are described in Tables 2, 3, 4, 5, and 6.

The properties of the product stream from the synthesis unit are described in Table 7.

Table 7. The properties of the product stream from the synthesis unit.

Parameter	Initial Value (uncalibrated)	Final Value (calibrated)
• Temperature	• 444 °C	• 433 °C
• Pressure	• 272.26 kg/sqcm	• 491.84kg/sqcm
• Total mole flow rate	• 5282.1 kmol/h	• 4696 kmol/h
• H ₂ molar fraction	• 49.14 %	• 34.54%
• N ₂ molar fraction	• 16.721 %	• 13.63%
• CH ₄ molar fraction	• 1.368 %	• 1.5%
• Ar molar fraction	• 0.3664 %	• 0.442%
• NH ₃ molar fraction	• 32.406 %	• 49.89%

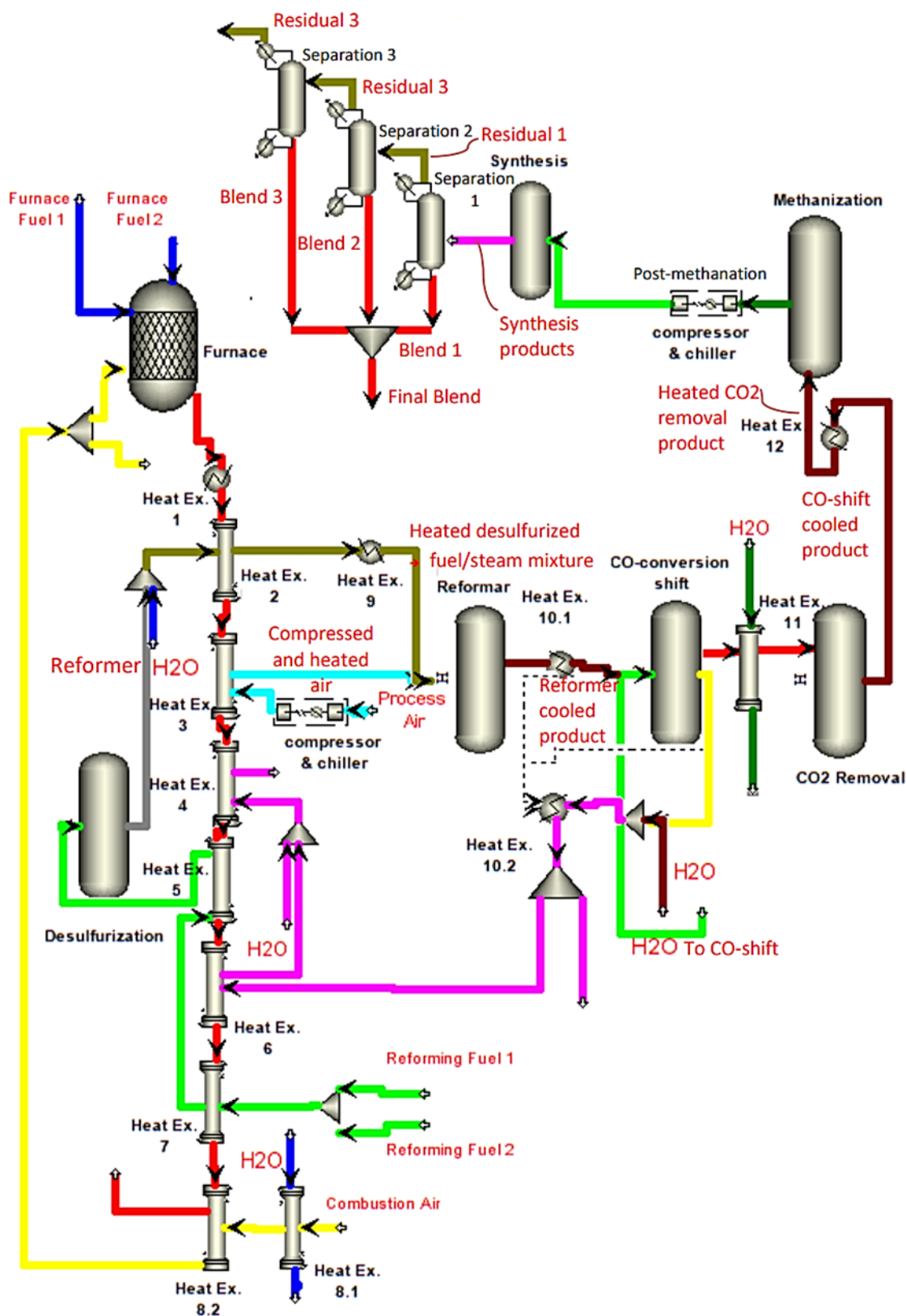


Figure 3. Reduced Ammonia plant (same stream colors within the same unit, however, not necessarily in the other units, are used for same stream composition).

The calibration process has been established by conducting a set of sensitivity analysis using Aspen Plus to identify the effects of the controlling parameters. Table 8 shows the methodology sequence of the calibration process.

Table 8. The methodology sequence of the calibration process.

Step order in the calibration process	Studied parameter	Varying interval	Dependent parameter	Controlled parameter
1	The calibrated model has reduced the separation and refrigeration units (flashing 0.0, 1.1, 1.2, 2.1, 2.2, 3, as Refrigeration 1 and 2, highlighted in light blue in Figure 2) and retained the units highlighted in light red in Figure 2 and integrated as shown in Figure 3.			
2	The post-methanation compressor-chiller discharge pressure.	[100-500] kg/sqcm	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
3	The post-methanation compressor-chiller outlet temperature.	[-160-280] °C	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
4	The outlet temperature of the heat exchanger prior to the CO-Shift conversion unit.	[150-900] °C	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
5	The outlet temperature of the heat exchanger prior to the methanization unit.	[40-400] °C	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
6	The reformer H ₂ O supply.	[10000-15000] kg/h	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
7	The reformer air supply.	[2330-2900] kmol/h	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
8	Observation: while varying the reformer air supply, the remaining parameters remained controlled at their initial values (including H ₂ sources such as Reformer H ₂ O and fuel supplies). This does mean that increasing the air supply shall be simultaneously accompanied by an increase in the H ₂ -containing supplies to increase the NH ₃ molar fraction through the synthesis unit (i.e., $N_2 + 3H_2 \rightarrow 2NH_3$).			
9	1. The reformer H ₂ O supply. 2. The reformer air supply.	1. [20000-140000] kg/h 2. [2000-10000] kmol/h	The synthesis product's molar fractions.	The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
10	Observation: Increase in the N ₂ molar fraction (i.e., due to the increase in the air supply) with a reduced NH ₃ molar fraction of NH ₃ is considered a sign that the reaction in the synthesis unit (i.e., $N_2 + 3H_2 \rightarrow 2NH_3$) is not further promoted at the uncalibrated temperature and pressure. Therefore, it is recommended to simultaneously accompany the increase in air supply with an increase in pressure and a reduction in the temperature of the supply streams to the synthesis process.			
11	1. The reformer H ₂ O supply. 2. The reformer air supply.	1. [20000-140000] kg/h 2. [2000-10000] kmol/h	The synthesis product's molar fractions.	<ul style="list-style-type: none"> Elevated pressure (500 kg/sqcm) and reduced outlet temperature (-160 °C) from the post-methanation compressor-chiller. The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6.
12	Observation: Although point E (elevated pressure (500 kg/sqcm) and reduced outlet temperature (-160 °C) from the post-methanation, the reformer H ₂ O and air supplies are 102041 kg/h and 2464.6 kmol/h, respectively) has approached the desired 70% NH ₃ -30% H ₂ (vol%) molar fraction compared to the uncalibrated values, the exact molar fractions have not yet been achieved. Therefore, a series of separation units has been integrated into the process to achieve the desired molar fractions. Further details are provided in section 3.9.			

3. Results

The sensitivity analysis in this paper is undertaken for the parameters that are the most effective in controlling the product's molar fractions to achieve the 70% NH₃-30% H₂ (vol%) molar fractions from the product stream from the synthesis unit. These are the post-methanation compressor discharge pressure and outlet temperature, process air mass flow rates (supplied to the reformer), superheated H₂O supply rates (supplied to the reformer, labeled as "Reformer H₂O", Figure 3), Untreated reformer air supply rate (supplied to the secondary reformer, labeled as "Process Air," Figure 3) and the heat exchanger prior to the CO-Shift conversion unit (labeled as "Heat Ex. 10.1", Figure 3) and the heat exchanger prior to the methanization unit (labeled as "Heat Ex. 12", Figure 3). The following results have been produced within the initial values of the parameters specified in Tables 2, 3, 4, 5, and 6.

The varying intervals have been chosen based on the allowable limits in Aspen Plus [. Beyond or below these limits, the results will not converge, indicating that the chemical process will not be activated to provide the desired performance range. For example, varying the parameters within the furnace unit is limited by the combustion operability limits of the used fuel blend (Table 2) [22-25]. Similarly, varying the parameters of the reformer and CO-shift methanization and synthesis units is limited by acceptable operation conditions (Tables 3, 4 and 5) [25-28].

3.1. The sensitivity of the synthesis product's molar fractions towards the post-methanation compressor-chiller discharge pressure

Figure 4 shows the sensitivity analysis when varying the post-methanation compressor-chiller discharge pressure with the interval of [100-500] kg/sqcm with respect to the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the discharge pressure, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. Increasing the discharge pressure of the post-methanation compressor has a significant effect on increasing the NH₃ molar fraction, reducing the H₂ molar fraction and the N₂ molar fraction. This is explained by referring to the high-pressure effect on activating a Haber-Bosch reaction [1%] that combines nitrogen with hydrogen to increase ammonia production. On the other hand, increasing the discharge pressure has a negligible effect on the CH₄ and Ar molar fractions (i.e., the corresponding CH₄ and Ar molar fractions to increasing the discharge pressure within the interval of [100-500] kg/sqcm are 1.2%-1.4% and 0.325%-0.375%, respectively).

As shown in line A-Figure 4, the uncalibrated discharge pressure is 280.4 kg/sqcm, and corresponding molar fractions of hydrogen, nitrogen and ammonia are 49.14 %, 16.721 %, and 32.406 %, respectively. Increasing the post-methanation compressor discharge pressure beyond 280.4 kg/sqcm essentially contributes to approaching the desired 70% NH₃-30% H₂ (vol%) molar fractions (i.e., increases the NH₃ molar fraction and reduces the N₂ and H₂ molar fractions from their uncalibrated values). By approximating the patterns (above the 280.4 kg/sqcm discharge limit and up to 500 kg/sqcm) of the NH₃, H₂, and N₂ molar fractions with respect to the post-methanation compressor discharge pressure into linear correlations, the sensitivity of the NH₃, H₂ and N₂ molar fractions towards the discharge pressure is $\partial M_{NH_3} / \partial P = 0.02037$ [mol.%]/[kg/sqcm], $\partial M_{N_2} / \partial P = -0.00486$ [mol.%]/[kg/sqcm], and $\partial M_{H_2} / \partial P = -0.0145$ [mol.%]/[kg/sqcm], respectively (Figure 5).

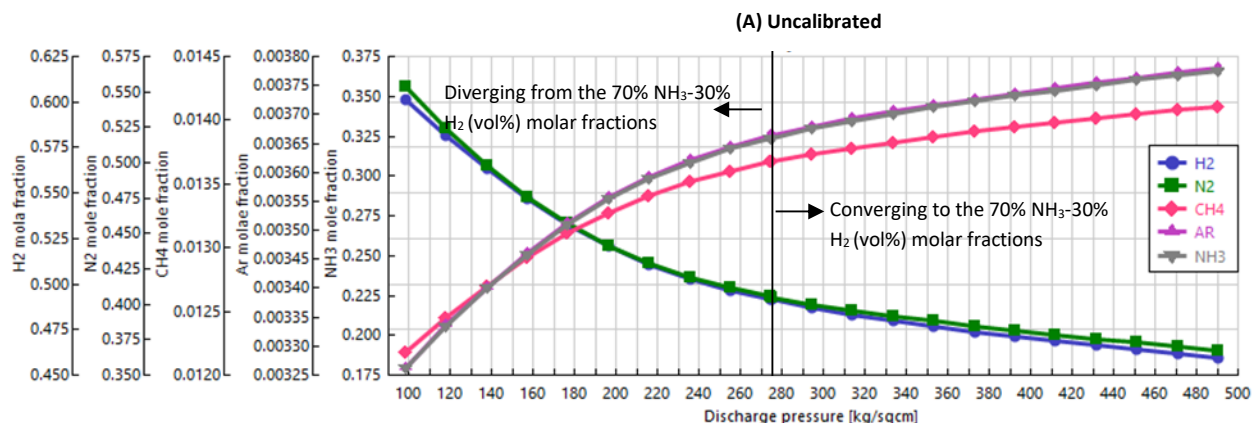


Figure 4. Sensitivity of the synthesis product's molar fractions towards the post-methanation compressor discharge pressure.

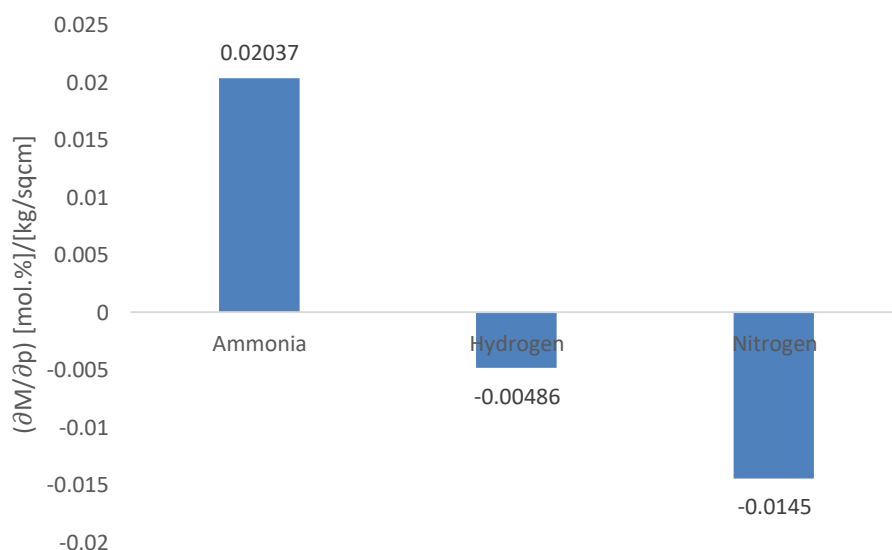


Figure 5. The sensitivity of the Ammonia, hydrogen and nitrogen molar fractions towards the discharge pressure ($\partial M / \partial P$) [mol.%]/[kg/sqcm]

3.2. The sensitivity of the synthesis product's molar fractions towards the post-methanation compressor-chiller outlet temperature

Figure 6 shows the sensitivity analysis when varying the post-methanation compressor-chiller outlet temperature with the interval of $[-160-280]$ °C with respect to the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the outlet temperature, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. It can be noted that reducing the outlet temperature of the post-methanation compressor-chiller has a significant effect on increasing the NH_3 molar fraction, reducing the H_2 molar fraction, and the N_2 molar fraction. This could be related to the Haber-Bosch reaction ($\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3 + 91 \text{ kJ}$), in which a decrease in temperature favors the forward exothermic reaction. The concentration of NH_3 in the system increases while the concentrations of N_2 and H_2 decreases. Decreasing the outlet temperature has a negligible effect on the CH_4 and Ar molar fraction.

As shown in line B-Figure 6, the uncalibrated outlet temperature is 5°C, and corresponding molar fractions of hydrogen, nitrogen and ammonia are 49.14 %, 16.721 %, and 32.406 %, respectively.

Decreasing the post-methanation compressor-chiller below outlet temperature below 5°C leads to approaching the desired 70% NH₃-30% H₂ (vol%) molar fractions (i.e., increases the NH₃ molar fraction and reduces H₂ and N₂ molar fractions from their uncalibrated values). The sensitivity of the NH₃, H₂, and N₂ molar fractions toward the compressor-chiller outlet temperature is $\partial M_{NH_3}/\partial T = -0.06$ [mol.%]/[°C], $\partial M_{N_2}/\partial T = 0.014$ [mol.%]/[°C], and $\partial M_{H_2}/\partial T = 0.04$ [mol.%]/[°C], respectively (Figure 7).

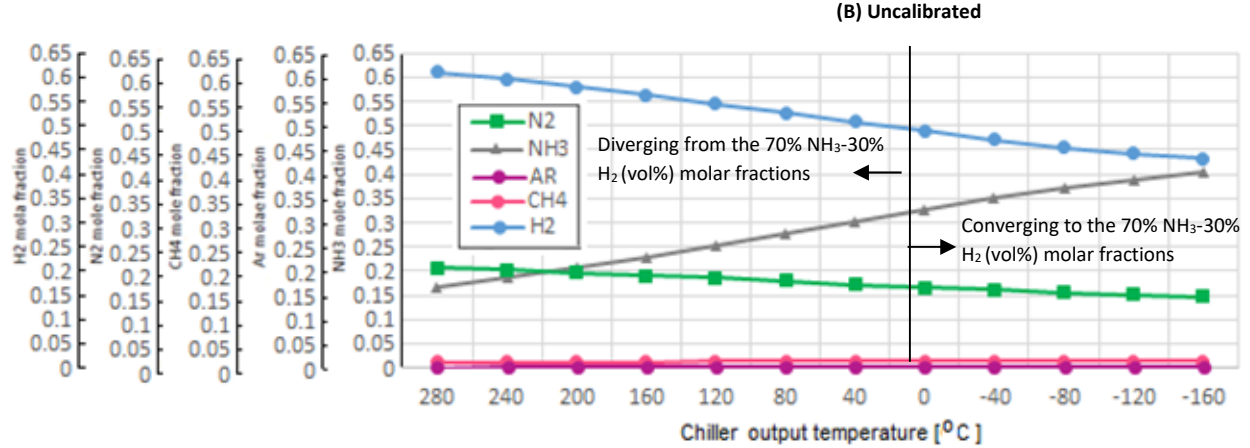


Figure 6. Sensitivity of the synthesis product's molar fractions towards the post-methanation chiller output temperature.

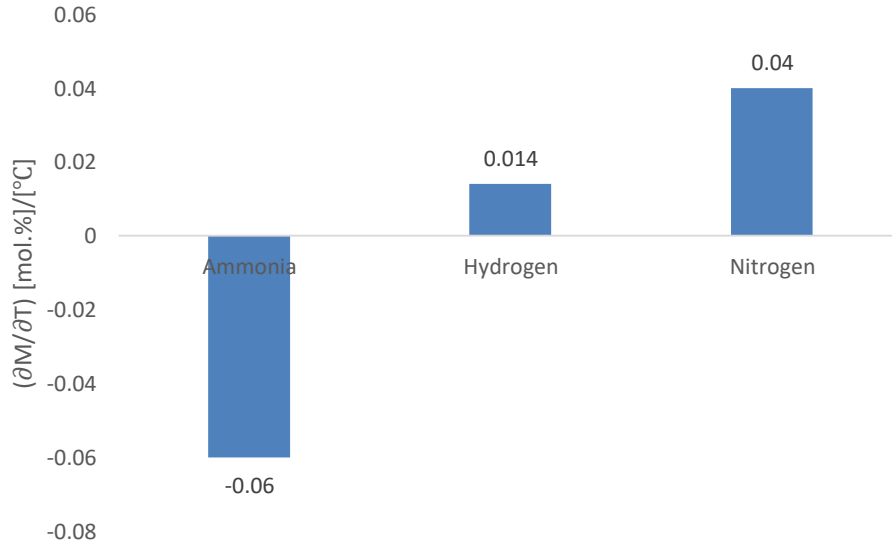


Figure 7. The sensitivity of the Ammonia, hydrogen and nitrogen molar fractions towards the post-methanation chiller output temperature ($\partial M/\partial T$) [mol.%]/[kg/sqcm]

3.3. The sensitivity of the synthesis product's molar fractions towards the heat exchanger prior to the CO-Shift conversion unit

Figure 8 shows the sensitivity analysis when varying the outlet temperature of the heat exchanger prior to the CO-Shift conversion unit (labeled as "Heat Ex. 10.1" in Figure 3) with the interval of [150-900] °C with respect to the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the reformer air supply, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. As shown in Figure 8, at both ends of the studied interval of the heat exchanger outlet temperature [150-900] °C, the molar fractions are approximately similar to each other. In addition, despite the fluctuating pattern of the NH₃ molar fraction,

the significance of this variance can be considered negligible (i.e., the molar fraction range, corresponding to the varying the heat exchanger outlet temperature [150-900] °C is only [0.32405-0.32435], Figure 8). The "Heat Ex. 10.1" heat exchanger cools down the products from the reformer unit from 977 °C to 380 °C and utilizes the extracted heat to increase the temperature of the H₂O supply to the desulfurization. Therefore, considering the important function of the heat exchanger within the process and the low sensitivity of the NH₃ molar fraction towards the Heat Ex. 10.1 outlet temperature, it is recommended to retain the Ex 10.1 at its uncalibrated operating conditions, line C-Figure 8.

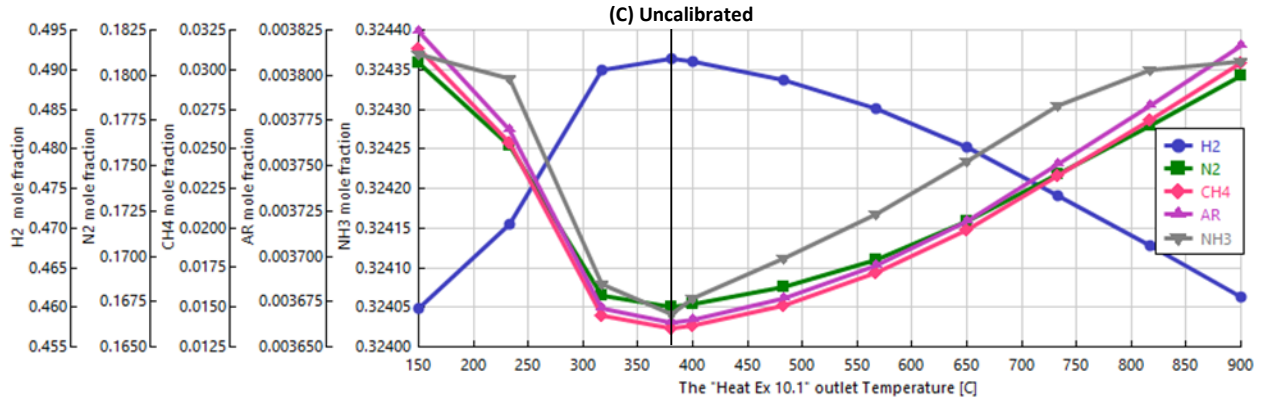


Figure 8. Sensitivity of the synthesis product's molar fractions towards the "Heat Ex. 10.1" outlet temperature.

3.4. The sensitivity of the synthesis product's molar fractions towards the heat exchanger prior to the methanization unit

Figure 9 shows the sensitivity analysis when varying the outlet temperature of the heat exchanger prior to the methanization unit (labeled as "Heat Ex. 12" in Figure 3) with the interval of [40-400] °C with respect to the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the reformer air supply, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. As shown in Figure 9, the NH₃ and Ar molar fractions are insensitive to the heat exchanger's outlet temperature. In addition, despite the fluctuating pattern of the molar fractions, the significance of this variance can be considered negligible (i.e., the molar fraction ranges corresponding to the varying heat exchanger outlet temperature [40-400] °C are only [0.49135-0.49155], [0.16714-0.16722] and [0.01356-0.0137] for H₂, N₂ and CH₄, respectively, Figure 9).

Therefore, a similar recommendation about the "Heat Ex.10.1" heat exchanger can be made about the "Heat Ex.12" heat exchanger; to retain the Ex 10.1 at its uncalibrated operating conditions, Line D-Figure 9.

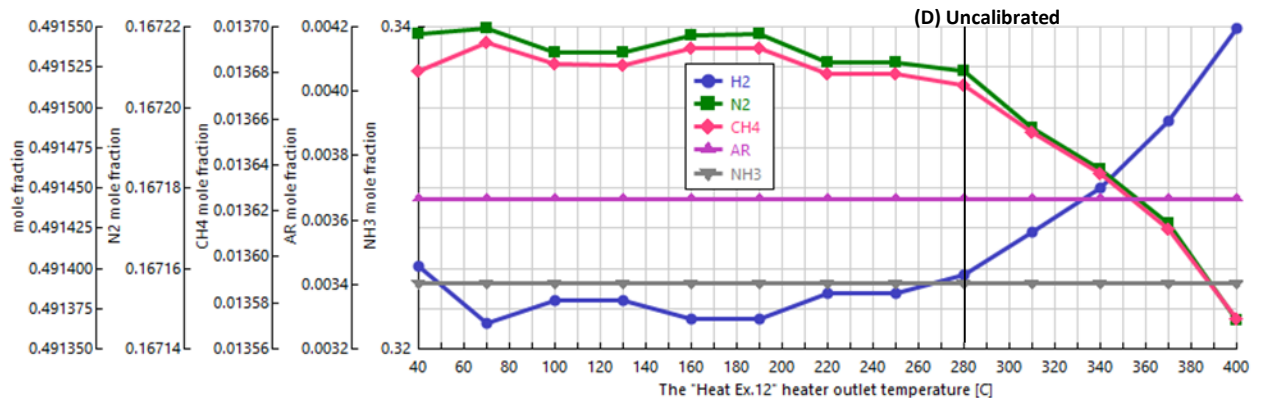


Figure 9. Sensitivity of the synthesis product's molar fractions towards the "Heat Ex. 12" heater outlet temperature.

3.5. The sensitivity of the synthesis product's molar fractions towards the reformer H₂O supply

Figure 10 shows the sensitivity analysis when varying the reformer H₂O supply with the interval of [10000-15000] kg/h with respect to the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the reformer H₂O supply, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. Increasing the reformer H₂O supply from 10000 kg/h to 40000 kg/h has a positive effect on increasing the NH₃ molar fraction. However, beyond the 40000 kg/h limit (Figure 10-Line E), the NH₃ molar fraction becomes independent of the H₂O supply. Nevertheless, beyond the 40000 kg/h limit, the H₂ molar fraction continuous to increase by increasing the H₂O supply up to approximately 8000 kg/h; however, beyond this limit, the H₂ molar fraction becomes insensitive toward the increase in the H₂O supply. As the target of this study is achieve the 70% NH₃-30% H₂ (vol%) molar fractions rather than maximizing hydrogen concentration, increasing the reformer H₂O supply up to, but not beyond, the 40000 kg/h limit would serve the target of the study.

It is worth noting that the uncalibrated reformer H₂O supply is 120401 kg/h (Line F-Figure 10) and the corresponding molar fractions of hydrogen, nitrogen, and ammonia are 49.14 %, 16.721 %, and 32.406 %, respectively. This essentially means reducing the uncalibrated reformer H₂O supply (i.e., 120401 kg/h) to the 40000 kg/h limit reduces H₂O consumption by (80,401 kg/h) while retaining the NH₃ molar fraction unaffected.

Increasing the H₂O supply with the [1000-4000] kg/h has the effect of increasing the NH₃ molar fraction accompanied by increasing the H₂ molar fraction. In fact, the direct reason for increasing the NH₃ molar fraction was the increase in the H₂ molar fraction, which resulted from converting H₂O into H₂ through the reforming reaction (i.e., $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$). Once the H₂ content is increased (i.e., by increasing the H₂O supply, thus increasing H₂ conversion), it is then converted into NH₃ through the synthesis unit (i.e., $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$). However, while the H₂ content continued to increase by increasing the H₂O supply, the NH₃ became independent beyond the 4000 kg/h limit because, as previously mentioned, the required N₂ content obtained from atmospheric air supply was maintained constant was not increased in parallel to the H₂O increase. This essentially means that enough hydrogen but not enough nitrogen contents were supplied as reactants in the ammonia synthesis unit (i.e., $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$) to increase the NH₃ molar fraction. Therefore, to further increase the NH₃ content, it is recommended to both simultaneously increase the reformer H₂O and air supplies in parallel (investigated in section 3.7).

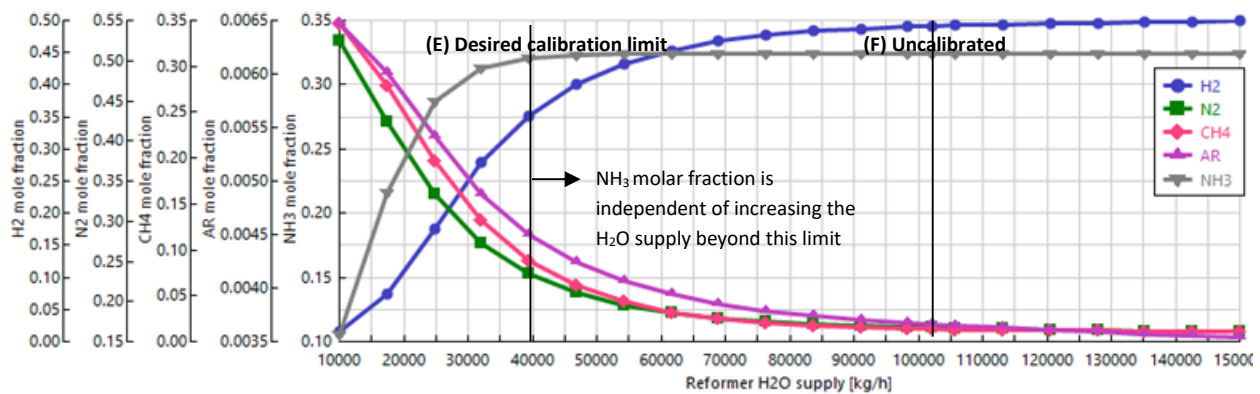


Figure 10. Sensitivity of the synthesis product's molar fractions towards the reformer H₂O supply.

3.6. The sensitivity of the synthesis product's molar fractions towards the reformer air supply

Figure 11 shows the sensitivity analysis when varying the reformer air supply with the interval of [2330-2900] kmol/h with respect to the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the reformer air supply, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. As shown in Figure 11, within the air supply interval of [2330-2600] kmol/h, the NH_3 molar fraction increases, and the H_2 molar fraction decrease as the air supply increases. This is directly attributed to the N_2 content, which activates the reaction in the synthesis unit (i.e., $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$) to convert H_2 into NH_3 . However, the effect of increasing the air supply on the NH_3 molar fraction is insignificant (i.e., the molar fraction ranges, corresponding to the varying the reformer air supply with the interval of [2330-2900] kmol/h is only [0.32405-0.3247], Figure 11). This is due to the increase of the excessive unreacted content of N_2 . As previously mentioned, while varying the reformer air supply, the remaining parameters remained controlled at their initial values (including H_2 sources such as Reformer H_2O and fuel supplies). This does mean that increasing the air supply shall be simultaneously accompanied by an increase in the H_2 -containing supplies to increase the NH_3 molar fraction through the synthesis unit (i.e., $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$). This was further investigated in section 3.5.

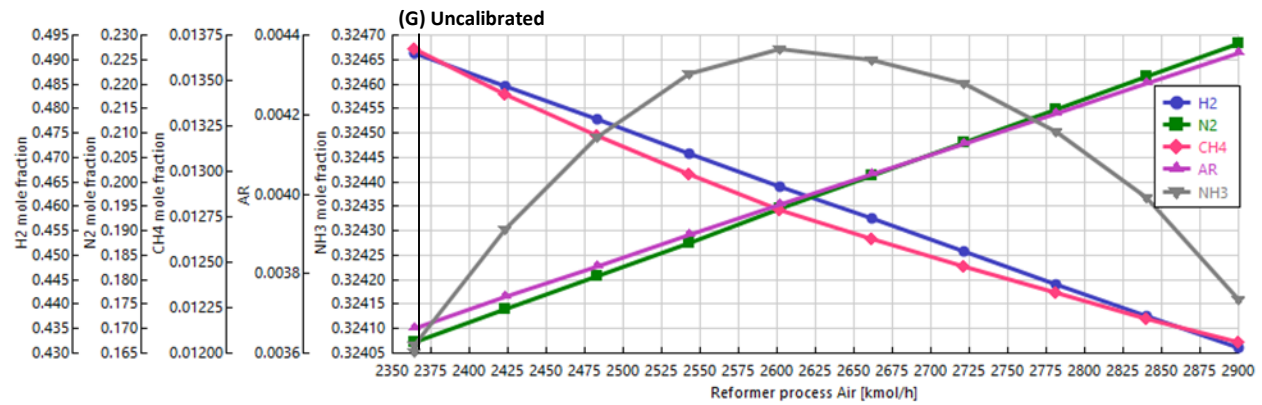


Figure 11. Sensitivity of the synthesis product's molar fractions towards the reformer air flow rate.

3.7. The sensitivity of the synthesis product's molar fractions towards the combined effect of the reformer H_2O and air supplies

Figure 12 shows the combined effect of simultaneously varying the H_2O and air reformer supply on the molar fractions of the product stream from the synthesis unit (labeled as "Synthesis products" in Figure 3). While varying the reformer air supply, the remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. The H_2O and air reformer supplies have been varied within the intervals of [20000-140000] kg/h and [2000-10000] kmol/h, respectively. As shown in Figure 12.C, the NH_3 molar fraction reaches the highest levels when the H_2O supply is increased, and the air supply is reduced. Similarly, as shown in Figure 12.A, the molar fraction of H_2 is increased as the H_2O supply increases and the air supply decreases. Increasing the H_2 molar reaction through increasing H_2O supply without increasing the supply of other hydrogen-containing supplies (Reformer fuel 1 and 2) is explained by the water-gas-shift reaction in the CO-shift unit ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), in which the production of hydrogen is maximized by reacting the CO content with H_2 . However, the increase in the N_2 molar fraction (i.e., due to the increase in the air supply) with a reduced NH_3 molar fraction of NH_3 is considered a sign that the reaction in the synthesis unit (i.e., $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$) is not further promoted at the uncalibrated temperature and pressure. Therefore, it is recommended to simultaneously accompany the increase in air

supply with an increase in pressure and a reduction in the temperature of the supply streams to the synthesis process (i.e., through the post-methanation compressor-chiller, as discussed in sections 3.1 and 3.2). This is further investigated in section 3.8.

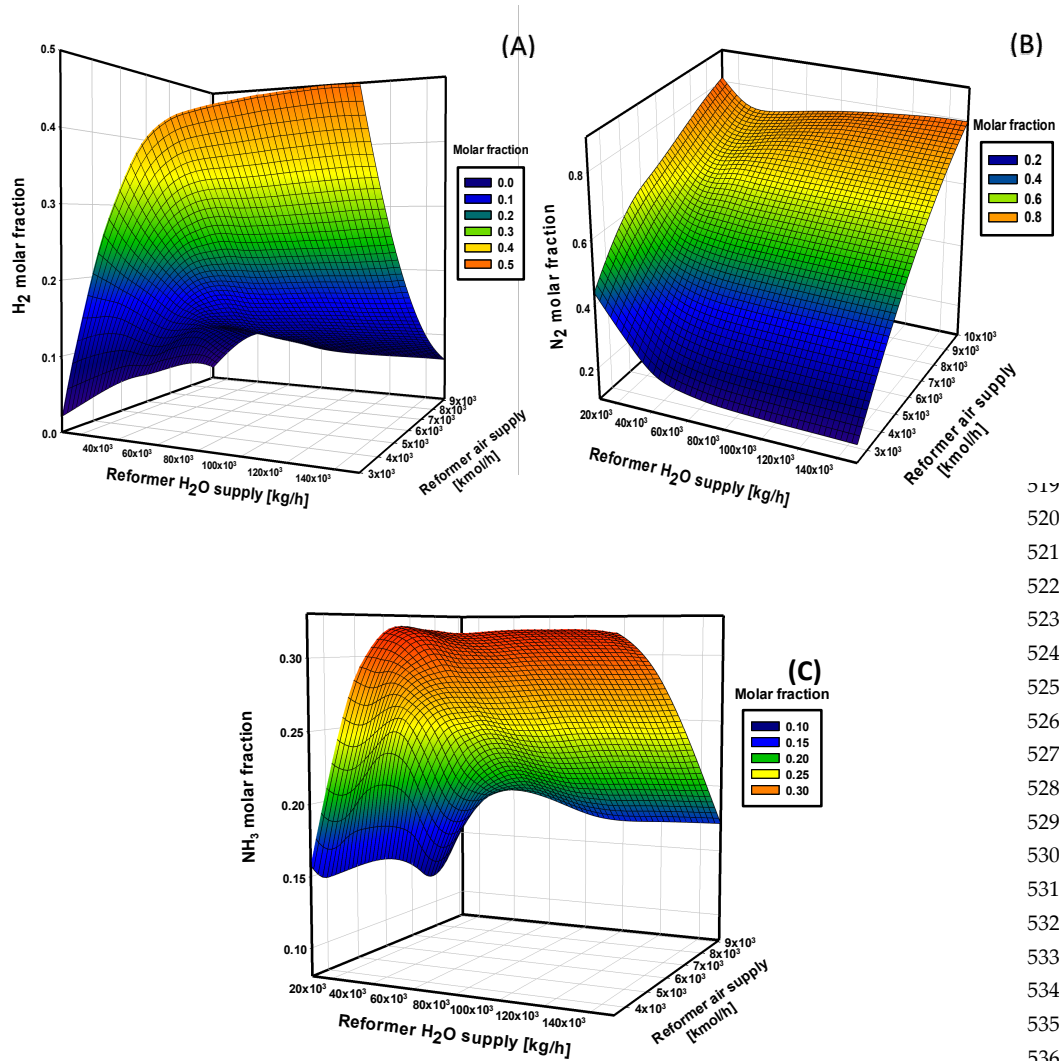


Figure 12. The sensitivity of the synthesis product's molar fractions towards the combined effect of the reformer H₂O and air supplies.

3.8. The sensitivity of the synthesis product's molar fractions towards the combined effect of the reformer H₂O and air supplies at elevated discharge pressure and reduced outlet temperature from the post-methanation compressor-chiller

Figure 13 shows the combined effect of simultaneously varying the H₂O and air reformer supplies on the molar fractions of the synthesis product at elevated discharge pressure (500 kg/sqcm) and reduced outlet temperature (-160 °C) from the post-methanation compressor-chiller. The remaining parameters remained controlled at their initial values, as described in Tables 2, 3, 4, 5, and 6. As shown in Figure 4, the highest molar fraction of NH₃ is achieved at 500 kg/sqcm; thus, the compressor discharge pressure has been increased from 280.4 kg/sqcm to 500 kg/sqcm. As shown in Figure 6, the highest molar fraction of NH₃ is

achieved at -160 °C; thus, the compressor-chiller outlet temperature has been decreased from 5 °C to -160 °C.

As discussed in section 3.7, at the uncalibrated setup of the post-methanation compressor-chiller (280.4 kg/sqcm and 5 °C), the increase in the N₂ molar fraction (i.e., due to the increase in the air supply) with a reduced NH₃ molar fraction of NH₃ is considered as a sign that the reaction in the synthesis unit (i.e., N₂ + 3H₂ → 2NH₃) is not further promoted. Therefore, the combined effect of the reformer H₂O and air supplies on the synthesis product's molar fractions has been studied, herein in this section at elevated discharge pressure and reduced outlet temperature.

As shown in Figure 13.B, compared to the uncalibrated conditions of the post-methanation-chiller (280.4 kg/sqcm and 5 °C), the conversion rate of N₂ has significantly increased as the variance range of the unreacted nitrogen molar fraction has reduced from [20-80] mol.% at the uncalibrated conditions (280.4 kg/sqcm and 5 °C, Figure 12.B) to [10-16] mol.% at the elevated pressure and reduced outlet temperature of the post-methanation compressor-chiller (500 kg/sqcm and -160 °C, Figure 13.B). In addition, the issue which was observed in the uncalibrated conditions of the post-methanation-chiller (i.e., the increase in the N₂ molar fraction (i.e., due to the increase in the air supply) with a reduced NH₃ molar fraction of NH₃, Figures 12.B and 12.C) has been resolved at the elevated pressure and reduced outlet temperature conditions, Figure 13.B and 11.C. As shown in Figure 13.C, increasing the air flow supply positively impacts increasing the NH₃ molar fraction at elevated pressure and reducing outlet temperature conditions. The highest NH₃ molar fraction can be found between the points D and E, labeled in Figure 13.C. Both points correspond to a high level of air supply.

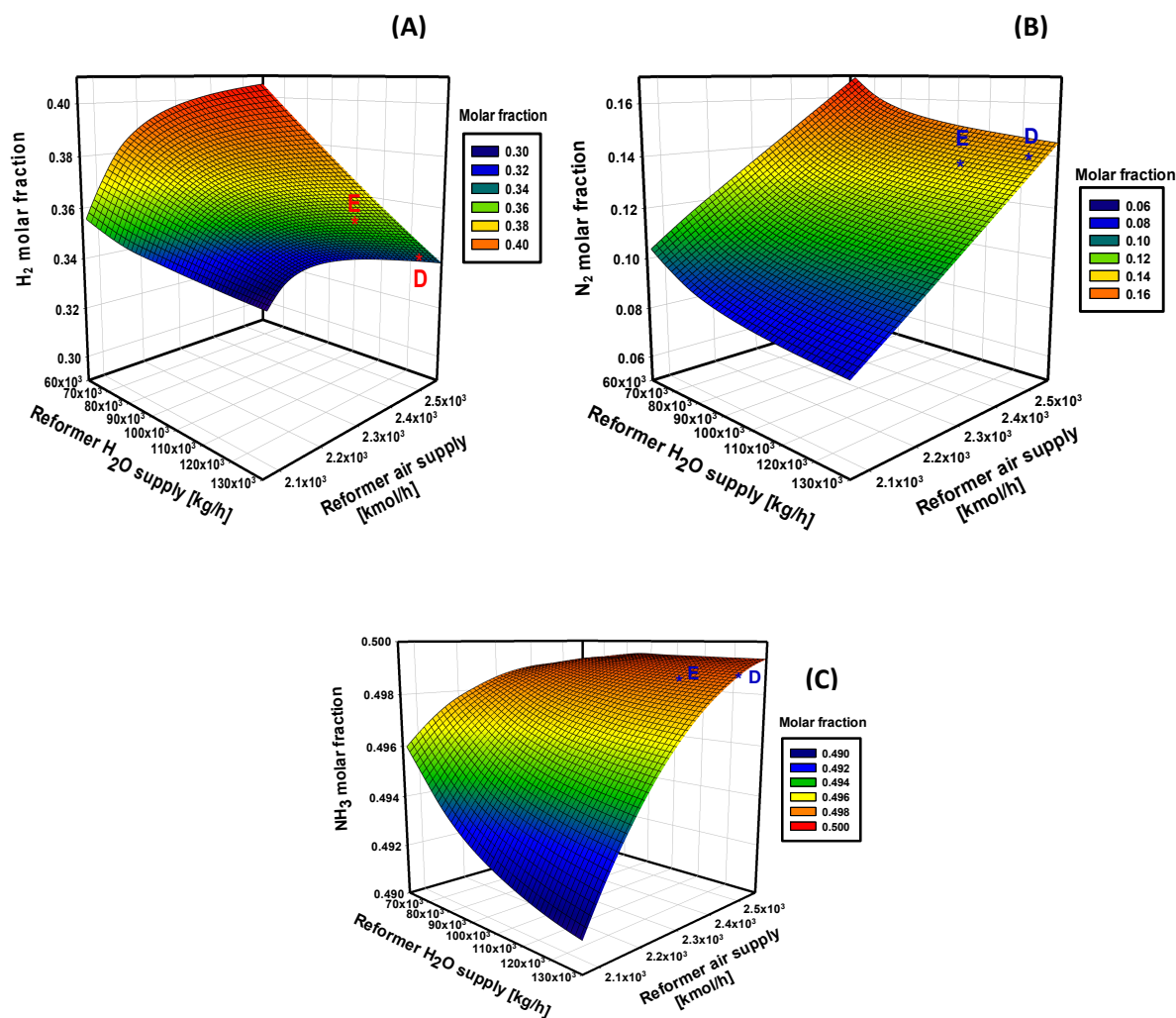


Figure 13. The sensitivity of the synthesis product's molar fractions towards the combined effect of the reformer H_2O and air supplies at elevated discharge pressure and reduced outlet temperature from the post-methanation compressor-chiller (500 kg/sqcm and -160°C).

While point D corresponds to a slightly higher NH_3 molar fraction than point E, however, point D corresponds to a significantly higher H_2O flow rate whilst E corresponds to low water supply; thus, point E has been chosen. In addition, since the target of this calibration is to achieve the desired 70% NH_3 -30% H_2 (vol%) molar fraction and neither to achieve pure H_2 nor pure NH_3 , point E has been chosen as it approaches the desired product fractions. Table 9 shows the corresponding molar fractions, reformer air, and H_2 supplies to points D and E.

Table 9. the corresponding molar fractions, reformer air, and H₂ supplies to points D and E, labeled in Figure 13.

Parameter	Initial Value (uncalibrated)	Point D	Point E	Desired
Post-mentalization compressor & chiller:				
• Discharge pressure	• 280.4 kg/sqcm	• 500 kg/sqcm	• 500 kg/sqcm	--
• Outlet Temperature	• 5 °C	• -160 °C	• -160 °C	
Reformer air supply	2364.6 kmol/h	• 2464.6 kmol/h	• 2464.6 kmol/h	--
Reformer H ₂ O supply	102041 kg/h	132041 kg/h	• 102041 kg/h	--
Synthesis product composition				
• H ₂ molar fraction	• 49.14 %	• 33.98%	• 34.54%	• 30%
• N ₂ molar fraction	• 16.721 %	• 14.36%	• 13.63%	• 0%
• CH ₄ molar fraction	• 1.368 %	• 1.28%	• 1.5%	• 0%
• Ar molar fraction	• 0.3664 %	• 0.44%	• 0.442%	• 0%
• NH ₃ molar fraction	• 32.406 %	• 49.93%	• 49.89%	• 70%

3.9. The sensitivity of the product's molar fractions of the separation units towards the heat duties of the separation units

As shown in Table 9, point E (labeled in Figure 13) has been chosen as a calibration point for the ammonia plant. Although point E has approached the desired 70% NH₃-30% H₂ (vol%) molar fraction compared to the uncalibrated values, the exact molar fractions have not yet been achieved. Therefore, a series of separation units has been integrated into the process to achieve the desired molar fractions. While the remaining parameters remained controlled at their initial values as described in Tables 2, 3, 4, 5, and 6, the conditions of the post-mentalization compressor & chiller, the reformer H₂O and air supplies have been adjusted as per point E, Table 9. As shown in Figure 3, the synthesis products are separated through the separation units (labeled as separation 1, 2, and 3, Figure 3). Each separation unit has two outlet streams (labeled as "blend" and "residuals" in Figure 3). The blend stream is required to have the desired 70% NH₃-30% H₂ (vol%) molar fractions while the residual stream is fed into the consecutive separation unit, which yields the following "blend" and "residual" streams. The separation units have been modeled using the ASPEN-PLUS model "SEP 2". To ensure that the streams blend 1, 2, and 3 have the desired 70% NH₃-30% H₂ (vol%), a sensitivity analysis has been performed for each separation unit to correlate the molar fractions of its "blend" stream to its heat duty. Figure 14 shows the correlation between the heat duty of the first separation unit "separation 1" with respect to the molar fractions of its blend stream "blend 1". As shown in Figure 14, the desired 70% NH₃-30% H₂ (vol%) molar fraction is achieved at line H, which corresponds to a heat duty of -0.173 Mmkcal/hr. Therefore, it has been chosen as a calibration point. At this calibration point, the resultant residuals "residuals 1" from the separation unit "separation 1" are then separated in the second separation unit "separation 2". Figure 15 shows the correlation between the heat duty of the second separation unit "separation 2" with respect to the molar fractions of its blend stream "blend 2". As shown in Figure 15, the desired 70% NH₃-30% H₂ (vol%) molar fraction is achieved at line I, which corresponds to a heat duty of -0.2 Mmkcal/hr. Therefore, it has been chosen as a calibration point. At this calibration point, the resultant residuals "residuals 2" from the separation unit "separation 2" are then separated in the third separation unit "separation 3". Figure 16 shows the correlation between the heat duty of the third separation unit "separation 3" with respect to the molar fractions of its blend stream "blend 3". As shown in Figure 16, the desired 70% NH₃-30% H₂ (vol%) molar fraction is achieved at line J, which corresponds to a heat duty of -0.1231 Mmkcal/hr. Therefore, it has been chosen as a calibration point. Finally, once the 70% NH₃-30% H₂ (vol%) molar fraction is achieved for the three "blend" streams (i.e., "blend 1", "blend 2" and "blend 3"), the streams have been mixed into a single stream (labeled as "final blend," Figure 3).

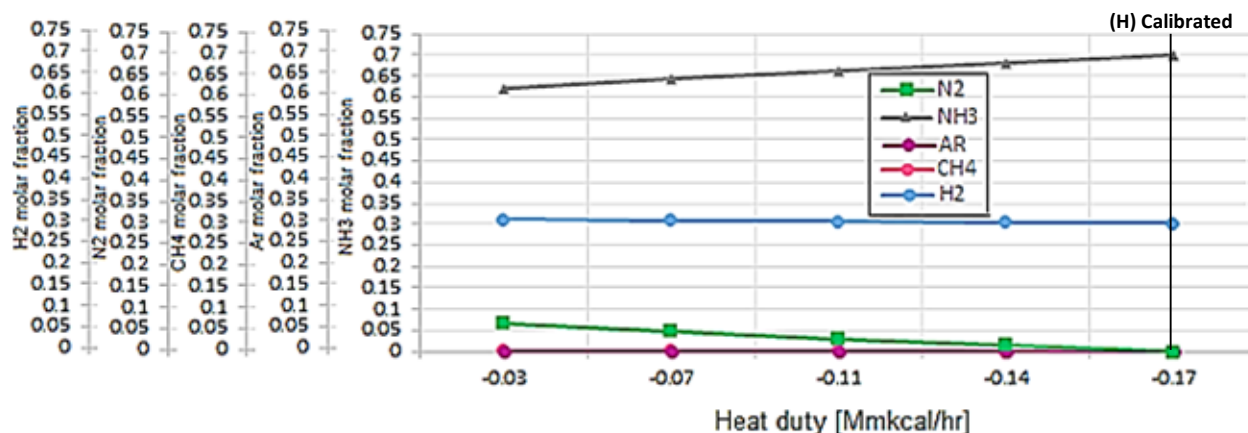


Figure 14. the correlation between the heat duty of the first separation unit “separation 1” with respect to the molar fractions of its blend stream “blend 1”.

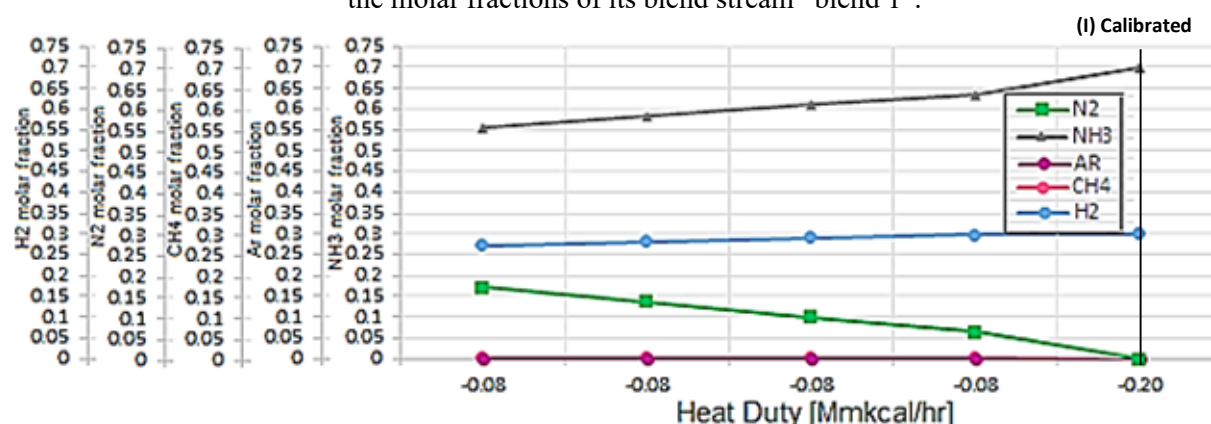


Figure 15. the correlation between the heat duty of the second separation unit “separation 2” with respect to the molar fractions of its blend stream “blend 2”.

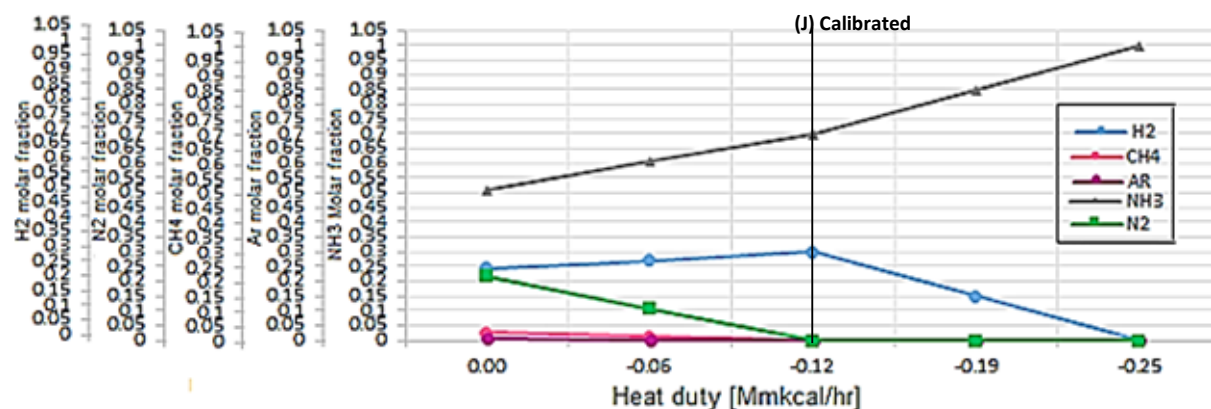


Figure 16. the correlation between the heat duty of the third separation unit “separation 2” with respect to the molar fractions of its blend stream “blend 3”.

4. DISCUSSION

In the uncalibrated ammonia model, after postprocessing, the products from the synthesis unit through a set of separation units and refrigeration units, high-purity ammonia (100% mol. of NH_3) is produced (labeled as Refrigeration 1 and 2, Figure 2). However, when a continuous supply of the 70% NH_3 -30% H_2 (vol%) fuel blend is required for a gas turbine cycle, producing ammonia is neither desired at a high level of purity nor a low level of temperature. Therefore, in the calibrated model, the methanization product

stream is compressed and fed directly to the synthesis unit (Figure 3), reducing the separation and refrigeration units.

In order to achieve the 70% NH₃-30% H₂ (vol%) molar fractions from the product stream from the synthesis unit, the sensitivity analysis in this paper is provided for the parameters that are the most effective at controlling the product molar fractions. These are the post-methanation compressor outlet pressure and temperature, process air mass flow rates (supplied to the reformer), H₂O supply rates (supplied to the reformer, labeled as "Reformer H₂O," Figure 3), and untreated reformer air supply rates (supplied to the reformer, labeled as "Process Air," Figure 3).

The molar fractions of the synthesis products in the reduced model have been studied in this paper in relation to the effects of individually and simultaneously varying the reformer air and H₂O supplies, while the other parameters have been kept under control at their initial values as shown in Tables 2, 3, 4, 5, and 6. It is advised to increase pressure and decrease the temperature of the supply streams to the synthesis process (i.e., through the post-methanation compressor-chiller) at the same time as increasing the air supply. The conversion rate of N₂ has significantly increased as the variance range of the unreacted nitrogen molar fraction has decreased from [20-80] mol.% at the uncalibrated conditions (280.4 kg/sqcm and 5 °C) to [10-16] mol.% after increasing the discharge pressure and lowering the outlet temperature of the post-methanation compressor-chiller to 500 kg/sqcm and -160 °C. Additionally, the dilemma with the post-methanation-uncalibrated chiller's conditions (i.e., the rise in N₂ molar fraction caused by an increase in air supply and a decline in NH₃ molar fraction of NH₃) has been resolved at the conditions of elevated pressure and reduced outlet temperature because increasing the air flow supply had a favorable effect on raising the NH₃ molar fraction at the conditions of elevated pressure and reduced outlet temperature. To achieve the desired 70% NH₃-30% H₂ (vol%) molar fraction ratio, a calibrated series of separation units have finally been added. The calibration parameters for the post-methanization compressor and chiller, reformer air supply, water supply, separations units, and corresponding parameters for the synthesis products and final blend stream are listed in Table 9.

Table 9. The calibration conditions of the post-methanization compressor & chiller, Reformer air supply, H₂O supply, separations units, the corresponding conditions of the synthesis products, and final blend stream.

Parameter	Final Value (calibrated)
Post-methanization compressor & chiller:	
• Discharge pressure	• 500 kg/sqcm
• Outlet Temperature	• -160 °C
Reformer air supply	• 2464.6 kmol/h
Reformer H ₂ O supply	• 102041 kg/h
Synthesis product composition	
• H ₂ molar fraction	• 34.54 %
• N ₂ molar fraction	• 13.63 %
• CH ₄ molar fraction	• 1.5 %
• Ar molar fraction	• 0.442 %
• NH ₃ molar fraction	• 49.89 %
Separation Units	
• Heat duty of Separation 1	• -0.173 Mmkcal/hr
• Heat duty of Separation 2	• -0.2 Mmkcal/hr
• Heat duty of Separation 3	• -0.1231 Mmkcal/hr
• Overall heat duty	• ~-0.5 Mmkcal/hr
Final blend stream	
• Total mole flow rate	• 3307.3 kmol/h
• H ₂ molar fraction	• 30.15 %
• N ₂ molar fraction	• 0 %
• CH ₄ molar fraction	• 0 %
• Ar molar fraction	• 0 %
• NH ₃ molar fraction	• 69.85 %

5. CONCLUSIONS

Without calibrating ammonia plants and simply mixing portions of the produced pure ammonia to hydrogen at the desired molar fraction requires coupling ammonia plants with other hydrogen-producing plants, leading to potential difficulties in commercializing the unused (as fuel in the $\text{NH}_3\text{-H}_2$ /air gas turbines) hydrogen portions from the hydrogen-producing plants. Moreover, the existing ammonia plants produce ammonia at a high purity level, which essentially requires extensive postprocessing after the synthesis loop (refrigeration and separation), which is unnecessary in the case of the 70% NH_3 -30% H_2 (vol%) fuel blend. Therefore, this paper has suggested a recalibrated and reduced ammonia plant. After identifying the sensitivities of the reduced ammonia plant, the discharge pressure and the outlet temperature of the post-methanation compressor-chiller have been set to 500 kg/sqcm and -160 °C, respectively. The reformer H_2O and air supplies have been set to 102041 kg/h and 2464.6 kmol/h, respectively. A calibrated 0.5 Mmkcal/hr series of three separation units ensure providing the required 70% NH_3 -30% H_2 (vol%) fuel blend.

As future work, it is recommended to conduct a comparable technoeconomic analysis between the calibrated and the uncalibrated ammonia plants to highlight the effects of the calibrated parameters on the technoeconomic sustainability of the plant.

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