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**DOI**
10.1016/j.compchemeng.2022.107951

**Publication date**
2022

**Document Version**
Final published version

**Published in**
Computers and Chemical Engineering

**Citation (APA)**
Rokhayati, E., & Kiss, A. A. (2022). Unraveling the effect of variable natural gas feedstock on an industrial ammonia process. *Computers and Chemical Engineering*, *166*, Article 107951. https://doi.org/10.1016/j.compchemeng.2022.107951

Computers and Chemical Engineering 166 (2022) 107951

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

# Unraveling the effect of variable natural gas feedstock on an industrial ammonia process

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ARTICLE INFO

*Keywords:*
Process integration
Process design
Process simulation
Process optimization
Energy savings

ABSTRACT

Ammonia plays critical role as the second most produced chemical commodity with around 80% used in producing nitrogen-based fertilizer. Considering the decline of reserves of fossil-based feedstocks it is imperative to shift towards greener alternatives. However, such green ammonia processes are far from being economically viable. This makes natural gas-based ammonia synthesis the best available technology currently, but this faces critical difficulties as natural gas supply could widely vary due to declining reserve or changing sources, posing another key challenge to improve the efficiency of affected ammonia production.

This study is the first to investigate the effect of variable natural gas composition (within the range of 83–99.99% vol dry methane; towards lean gas) on an industrial ammonia production process with maintained key operating parameters value such as steam to carbon ratio (S/C), hydrogen over nitrogen ratio (H/N), etc. The sensitivity analysis shows that sustained energy efficiency of the process is possible, confirming the conventional ammonia plant's ability to withstand changes in feedstock and fuel supply. In addition, lean gas yielded a positive impact on the raw material intensity and $CO_2$ emissions with average reductions of 1.17% and 1.79% per each 4% methane content increase, respectively.

## 1. Introduction

Ammonia has a vital role as the second most produced chemical commodity globally with approximately 144 million tonnes synthesized in 2020 (YARA, 2021a; U.S. Geological Survey, 2021). Around 80% of the ammonia was used in making nitrogen-based fertilizer as it contains nitrogen, a key nutrient required by the plants (Laval et al., 2020; Pfromm, 2017; Sadeek et al., 2020). Other derivatives such as ammonium nitrate, nitric acid, ammonium phosphate and ammonium sulphate share the remaining balance of ammonia consumption.

The roadmap towards zero net carbon in 2050 amplifies ammonia's criticality due to its potential as a green fuel (Laval et al., 2020; International Energy Agency, 2021) that does not emit $CO_2$ (Chai et al., 2021; Hansson et al., 2020; Morgan et al., 2014; Palys and Daoutidis, 2020) and an increase of its demand is predicted (Laval et al., 2020). The growing human population is also a key driver for providing more feedstock for the fertilizer industry (Erisman et al., 2008). As the use of fossil-based feedstocks is declining (BP, 2021), it is crucial to shift towards greener options but these are not yet economically justified (YARA 2021a; Hansson et al., 2020; Morgan et al., 2014; Palys and Daoutidis, 2020). Hence the natural gas based ammonia synthesis remains the best available technique (Smith et al., 2020a).

The discovery of ammonia synthesis process by Fritz Haber and Carl Bosch in 1909, widely known as Haber-Bosch process, enabled large-scale production of ammonia (Smil, 2001; Brightling, 2018). Currently, more than 90% ammonia produced is synthesized through this process (Tock et al., 2015). Although the reaction to produce ammonia from nitrogen and hydrogen in the Haber-Bosch process is quite straightforward, the whole process is very energy intensive due to many chemical reactions involved to provide the reactants. Hydrogen is mainly sourced from fossil-based feedstock such as natural gas (NG) and coal and is produced by steam methane reforming (SMR). The requirement for non-moderate operating condition in ammonia converter with pressure over 100 bar and temperature range of 400–500 °C added with low typical conversion (which leads to recirculation of the synthesis gas) further increases the energy intensity of the process. Numerous improvements over decades resulted in more efficient processes with about 30% less energy used per tonne $NH_3$ as compared to 1970′s (Smil, 2001; International Fertilizer Association, 2014).

Most hydrogen required for ammonia synthesis is produced from fossil-based feedstock such as NG that accounts for 65% of total supply

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https://doi.org/10.1016/j.compchemeng.2022.107951
Received 25 February 2022; Received in revised form 12 July 2022; Accepted 4 August 2022

## Nomenclature

| | |
|---|---|
| BFW | boiler feed water |
| GHG | green house gas |
| HTSC | high temperature shift converter |
| LTSC | low temperature shift converter |
| NG | natural gas |
| S/C | steam to carbon ratio |
| SMR | steam methane reforming |
| VHP | very high pressure (steam) |
| WHB | waste heat boiler |
| WGS | water-gas shift reaction |

and followed by coal at 34% (International Fertilizer Association, 2014). Abundant reserves across many regions, its competitive price, and low $CO_2$ emissions are the main reasons for NG domination (I.G. Union, 2020; Chai et al., 2021; Smith et al., 2020a). However, warnings have emerged over years pointing out the declining NG ability to fulfill the global demand, termed as *reserve-to-production ratio* (R/P), with current state at only 48.8 years (BP, 2021). Preventing R/P ratio from further fall by improving existing ammonia production efficiency is therefore very important.

A study of an ammonia plant found that there was 98% gas charge threshold where further fall of NG supply would increase the energy demand up to 10% (Sadeek et al., 2020), amplifying the importance of energy efficiency in ammonia plant not only due to non-renewable nature of NG, but also its tendency to become less energy efficient at lower rate. Diverse composition of NG due to fluctuation of production condition (Speight, 2019) poses another challenge in improving existing ammonia plant's efficiency. A steep increase of the methane content in NG feedstocks for an ammonia plant in Indonesia (PT Pupuk Kalimantan Timur) over the past eight years from around 83 to 96% volume dry due to addition of a gas well that is newly in operation to replace the depleting reserves of existing supply brings many challenges related to the energy efficiency as well as $CO_2$ emissions as the plant (similar to others worldwide) was not designed for NG with such high methane content. In the gas processing industry, NG with higher methane content has lower heating value and often referred to as lean gas (Speight, 2019).

The energy intensive nature of Haber-Bosch process, the use of non-renewable feedstock and energy sources, and more stringent regulations on $CO_2$ emissions are the key factors for improvements in ammonia synthesis. However, a notable gain can only be achieved by major changes, i.e. by shifting the feedstock and energy source to renewable ones to eliminate the $CO_2$ emissions (Smith et al., 2020b). The question remains on whether green ammonia would eventually exist despite the technical, economic and regulation challenges. The production of green ammonia is highly dependent on the intermittent nature of the renewable supply with generally much lower magnitude compared to well-established fossil-fuels (BP, 2021; Tock et al., 2015) hindering the development of large capacity plant. From an economics viewpoint, capital costs of renewable energy are higher in many regions (Beck and Martinot, 2004) due the low efficiency of electrolysers. Those factors added with the needs to store hydrogen and renewable electricity (Valera-Medina and Bañares-Alcántara, 2020), resulted in 2–4 times more expensive green ammonia than the conventional one (YARA, 2021b). To date, a large-scale production facility does not exist yet, and the most advanced project is expected to operate in 2026 (YARA, 2021b). Alternatively, a hybrid or revamped ammonia plant using renewable hydrogen could be an excellent transition towards green ammonia (Laval et al., 2020) although a renewable contribution of more than 10% of hydrogen supply should be carefully studied to check if it would be commercially compelling (Noelker, 2021).

Therefore, improving existing ammonia processes is imperative to reduce the environmental burden as well as to sustain the fossil-fuel reserve for longer periods. Various research related to conventional ammonia production have been conducted. The SMR-based route is currently identified as best available technique (BAT) in producing ammonia due to greater efficiency and lower emissions (Smith et al., 2020b) and is widely used as a benchmark. Vast array combinations of feedstock and fuel resources for the classic ammonia plant have been investigated and the SMR-based routes proved to have a relatively small impact across several parameters (Tock et al., 2015; Zhang et al., 2020; Bicer et al., 2016). Acknowledging the maturity of SMR-based ammonia production technology, numerous studies have been performed to further increase its efficiency via several methods, i.e. operational, revamping, retrofit, etc. (Sadeek et al., 2020; Rafiqul et al., 2005; Panjeshahi et al., 2008; Song et al., 2017; Tran et al., 2017; Pedernera et al., 1999).

Although most ammonia produced today is synthesized from NG, no study about variable NG composition has been reported. One of the closest study available (Tanvir Sowgath and Mujtaba, 2019) was limited to a very narrow variance of NG composition (i.e. from 97.2 to 98.13%) and was more focused on the safety aspect (i.e. fire load point). Therefore, the NG composition fluctuation remains a challenge and has not been well understood. This study fills this research gap and provides insights on how an ammonia production process could be affected and what is required to maintain its efficiency regardless of the disruption caused by its feedstock and energy source. It is also the first study to focus on the optimization of a conventional ammonia production with variable NG feedstock. An ammonia plant in Indonesia with a typical capacity of 1180 metric tonnes per day (MTPD) is used as an industrial case study. Aspen Plus® was used for the rigorous modeling and simulation of the ammonia plant, based on validated industrial data.

## 2. Problem statement

The green ammonia synthesis is far from being economically viable, thus optimizing the existing ammonia production routes is vital to sustain natural gas reserve and to minimize the $CO_2$ emissions. Moreover, the declining reserve of natural gas and operational fluctuation during exploration may cause its composition to change towards lean gas with more methane content and less energy, which in turn affects the hydrogen and ammonia production, as well as the energy efficiency and the sustainability aspects of the ammonia synthesis. To solve this problem and understand the impact of variable NG composition, this study performs a sensitivity analysis using an industrially validated model built in a rigorous process simulator.

More specifically, motivated by these concerns, the aims of this study are:

- To investigate the impact of natural gas composition changes towards lean gas with methane content ranging 83–99.99% vol dry on ammonia production, on the specific energy use and sustainability aspects of a conventional Haber-Bosch process.
- To propose educated operational recommendations for improving the energy efficiency and sustainability of conventional ammonia plants.

In comparison with existing tools or literature, the simulation techniques of this study offers as main contributions the following:

- First simulations of complex ammonia processes with variable compositions of NG as feedstock and energy source, which maintains the values of key operational parameters. As the feedstock and energy sources of ammonia processes will change due to the transition to the more sustainable alternatives, such process simulations are beneficial more than ever.
- In-depth analysis on simulating an ammonia production process which poses challenges not addressed before such as the simulation

of ammonia synthesis loop, $CO_2$ capturing, consideration on various reactor models used, performing a sensitivity analysis and process optimization, which overall is difficult due to the complex nature of the ammonia process.

## 3. Basic data

The ammonia production of the studied plant was simulated using a widely used process simulator Aspen Plus® V8.8 due to its capability to predict system behavior through rigorous calculations. A template file provided by Aspen Plus® called "*Ammonia*" was used as starting point, with the equipment configuration modified accordingly. This was done to utilize the improved preloaded property package for increased model accuracy. For the property method, the Redlich-Kwong-Soave Boston-Mathias (RKS-BM) model was used throughout the model, except for the $CO_2$ removal section and the very high pressure (VHP) steam generation unit where ELECNRTL (electrolyte non-random two liquid) and steam tables (STEAMNBS2) were used, respectively. The equation-of-state models such as RKS-BM are capable to present a highly accurate description of the thermodynamic properties of the high-temperature and high-pressure environment found in ammonia processes (Aspentech, 2015).

The validation of the model involved two steps: using design data and actual plant data to obtain high degree of accuracy. The design data was provided by the process licensor, therefore a simulation model that agrees well with such data could give confidence in the model accuracy. However, due to intellectual property rights, only certain industrial parameters are presented in the section about process design and simulation. Simulation of any real plant data poses different challenges as several key parameters such as chemical reactions, equipment efficiency, flowmeter accuracy, may not be in ideal or equilibrium state. Using real data, the validated simulation model was then used as base case in the sensitivity analysis. Data from various sources such as plant's distributed control system (DCS) that were assumed to be accurate as measured data, manual log sheet as well as laboratory analysis results were used for process simulation. The percent of difference was used to assess the variance between simulation results and design data or plant data from the ammonia plant: $\%\,difference = 100 \times (data - simulation\_result)/data$.

## 4. Process simulation approach

The studied ammonia production process is divided into four sections: front end, middle end, back end and VHP steam generation unit as shown in simplified process diagrams (Fig. 1).

Ammonia production is a complex process involving diverse operating conditions ranging from −33°C until above 500°C combined with pressure from vacuum up to more than 100 bar. In addition, it involves many equipment units including reactor, heat exchanger, absorber and stripper, as well as compressor and pumps with several loops/recycle streams. Therefore, a strategy was needed to aid the simulation convergence and to accelerate the simulation run time. Equipment with similar operating conditions (i.e. part of a section) was put together into a dedicated simulation *hierarchy*. In this way, it is possible to apply different property methods and components that suit a certain unit the most and keep the whole simulation into a single file. Another benefit was only equipment and streams within the *hierarchy* were considered during the simulation run, thus minimizing complexities and running time.

### 4.1. Process modeling

#### 4.1.1. Front end model

The feedstocks for the studied ammonia plant were natural gas (referred as NG process), air and medium pressure steam. Natural gas also served as the main energy source for the primary reformer (referred as NG fuel). Both NG process and process air were compressed to around 35–42 bar using two dedicated steam-driven compressors. The two raw materials were then preheated to the expected temperature range in the primary reformer convection section by utilizing waste heat from the flue gas of primary reformer furnace. The NG process was sent to the desulfurizer before entering primary reformer to eliminate any sulfur impurity that may cause catalyst poisoning in primary reformer and low temperature shift converter (LTSC). The desulfurizer section consists of a hydrogenator to convert the organic sulfur compounds into inorganic one that was modeled as an RSTOIC block with 100% conversion and a sulfur adsorber (modeled as Sep2 block) where all inorganic sulfur was taken out. This is supported by the plant data where no sulfur slip was detected in the outlet stream. Next, NG process was further preheated in the convection section, mixed with process steam and preheated once more before was sent to the catalyst tubes in primary reformer.

*Primary reformer and steam generation*. There are two sections in the primary reformer, radiant section where NG and other fuels were burnt with the aid of combustion air to provide heat required by the endothermic reforming reactions inside the nearby catalysts tube, and convection section where the waste heat from flue gas was utilized to provide heating to NG process, process air, steam and boiler feed water (BFW). Most of the hydrogen for the ammonia synthesis was produced inside the catalyst tubes in radiant section by reacting natural gas and steam via reactions (1)–(10).

$$3C_2H_{6(g)} + H_2O_{(g)} \leftrightharpoons 5CH_{4(g)} + CO_{(g)} \quad \Delta H^o = 3441.63\,kJ\,mol^{-1} \tag{1}$$

$$3C_3H_{8(g)} + 2H_2O_{(g)} \leftrightharpoons 7CH_{4(g)} + 2CO_{(g)} \quad \Delta H^o = 18459.8\,kJ\,mol^{-1} \tag{2}$$

$$3n - C_4H_{10(g)} + 3H_2O_{(g)} \leftrightharpoons 9CH_{4(g)} + 3CO_{(g)} \quad \Delta H^o = 33739.1\,kJ\,mol^{-1} \tag{3}$$

$$3i - C_4H_{10(g)} + 3H_2O_{(g)} \leftrightharpoons 9CH_{4(g)} + 3CO_{(g)} \quad \Delta H^o = 42927.2\,kJ\,mol^{-1} \tag{4}$$

$$3n - C_5H_{12(g)} + 4H_2O_{(g)} \leftrightharpoons 11CH_{4(g)} + 4CO_{(g)} \quad \Delta H^o = 48887.1\,kJ\,mol^{-1} \tag{5}$$

$$3i - C_5H_{12(g)} + 4H_2O_{(g)} \leftrightharpoons 11CH_{4(g)} + 4CO_{(g)} \quad \Delta H^o = 55811.6\,kJ\,mol^{-1} \tag{6}$$

$$3C_6H_{14(g)} + 5H_2O_{(g)} \leftrightharpoons 13CH_{4(g)} + 5CO_{(g)} \quad \Delta H^o = 63250.2\,kJ\,mol^{-1} \tag{7}$$

$$3C_7H_{16(g)} + 6H_2O_{(g)} \leftrightharpoons 14CH_{4(g)} + 6CO_{(g)} \quad \Delta H^o = 78146.9\,kJ\,mol^{-1} \tag{8}$$

$$CH_{4(g)} + H_2O_{(g)} \leftrightharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H^o = 205.91\,kJ\,mol^{-1} \tag{9}$$

$$CO_{(g)} + H_2O_{(g)} \leftrightharpoons CO_{2(g)} + H_{2(g)} \quad \Delta H^o = -41.1\,kJ\,mol^{-1} \tag{10}$$

RStoic block from Aspen Plus® was used to model the pre-reforming reactions Eqs. (1)–((8)) with 100% conversion of the hydrocarbons given by the plant data that no hydrocarbons heavier than methane were detected in the outlet stream of primary reformer. For the methane reforming and water gas shift (WGS) reaction Eqs. (9) and ((10)), REquil block was used with temperature approach of equilibrium was set to −2°C to match the plant data in the base case (Case 4). The heat requirement for reactions was fulfilled by the primary reformer furnace that was modeled as complete combustion with RStoic block following reactions (11)–(14). The presence of excess oxygen at 2.54% vol according to plant data in the flue gas supports this assumption. The combustion air flowrate was adjusted to fit the excess $O_2$ of the plant data. To aid heat transfer from furnace to the primary reformer REquil model, a simple cooler with specified temperature as in the furnace and a heat stream were used.

$$2H_{2(g)} + O_{2(g)} \leftrightharpoons 2H_2O_{(g)} \tag{11}$$

$$C_nH_{2n+2(g)} + (2n - (n-1)/2)O_{2(g)} \leftrightharpoons nCO_{2(g)} + (n+1)H_2O_{(g)} \tag{12}$$

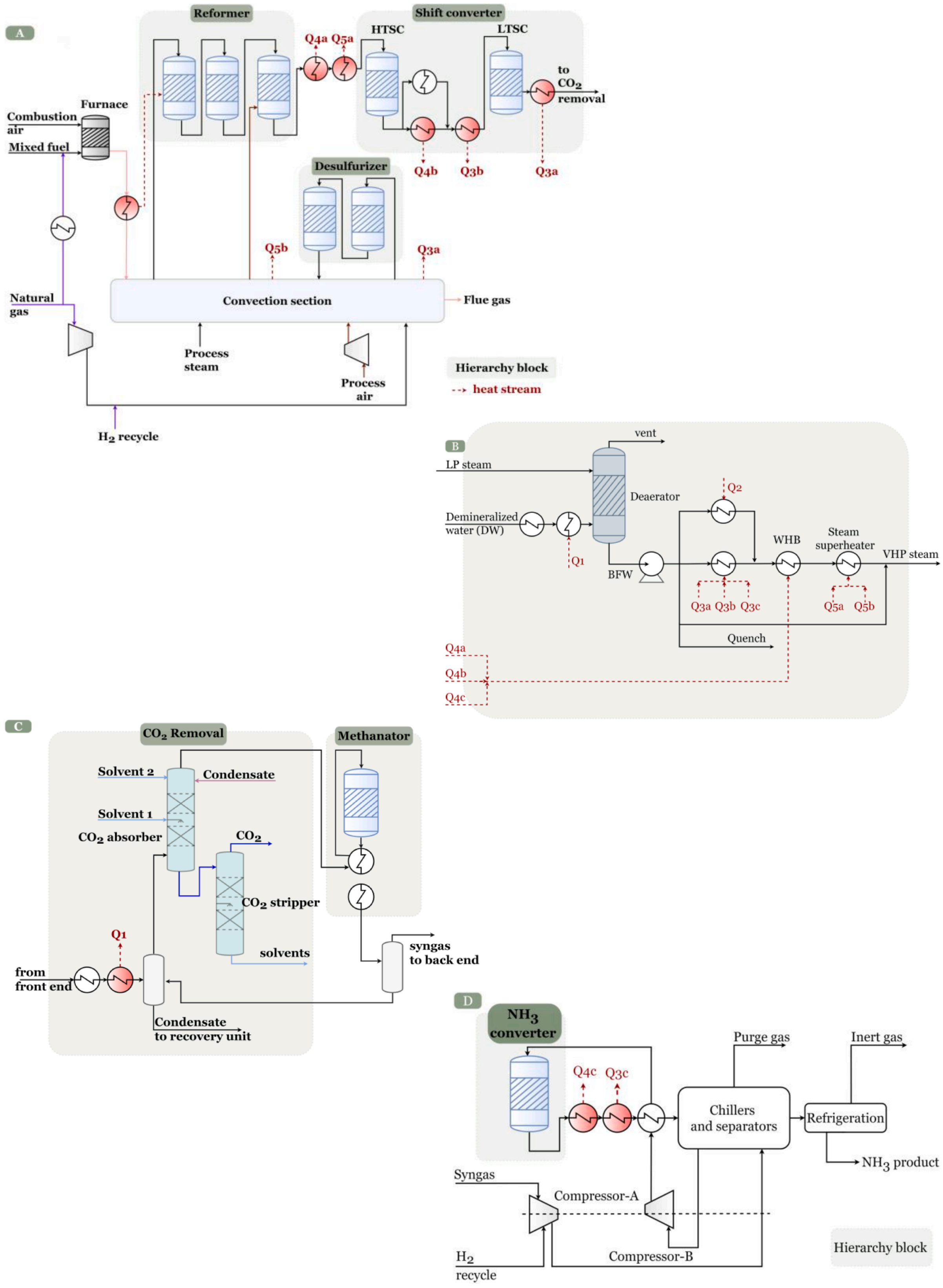

**Fig. 1.** Simplified diagram of ammonia production process in the studied plant: (A) Front end model; (B) VHP steam generation unit; (C) Middle end model; (D) Back end model.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} \tag{13}$$

$$NH_{3(g)} + 1.5\,O_{2(g)} \rightleftharpoons N_{2(g)} + 3H_2O_{(g)} \tag{14}$$

where $n = 1 - 7$

In the convection section, all heat exchangers were modeled with HeatX blocks to allow heat transfer between two process streams except for boiler feed water (BFW) preheater and steam superheater that were modeled as Heater blocks with outlet heat streams to the VHP steam generation unit. A dedicated hierarchy block was used for the steam generation unit as only water was involved (trace impurities may occur but this was not the focus of this study). This strategy enabled a swift simulation run time and easy monitoring of the results. The STEAMNBS2 property method from Aspen Plus® was selected for the hierarchy due to its superiority (compared to other methods for steam system, e.g. STEAMTA and STEAMNBS) in providing accurate temperature results as compared to the plant data.

*Secondary reformer.* The process gas from primary reformer was sent to secondary reformer where the process air is introduced according to the stoichiometric requirement of nitrogen to produce ammonia. The SMR and WGS reactions Eqs. (9) and ((10)) continue to take place. The heat requirement for the SMR reaction is provided by combustion of hydrogen and methane with oxygen that was contained in the process air as the limiting reactant Eqs. (11) and ((12)). An RStoic block was used to model the combustion reactions with 100% of oxygen conversion.

In modeling the SMR and water gas shift reaction, an REquil block with zero °C temperature approach to equilibrium was found to provide a good match between simulation results and the design data. This may indicate that the reactions were in equilibrium and the catalyst's performance was good. However, in modeling the plant data, the methane content in% mole dry in the outlet stream, referred as methane slip, was too low for a given outlet temperature. This finding may indicate the declining performance of the catalysts as methane slip is an important indicator to access the performance of the primary and secondary reformers, where its value within the expected range indicates good reforming reaction to produce hydrogen. Hence, a reactor block that allows a custom catalyst's performance parameter such as RPlug is more suitable. The reaction system subroutine provided by Aspen Plus® was used hence it is required to specify certain parameters, including the "*Kinetic subroutine*". According to the simulation, the value of parameter "real" (catalytic activity) in the "*Kinetic subroutine*" at 0.28 agreed well with the plant data. The outlet stream from secondary reformer provides useful heat for the VHP steam generation by means of waste heat boiler (WHB) and steam superheater that were modeled with Heater blocks with heat stream output.

*High temperature and low temperature shift converters*. The remaining gaseous carbon monoxide (CO) content in the process stream must be removed to protect ammonia converter catalysts from poisoning. CO was converted into $CO_2$ via water gas shift reaction (Eq. (10)) so that it can be absorbed by a solvent in the $CO_2$ removal section. The water gas shift reaction occurred in two stages, high and low temperature shift converter (HTSC and LTSC). RPlug block from Aspen Plus® yields a good fit for the composition and temperature of the outlet streams compared to design and real plant data. The reaction subroutine called HTSHIFT and LTSHIFT were utilized with real parameter value for HTSC and LTSC were 0.8 and 0.1, respectively. Due to the exothermic nature of water gas shift reaction, the waste heat was recovered in the subsequent heat exchangers including WHB and BFW preheaters that were modeled with Heater blocks with heat stream output.

### 4.1.2. Middle end model

Further purifications to remove the oxygen contained in CO and $CO_2$ from the process gas were done in middle end section.

*Carbon dioxide removal section.* The $CO_2$ removal section consists of two major units: $CO_2$ absorber and $CO_2$ stripper; equipped with heat exchangers including stripper reboiler and pumps for solvent circulation. Majority of the $CO_2$ content in the process gas was absorbed using aqueous methyl di-ethanol amine (MDEA) and piperazine (PZ) as an activator (designed by BASF®). Next, the absorbed $CO_2$ was removed in $CO_2$ Stripper and majority of it was sent to the adjacent urea plant with purity of approximately 99.2% mol dry. For the validation stage, the $CO_2$ Absorber was modeled using a RadFrac block. The reaction set provided by Aspen Plus® with chemical ID "P-M-RXN" was utilized to simulate the reactive $CO_2$ absorption (Tanvir Sowgath and Mujtaba, 2019; Aspentech 2015). Reactions involving $CO_2$ with OH- and $CO_2$ with PZ and PZCOO- are kinetics based (Aspentech, 2014).

Referring to reactions Eqs. (15)–((27)), it is implied that the $CO_2$ removal unit itself is complex with the addition of ions, as compared to other sections with only hydrocarbons, steam, and ammonia. Therefore, in the validation stage, the $CO_2$ removal unit was modeled in a separate simulation to avoid complexities due to its interaction with other sections. An application file from Aspen Plus® called "*ENRTL-RK Rate Based PZ+MDEA Model*" was used. A special data package of MDEA (called KEMDEA) was inserted in the model (Mudhasakul et al., 2013). A property method that is more suitable for the electrolyte system called "ELECNRTL" was utilized. As $CO_2$ was removed through reactive absorptions, the equilibrium approach was unsuitable do to its failure to predict the reaction impact to the mass and heat transfer (Mudhasakul et al., 2013), hence the rate-based model of the RadFrac block was used. Meanwhile, inside the main simulation file, the $CO_2$ absorber was modelled as a separator Sep2 block where the split parameters and other key properties were obtained from the rigorous $CO_2$ removal simulation file.

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(l)} + OH^-_{(l)} \quad \text{(equilibrium)} \tag{15}$$

$$CO_{2(g)} + OH^-_{(l)} \rightarrow HCO^-_{3(l)} \quad \text{(kinetic)} \tag{16}$$

$$HCO^-_{3(l)} \rightarrow CO_{2(g)} + OH^-_{(l)} \quad \text{(kinetic)} \tag{17}$$

$$HCO^-_{3(l)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(l)} + H_3O^+_{(l)} \quad \text{(equilibrium)} \tag{18}$$

$$PZ_{(l)} + CO_{2(g)} + H_2O_{(l)} \rightarrow PZCOO^-_{(l)} + H_3O^+_{(l)} \quad \text{(kinetic)} \tag{19}$$

$$PZCOO^-_{(l)} + H_3O^+_{(l)} \rightarrow PZ_{(l)} + CO_{2(g)} + H_2O_{(l)} \quad \text{(kinetic)} \tag{20}$$

$$PZCOO^-_{(l)} + CO_{2(g)} + H_2O_{(l)} \rightarrow PZCOO^{2-}_{(l)} + H_3O^+_{(l)} \quad \text{(kinetic)} \tag{21}$$

$$PZCOO^{2-}_{(l)} + H_3O^+_{(l)} \rightarrow PZCOO^-_{(l)} + CO_{2(g)} + H_2O_{(l)} \quad \text{(kinetic)} \tag{22}$$

$$PZH^+_{(l)} + H_2O_{(l)} \rightleftharpoons PZ_{(l)} + H_3O^+_{(l)} \quad \text{(equilibrium)} \tag{23}$$

$$HPZCOO_{(l)} + H_2O_{(l)} \rightleftharpoons PZCOO^-_{(l)} + H_3O^+_{(l)} \quad \text{(equilibrium)} \tag{24}$$

$$MDEA^+_{(l)} + H_2O_{(l)} \rightleftharpoons MDEA_{(l)} + H_3O^+_{(l)} \quad \text{(equilibrium)} \tag{25}$$

$$MDEA_{(l)} + CO_{2(g)} + H_2O_{(l)} \rightarrow MDEA^+_{(l)} + HCO^-_{3(l)} \quad \text{(kinetic)} \tag{26}$$

$$MDEA^+_{(l)} + HCO^-_{3(l)} \rightarrow MDEA_{(l)} + CO_{2(g)} + H_2O_{(l)} \quad \text{(kinetic)} \tag{27}$$

*Methanator.* The remaining CO and $CO_2$ content in process gas must be eliminated by converting them to an inert gas, methane, in methanator through the following reactions:

$$\begin{gathered} CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)} \\ \Delta H^o = -205.91\,kJ\,mol^{-1} \end{gathered} \tag{28}$$

$$\begin{gathered} CO_{2(g)} + 4H_{2(g)} \rightarrow CH_{4(g)} + 2H_2O_{(g)} \\ \Delta H^o = -164.83\,kJ\,mol^{-1} \end{gathered} \tag{29}$$

The RStoic block with 100% conversion of CO and $CO_2$ was used to model the methanator. The heat generated by the exothermic reactions was utilized to preheat the inlet process gas. Further cooling for the outlet process stream was provided by cooling water. Both exchangers were modeled using Heater blocks. The process stream then was sent to the syngas compressor and referred as make up synthesis gas (syngas).

### 4.1.3. Back end model

*Ammonia synthesis loop*. Reaction (30) takes place in the ammonia converter that has two catalyst beds with an interbed heat exchanger in between. The syngas feed was first preheated in the interbed exchanger, allowing the outlet stream from the first catalyst bed to be cooled down, away from the reaction equilibrium to obtain higher conversion in the next bed. Each catalysts bed was modelled with RPlug block that provided a better match as compared to REquil, when using real plant data in the base case (Case 4). The reaction system subroutine NH3SYN was used. The real parameter value for user kinetic subroutine was adjusted to match the outlet temperature during validation using plant data, yielded in 1.9 and 1.6 for catalyst bed 1 and 2, respectively. For the interbed heat exchanger, a HeatX block was used.

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \quad \Delta H^o = -91.4\,kJ\,mol^{-1} \tag{30}$$

Next, waste heat contained in the gas exiting the second catalyst bed was recovered in final WHB, BFW preheater and process heat exchangers. Following this, the gas was mixed with compressed make up syngas exiting the third stage of syngas compressor. The mixture was then cooled, separated from the liquid ammonia, and circulated back to the ammonia converter while undergone several stages of preheating provided by waste heat from ammonia converter outlet followed by compression by the fourth stage of syngas compressor. The liquid ammonia was drawn and sent to the refrigeration unit for further cooling.

A certain amount of the circulated gas should be removed as purge gas from the synloop section to prevent the buildup of inerts. This purge gas was sent to a dedicated hydrogen recovery unit (HRU) outside the ammonia plant battery limit to recover the hydrogen and ammonia (not simulated in this study). HeatX, Heater and flash separator blocks were used to model the heat exchangers, chillers, and separators in ammonia synloop. As the ammonia plant model was built gradually from the front end unit, the first three stages of syngas compressor were modeled with a multistage compressor MCompr and the last stage was modeled as a separate Compr block to aid convergence due to the presence of recycled streams.

*Refrigeration unit*. The liquid ammonia from synloop was sent to refrigeration unit where it was flashed from around 130 to 1 bar in flash vessels and was drawn as ammonia product at approximately $-33^\circ$C. The ammonia vapor from flash vessels was sent to the refrigerant compressor, condensed with cooling water, and then was circulated as refrigerant in the synloop. A combination of HeatX, Heater, Flash2 Separator and MCompr multistage compressor blocks from Aspen Plus® were used.

## 4.2. Sensitivity analysis and optimization

The validated simulation model using real plant data was used as a base case for the sensitivity analysis (Case 4) and represents the current operational mode of the studied plant. The sensitivity analysis involved procedures below.

### 4.2.1. Determine the natural gas composition range

While natural gas composition can vary greatly, the general representability is very important. The methane content range between 83 and 99.99% vol dry was selected, with increment of approximately 4% between each case that allowed obtaining a representative trend within timely manner. Methane content below 80% was not studied as this can be rarely found (Pustišek and Karasz, 2017).

### 4.2.2. Build the simulation model for each case

Aspen Plus® provides model analysis tool than can be used for sensitivity analysis. However, this feature was not suitable for a complex simulation involving many reactions, heat transfer between process streams, as well as recycle loops that are heavily affected by the stream composition including NG as raw material and fuel. As the NG composition changes, other consequences follow, including (but not limited to) the different process requirement for each case, the chemical conversion as well as the heat generation/requirement for each reaction, the heat transfer between process streams, etc. In addition, the change of heat combustion from different NG composition affects the endothermic reactions in primary reformer as well as heat transfer in its convection section. Therefore, for each NG composition, certain key parameters should be carefully examined, and manual adjustments may be required to maintain the expected range (as design spec feature was not suitable for similar reasons). For each case, the base case simulation file was duplicated, and the NG composition was adjusted accordingly. To allow a fair comparison, each model was optimized to obtain similar key parameters values as in the base case.

### 4.2.3. Perform process optimization

The process optimization means maximizing ammonia production subject to the constraints of maintaining the values of key parameters within a reasonable tolerance, where the deviations towards the base case were $< 0.2\%$ except for oxygen excess with $< 10\%$. As discussed in the previous section, changing the NG composition leads to several consequences. Therefore, this procedure is critical to ensure a fair comparison between cases as the only variable present would be change in the NG composition. No optimization tool from Aspen Plus® was utilized as each parameter was maintained by manually adjusting the corresponding input value as discussed next. The key results from each simulation were recorded (i.e. in Microsoft Excel) to help directing the trial towards the objective.

* *Steam to carbon ratio (S/C)*

$$S\Big/C = steam\,flow\left(kmol\,hr^{-1}\right)\Big/\sum C\left(kmol\,hr^{-1}\right) \tag{31}$$

where ΣC is the total carbon content and

$$\sum C = \left[\sum\left(x_i \times nC_i\right)\right] \times NG\,flow\left(kmol\,hr^{-1}\right) \tag{32}$$

where $i$ is hydrocarbon in natural gas, $x_i$ is dry mol percent of hydrocarbon $i$, and $nC_i$ is the number of carbon atom in hydrocarbon $i$. The carbon number represents the carbon-hydrogen bond in NG where the hydrogen itself is one of the reactants to produce ammonia. The higher the number, the higher the hydrogen equivalent in NG, hence more ammonia could be synthesized. It is taken into account that most hydrogen was produced in primary reformer and that the SMR reactions (1–10) imply more hydrogen could be obtained by either increasing the primary reformer temperature and /or increasing the steam mole flowrate. However, there is a limitation where too much steam will burden the plant's energy requirement as more heat was needed from the combustion furnace to achieve certain temperature in the primary reformer catalyst tubes due to higher total mole flowrate. The process steam was added at a flowrate that corresponds to a certain S/C ratio to obtain optimum hydrogen product from SMR reaction in reformer and thus minimize the excess methane (referred as methane slip). The S/C ratio was maintained at ~2.99 for all cases following the base case that represents daily normal operating mode of the studied plant to ensure an "equal degree" of hydrogen production.

* *Primary reformer outlet temperature and excess oxygen*

As NG composition changes, the process steam requirement varies for a constant S/C ratio. Therefore, the flowrate of NG fuel and combustion air were adjusted to keep the primary reformer outlet temperature and excess oxygen in the flue gas reasonably constant at 788°C and 2.3% mol dry, respectively, as in the base case. As for S/C ratio, the primary reformer temperature outlet and oxygen excess value were maintained as in the base case.

* *Hydrogen to nitrogen ratio (H/N)*

The H/N ratio is ratio between hydrogen to nitrogen mole flowrate in make up syngas, following the stoichiometric requirement at ammonia converter. The process air flowrate entering secondary reformer was trialed to obtain H/N ratio of 2.99 as in the base case.

* *Very high pressure (VHP) steam temperature*

As NG composition changes, the carbon number varies, resulted in different requirements of process steam and NG fuel for the SMR reaction which finally affected the amount of waste heat rejected by process streams and combustion flue gas for VHP steam generation. In this way, the VHP steam temperature could only be maintained by adjusting the demineralized water feed flowrate. The design spec feature of Aspen Plus® was used with steam temperature specified at 515°C following the requirement as in the base case.

#### 4.2.4. Analyze the simulation results

The following results were compared and analyzed: ammonia production, raw material consumption figure, energy consumption figure (natural gas, electrical power, and steam production). To assess the independency of the studied ammonia plant in fulfilling its energy requirement, the network required by significant energy users was correlated with the steam driver requirement as well as VHP steam generation. The requirement for steam-driven compressors ($Steam_{req,\ i}$) was calculated as below:

$$Steam_{req,i} = \left(Steam \big/ W_{comp}\right) \times Network_{comp,i} \tag{33}$$

where the $Steam/W_{comp}$ parameter was obtained from the base case, assuming a constant compressors efficiency for all cases.

$$\left(Steam \big/ W_{comp}\right) = \left[VHP_{steam\ to\ turbine} \big/ Network_{comp}\right]_{base\ case} \tag{34}$$

### 4.3. Sustainability analysis

The sustainability analysis focuses on the raw material intensity, energy intensity and the $CO_2$ emissions per tonne of ammonia. The results that represent the conventional process were compared with the current global average and green ammonia.

## 5. Results and discussion

### 5.1. Process design and simulation

Table 1 shows the key parameters results from the two validation stages which reveals a good agreement with% *difference* below 10%, except for methane slip in secondary reformer and $CO_2$ slip ($CO_2$ content in the outlet stream) of absorber in validation using design data and $NH_3$ content at outlet ammonia converter in validation using plant data.

In the validation using plant design data, only the% *difference* is shown due to copyright matter. For the front end model, a zero temperature approach to equilibrium of REquil block gives the best fit to the design data in primary and secondary reformer, revealing the dependency to the temperature as the most influential factor. Although the difference was 19.05%, the methane slip in secondary reformer was still within normal operation range at below 0.6% mol dry. For $CO_2$ removal unit, challenges arose to simulate the rate based absorption model, although a simulation template and a special insert package have been provided by Aspen Plus®, added with previous study in a similar process (Mudhasakul et al., 2013), mainly due to limited liquid holdups data. However, the rate-based model demonstrated a great capability to perform the heat balance calculation indicated by the outlet stream temperature that agrees well with design (49.91 vs 50°C for process gas outlet). In addition, the $CO_2$ slip of absorber at 0.25% mol dry was found to be lower than similar study on ammonia process at 0.30% mole dry (Sadeek et al., 2020) with the overall absorption efficiency fits well within the normal range of the plant. As $CO_2$ slip refers to $CO_2$ content in the outlet stream of $CO_2$ absorber, lower $CO_2$ slip means more $CO_2$ that is removed from the process gas through absorption using liquid absorbent. For the back end, overall parameters agree well with the plant data.

Next, the simulation was used to model the process using plant data in second validation stage and later to be used as base case. For the front end model, the overall key parameters agree well with the plant data with% *difference* less than 10%. In $CO_2$ removal unit, the absorber and stripper were modeled with Sep2 blocks (as performance of the $CO_2$ removal unit is not the focus of the study) by providing the split fraction for each component according to plant data at the inlet and outlet streams. Furthermore, plant data shows that key parameters of process gas exiting $CO_2$ removal unit i.e., maximum $CO_2$ slip were managed to be maintained regardless of the fluctuation of NG feed composition. For the middle end, the H/N ratio at outlet of the methanator agrees well with the plant data with 4.17% *difference*.

**Table 1**
Ammonia plant model validation results.

| Parameter | Unit | Design data<br>% difference*) | Plant Data<br>Actual data | Model result | % difference*) |
|---|---|---|---|---|---|
| Primary reformer: | | | | | |
| methane slip | % mol dry | −1.33 | 13.29 | 13.27 | 0.17 |
| outlet temperature | °C | 1.44 | 788.39 | 788.38 | 0.001 |
| $O_2$ excess of the flue gas | % mol dry | N/A | 2.54 | 2.48 | 2.37 |
| Secondary reformer: | | | | | |
| methane slip | % mol dry | 19.05 | 0.56 | 0.51 | 8.78 |
| outlet temperature | °C | 0 | 967.08 | 969.00 | −0.20 |
| $CO_2$ removal: | | | | | |
| $CO_2$ slip of absorber | % mol dry | −406.28 | 0.01 | 0.01 | −0.82 |
| $CO_2$ product flowrate | $Nm^3\ h^{-1}$ | 1.57 | 30,701.21 | 29,894.26 | 2.63 |
| Methanator: | | | | | |
| H/N ratio**) | – | 0.63 | 3.12 | 2.99 | 4.17 |
| Ammonia converter: | | | | | |
| $NH_3$ content at inlet | % mol dry | −2.76 | 3.93 | 4.26 | −8.43 |
| $NH_3$ content at outlet | % mol dry | −1.46 | 15.15 | 18.40 | −21.42 |
| outlet temperature | °C | −0.18% | 435.79 | 438.79 | −0.69 |
| Ammonia product | tonne $day^{-1}$ | 0.0001 | 1044.75 | 1044.97 | −0.02 |
| VHP steam product | tonne $h^{-1}$ | 2.95 | 183.73 | 186.25 | −1.37 |

*) (data-model)/data.

**) $H_2$ content:$N_2$ content.

The back end model involves a highly iterative procedure to obtain the appropriate user subroutine of the kinetic parameter values for the RPlug block of ammonia converter. Such kinetic parameters highly affect the catalyst activity of ammonia converter that in turns will affect the quantity of ammonia produced as well as heat generated from the exothermic reaction. Subsequently, heat transfer in several downstream exchangers was affected, and eventually, the inlet stream of the ammonia converter was affected as there are recycle loops due to low single-pass conversion. Therefore, it is critical to observe several parameters involved during the simulation to prevent errors. Overall, a good agreement with plant data has been attained with 0.02*% difference* for the ammonia product.

Notably there was a limitation of the Aspen Plus® model for the ammonia converter. When validating the model using real plant data, either the composition or temperature of the outlet stream from ammonia converter was compromised, which to the best of our knowledge has never been addressed before by similar studies (Sadeek et al., 2020; Tran et al., 2017). It was observed that when the outlet stream compositions were matched with the plant data, the calculated outlet stream temperature was lower. On the other hand, if the temperature of the outlet stream was made to match the plant data, the calculated ammonia content is higher. Given that the inlet temperature was the same for the previously discussed two cases, this finding may imply the limitation of the heat of reaction calculation provided by the reaction subroutine "NH3SYN". As this study was aimed to investigate the effect of NG composition to the VHP steam generation, the case that favors a good agreement for the ammonia converter outlet temperature was selected by fully considering the overall good agreement of ammonia production quantity (this is detailed in *Supplementary Information,* see Table S1).

### 5.2. Sensitivity analysis

The detailed natural gas composition for each case is available in *Supplementary Information* (see Table S2), considering the representative chosen range according to globally available NG compositions (Tran et al., 2017; Aspentech 2014; Mudhasakul et al., 2013). Natural gas composition for the base case was taken from the studied plant data while the methane content was varied in other cases, sustaining the $H_2S$ content as in the base case. Accurate NG heating values were obtained from a property calculator (Unitrove, 2021), as this was not readily available in Aspen Plus®. The result for the base case demonstrates a very good match with the laboratory analysis data of the studied plant.

#### 5.2.1. Ammonia production

Increasing methane content in natural gas indicates lower hydrogen content due to declining proportion of heavier hydrocarbons such as ethane, propane, butane, pentane and so forth that have higher carbon-hydrogen bond number. Therefore, being the first place where majority of such carbon-hydrogen bonds break via SMR reaction, primary reformer provides a useful figure to analyze the effect of NG composition towards hydrogen product for ammonia synthesis in its outlet stream as detailed in Fig. 2. Case 1 with the lowest methane content yielded highest hydrogen product as predicted with the average fall at −2.15% for every 4% increase of methane content. The variation of hydrogen production fall as can be seen from Fig. 2(A) were mainly due to variation of higher hydrocarbons constituent in NG although a similar increment of methane content was applied for each case.

Next, other reactions in the subsequent reactors contributed to a slight rise and fall of the hydrogen content in process gas as more of it were synthesized in secondary reformer, HTSC and LTSC; while a minor amount of it was consumed to convert CO and $CO_2$ back into methane in methanator. Finally, Fig. 2(B) shows how the hydrogen available was directly proportional with the ammonia produced at a constant H/N ratio as it reacts with nitrogen in ammonia converter, with average fall of ammonia product at −2.86% per case. This finding implies the production opportunity loss that may occur as leaner gas was fed. An increase of NG charge may be needed to sustain the production quantity. Yet, increasing feedstock rate may not be simple as there may be capacity limitations following the original design of an ammonia plant, posing a challenge to sustain the conventional ammonia plant efficiency.

#### 5.2.2. Raw materials consumption figures

*Natural gas.* As feedstock and main energy source, natural gas contributes most towards the ammonia production costs. According to the data of the studied ammonia plant in 2020, NG provided energy that equals about 88% of the total requirement. Although the figure may vary depends on the process technology, the previous data suggests the importanceof investigating the effect of natural gas composition change towards its consumption figure.

As increasing methane content in natural gas yielded lower hydrogen, it becomes clear that Case 1 resulted in the lowest volumetric NG consumptions per tonne ammonia product with increasing trend towards Case 5 (Fig. 2(C)) at an average of 2.52% per case. This amplifies the criticality of further assessment regarding the equipment and piping capacity when dealing with drastic change of natural gas composition. This finding could force the conventional ammonia plants to shift towards a more sustainable process, i.e. by introducing hydrogen from renewable sources when the NG composition change becomes unmanageable.

The finding about volumetric NG consumption may spark concerns on whether the ammonia production costs will increase. Further analysis suggests that natural gas consumption figure based on its heat content, i.e. in MJ tonne $NH_3^{-1}$ could be sustained across all cases despite the increasing trend of its volumetric requirement. As detailed in Table S2, natural gas in Case 1 has the highest heat content per mol due to lower methane content with decreasing trend towards Case 5. Therefore, through a simple procedure to obtain the energy requirement from NG by multiplying the total volumetric consumption (process and fuel) with its heating value, a stable figure with very small average of decrease across all cases at −0.02% was revealed.

The method to consider the NG process in the energy calculation of an ammonia plant is commonly applied globally (International Fertilizer Association, 2014; Brown, 2021; Smith et al., 2020b; Mokhatab and Poe, 2012). Extending the analysis by multiplying NG use in MJ tonne $NH_3^{-1}$ with its price in relevant units, shows a similar trend for NG costs (Fig. 2(D)) as in energy basis (price basis 7 USD mmbtu$^{-1}$ (The Ministry of Energy and Mineral Resources of the Republic of Indonesia, 2021), may vary in other regions (EIA, 2021)). From the economic stance, this finding is paramount by confirming that despite any composition change towards lean gas, the NG and ammonia production costs could be sustained. The key here is to maintain the optimum range of key parameters as pointed out in the methodology section.

*Process steam.* Medium pressure steam is required for SMR reaction in accordance with the S/C ratio. Any small change in the S/C ratio may affect the ammonia process, i.e. NG fuel requirement for SMR reaction, ammonia production quantity, etc., hence, a constant S/C ratio at 2.99 as in the base case was selected. The sensitivity analysis reveals the decreasing trend of process steam requirement as methane content in natural gas increase with the average fall at −1.21%, putting Case 1 with the highest number at 1.65 tonne steam per tonne ammonia. This is due to lower carbon number that represents the number of hydrocarbons involved in SMR reaction in lean natural gas.

*Net work requirement and steam generation.* This section assesses whether the studied ammonia plant could continue to be independent in providing its thermal energy requirement for compressors and large pumps (refer to Fig. S1 for the steam system diagram). In addition to primary reformer as the major energy user, the studied ammonia plant

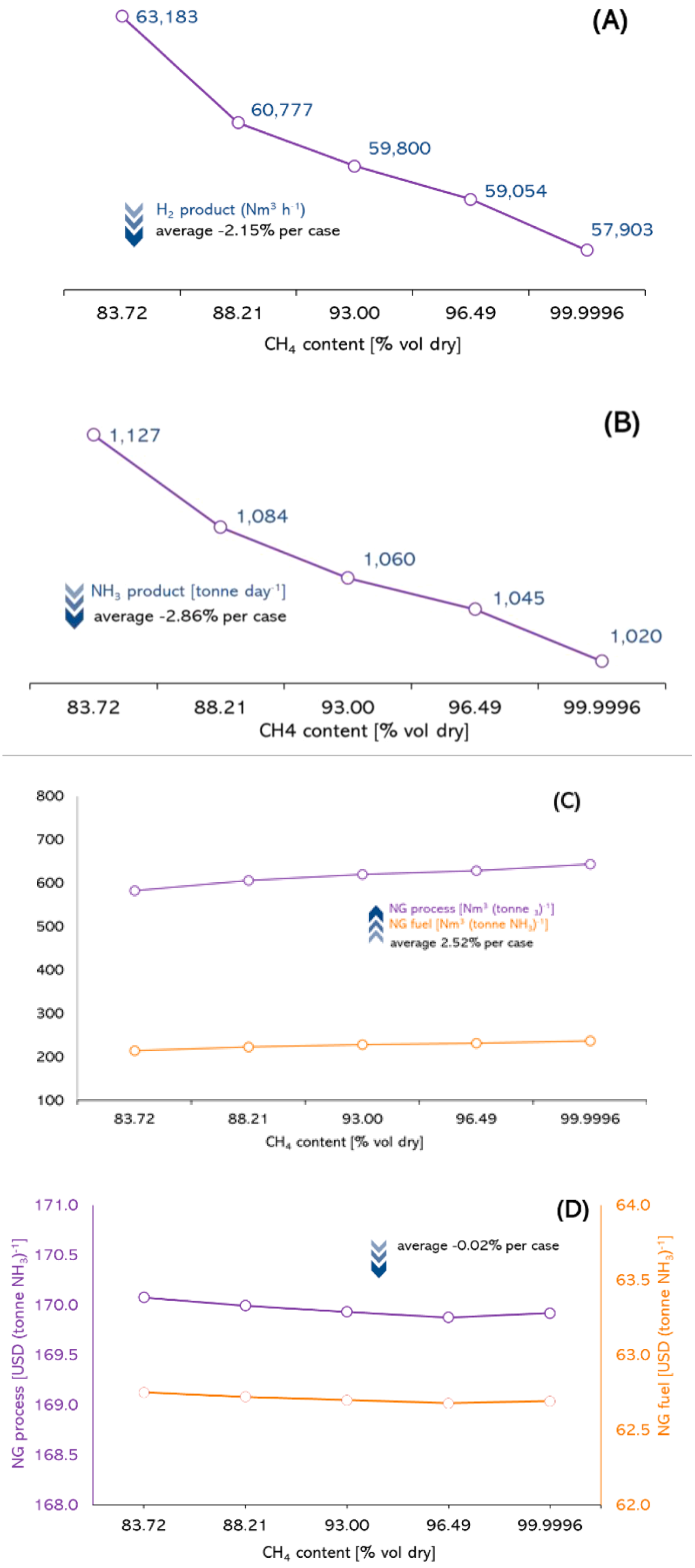

**Fig. 2.** Effect of NG composition towards: (A) Hydrogen product at primary reformer outlet; (B) Ammonia product per day; (C) Natural gas consumption figure; (D) NG fuel costs.

has compressors and BFW pump that were driven by the generated VHP steam. Therefore, to assess the steam balance due to variable natural gas composition, the net work requirement of such compressors and pump will be analyzed and correlated with the VHP steam production.

Five most significant energy users were considered in this sensitivity analysis, including four compressors: syngas, refrigerant, process air, and natural gas process; and BFW pump which account for 92% of the total thermal energy consumption (PKT, 2020). The net work required were obtained from Aspen Plus® by specifying discharge conditions and related efficiencies for compressors and pump, resulted in an almost stable trend across five cases with Case 1 as the lowest at 793.27 kW tonne $NH_3^{-1}$ (Fig. 3(A)).

The effect of variable NG composition became clearer as further investigation into the individual net work requirement of each energy user was performed (Fig. 3(B)). Similar trends where the net work requirement decreased as methane content increase were exhibited by all compressors except for NG. This finding is related to the fact that the carbon number is inversely proportional with the methane content. NG with higher methane content yielded in lower hydrogen product, thus required lower process air flowrate to maintain the H/N ratio in make up syngas, causing the syngas compressor's load to decrease; and finally, as lower quantity of ammonia produced, the load of the refrigerant compressor decreased accordingly. The different trend for the NG compressor was caused by the NG density that is inversely proportional with the methane content (Speight, 2019), and that net work required is a function of gas volume (Smith, 2016). For BFW pump, the declining net work requirement was caused by the design specification that was applied to maintain the VHP steam product temperature by varying demineralized water feed flowrate. This indicates lower quantity of VHP steam produced as lean gas was fed.

From a steam generation perspective, a lower heat of reaction was generated in HTSC and ammonia converter when lean gas was fed, as lower hydrogen was produced via SMR reactions. This resulted in lower heat available in waste heat boilers and BFW preheaters at the downstream of HTSC and ammonia converter. Lower hydrogen produced brings another effect, lower nitrogen required to maintain the H/N ratio in make up syngas. As nitrogen was feed in form of process air, the associated oxygen content was lower as well, further decreasing the waste heat available in WHB and VHP steam superheater at secondary reformer outlet. From the natural gas fuel side, lean gas means lower heat of combustion that was generated in primary reformer furnace, resulted in a lower heat available in BFW preheater and steam superheater in the convection section (Fig. 3(C)), and combined with previously discussed effects caused lower quantity of VHP steam production (Fig. 3(D)) with an alarming average of decrease at 2.24% per 4% vol dry methane content increase.

To provide a meaningful analysis, the VHP steam requirement for syngas and refrigerant compressor across five cases were calculated according to Eqs. (33) and (34) given the fact that they are the only users in VHP header. In the studied ammonia plant, the VHP steam could only be produced in the plant, therefore, ensuring the plant independency to its requirement is critical, otherwise plant cut rate may be put in place leading to an economic loss. No analysis is needed for the lower pressure steam header as their requirements were fulfilled either by extraction or let down from the above headers. Fig. 3(D) confirms that despite the declining VHP steam product quantity as lean gas was introduced; the VHP steam requirement followed the production trend well with the average decrease at 2.52% for five cases, sustaining the independency of conventional ammonia plant towards any drastic changes in NG composition.

The ammonia production quantity is the most affected factor with possible opportunity loss. However, this comes with a promising chance to introduce more sustainable hydrogen if the composition change of NG becomes unmanageable. Other parameters were shown to be affected as

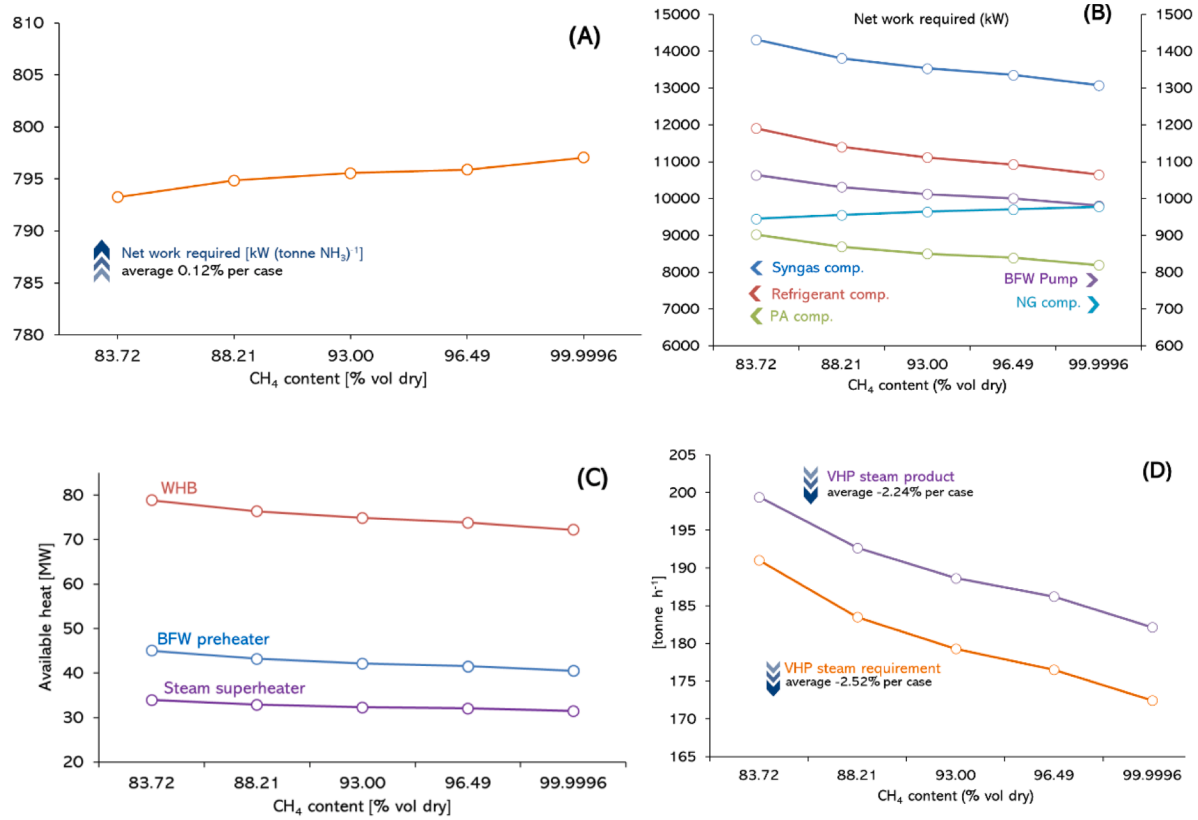

**Fig. 3.** Effect of NG composition towards: (A) Total net work required of key energy users per tonne ammonia; (B) Net work required breakdown; (C) Available for steam generation; (D) Steam generation and requirements.

well, but overall the changes cancel each other and it is possible to sustain the ammonia plant efficiency if the key operating parameters were maintained. The relatively unaffected NG cost implies that the overall ammonia production costs follow a similar trend.

### 5.3. *Operation improvements*

Despite the major sustainability gain that could be achieved by switching to renewable energy and feedstock, this process relies on the intermittent and smaller capacity of renewables as compared to the conventional process (Smith et al., 2020a). Therefore, it is imperative to continue in improving the current BAT while expecting the greener ammonia process to be ready. Admitting that a better understanding leads to appropriate actions, this section offers valued daily operation controls to obtain an acceptable gain towards more efficient ammonia process in a more affordable and executable way compared to major revamping or retrofit. Key operational parameters for primary reformer are discussed given the fact that it was the largest energy user in most classic ammonia plants. All calculations were performed based on Case 4.

#### 5.3.1. *Primary reformer temperature outlet*

The nature of endothermic reactions in primary reformer makes it beneficial to obtain higher hydrogen product when the temperature is increased. Assuming that such reactions were in equilibrium, the temperature could be observed from the outlet process stream. However, given the relatively constant heat duties in the primary reformer convection section, combusting more natural gas fuel to increase the reaction temperature resulted in higher heat loss and emissions to the environment, implying a trade-off between related parameters (Fig. 4(A, B)). According to the studied plant data, a 7°C stack temperature increase may occur when the natural gas fuel flowrate was increased from ~8,200 to 10,800 Nm$^3$ h$^{-1}$(Fig. 4(B)). Acknowledging another important factor, the catalyst tube lifetime, the recommended range for optimum primary reformer temperature is around 790–800°C, resulted in methane slip at approximately 10–13% mol dry (Mardiani, 2012). A higher methane slip for the same temperature may indicate the declining performance of the catalysts. The actual data from the studied plant were indicated with “A” compared to the reference value “R” (Fig. 4(A)).

#### 5.3.2. *Steam to carbon (S/C) ratio*

Another way to suppress the primary reformer methane slip is to maximize the hydrogen production by increasing the S/C ratio that will shift the SMR reaction equilibrium towards hydrogen product as more steam available. However, to achieve the same temperature, the heat requirement for SMR reaction will increase accordingly, due to higher total mass flowrate. Finally, heat loss via flue gas may be affected, i.e. increase as well (Fig. 5). Generally, the S/C ratio is maintained at optimum range between 2.8 and 3, and the primary reformer temperature is varied to obtain the expected methane slip. An optimum S/C ratio yielded in an acceptable methane slip without increasing the heat loss through primary reformer stack. Then again, a low S/C ratio, i.e. $\leq 1.9$ is not preferred as it may cause carbon formation inside the primary reformer catalyst tubes(Mardiani, 2012).

#### 5.3.3. *Excess oxygen in primary reformer flue gas*

Excess oxygen is a crucial parameter that indicates a complete combustion of natural gas and other fuels (if any). From a safety aspect, any unburned fuel may pose a risk of explosion. The excess oxygen for the base case at approximately 2.3% mol dry could be improved further

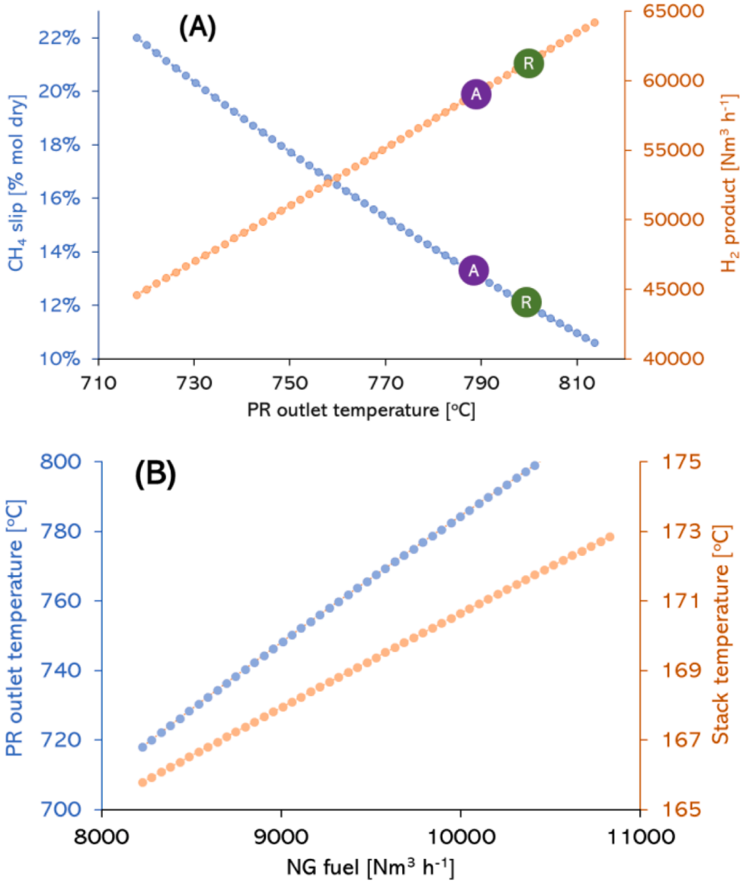

**Fig. 4.** Primary reformer temperature: (A) correlation between primary reformer temperature, methane slip, and hydrogen product; (B) correlation between natural gas fuel consumed, primary reformer temperature, and stack temperature.

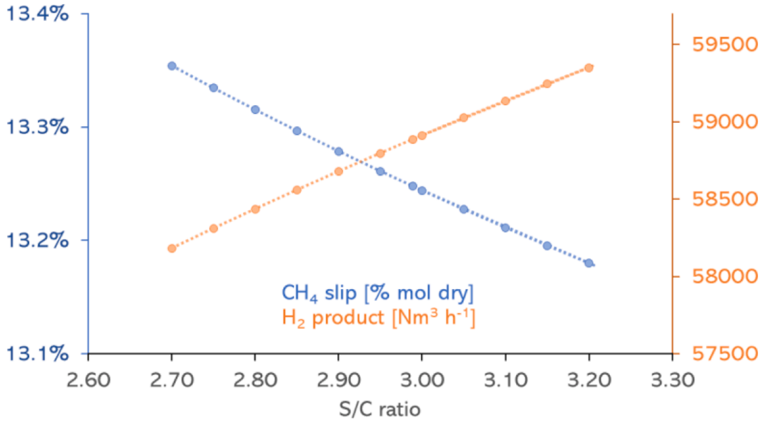

**Fig. 5.** Correlation between S/C ratio, methane slip and hydrogen product.

to around 1–1.5% mol dry to minimize the heat loss from flue gas. Conversely, excess oxygen may not be too low, i.e. less than 1% mol dry to account any operational fluctuation that may lead to incomplete combustion in the furnace.

## 5.4. Sustainability metrics

Admitting the use of non-renewable resources in the studied ammonia plant, this section will discuss the sustainability aspect of the process and find the relative position towards more sustainable processes.

### 5.4.1. Raw material intensity and energy intensity

Fig. 6(A) shows how the increasing methane content in natural gas yielded positive results towards sustainability with decreasing natural gas process intensity at −3.52% of overall average across five cases. This finding is in line with the fact that natural gas with higher methane content has lower volume density. Considering the reduction of ammonia product for each case at 2.86%, it may be implied that the percentage of natural gas volumetric density fall is greater to obtain such

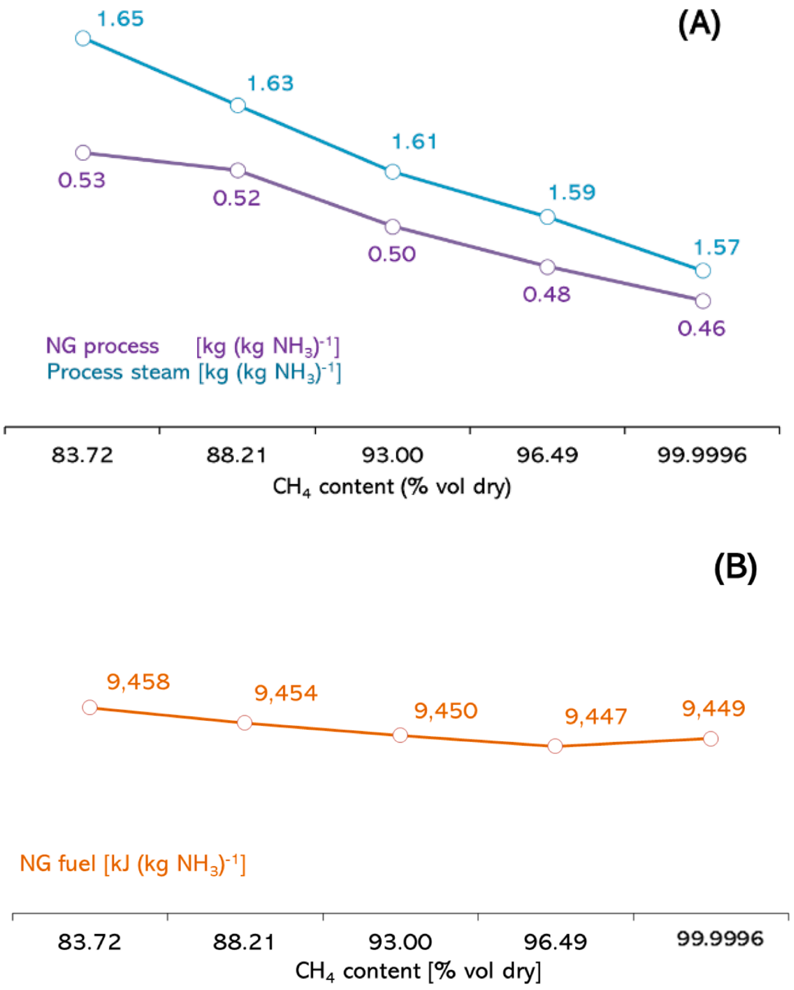

**Fig. 6.** Sustainability analysis for the studied ammonia plant: (A) raw material intensity; (B) energy intensity.

natural gas intensity profile. The positive trend was also observed for the process steam intensity although the average decrease was lower, at −1.21%. The improved raw material intensity could offer a chance to prolong the natural gas reserve which have shown an alarming decrease across the last two decades (BP, 2021). Although the NG quality is often a given parameter, operating the ammonia plant with natural gas that is rich in methane content will further be beneficial towards sustainability aspect if added with operational control to improve the process efficiency.

In terms of energy intensity, only NG as the main energy source was considered. This is also supported by the fact that the studied ammonia plant is self sufficient in providing its steam requirement for the next largest energy users after the primary reformer. Fig. 6(B) shows that the energy intensity could be preserved despite the increasing methane content in NG.

### *5.4.2. Carbon dioxide emissions*

The $CO_2$ emissions analysis was carried out within the studied ammonia plant boundary, where the emissions from the NG exploration and its subsequent supply chain were not part of the study. The steam generation was considered to be carbon neutral as it is produced by utilizing the waste heat from flue gas as well as from the process streams, although the provision of demineralized water from the utility plant may emit some $CO_2$ gases. Four categories were found to contribute most towards total $CO_2$ emissions: primary reformer, $CO_2$ stripper, electricity use and vents.

A more detailed result for the $CO_2$ emissions is available in the *Supplementary Information* (see Table S5) where a positive impact of increasing methane content in natural gas towards $CO_2$ emissions is demonstrated (Smith, 2016; Mardiani, 2012). The fall of the carbon number, as well as $CO_2$ that is naturally contained in natural gas, as the methane content increase contributed to the positive impact. Primary reformer furnace contributed most toward the $CO_2$ emissions as combustion occurred, while the fact that up to 92.30% $CO_2$ released from the $CO_2$ removal unit was fed to the adjacent urea plant resulted in a positive impact by significantly reducing the $CO_2$ emitted (Table 2).

**Table 2**
Total $CO_2$ equivalent emissions for the ammonia plant in kg CO2eq per tonne $NH_3$.

| $CO_2$ from: | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 |
|---|---|---|---|---|---|
| Primary reformer (a) | 567.52 | 561.16 | 547.23 | 537.29 | 528.41 |
| $CO_2$ stripper (b) | 82.10 | 82.16 | 82.10 | 82.15 | 82.08 |
| Electricity (c) | 22.86 | 22.86 | 22.86 | 22.86 | 22.86 |
| Inert and let-down gas (d) | 43.21 | 41.63 | 39.98 | 39.24 | 38.19 |
| Total (kg CO2eq / ton $NH_3$) | 715.68 | 707.81 | 692.17 | 681.54 | 671.55 |

Several figures for $CO_2$ emissions of a conventional ammonia plant with Haber Bosch process are available from various publications. For instance, the European average in 2005 was 2.7 tonnes $CO_2$ per tonne $NH_3$ (Rafiqul et al., 2005), while a contemporary more efficient HB process plant emits 1.5–1.6 tonnes $CO_2$ per tonne $NH_3$ (Bicer et al., 2016). Certainly, compared to previously mentioned figures, the studied ammonia plant demonstrates much lower $CO_2$ emissions with average across five cases at 0.69 tonnes $CO_2$ (tonne $NH_3$)$^{-1}$, lower values than the range from literature. The major contributor for low $CO_2$ emissions was the $CO_2$ utilization as raw material for an urea fertilizer plant, followed by operational control and optimization. Finally, as ammonia production is accountable for approximately 1.8% of total global $CO_2$ emissions, lowering the $CO_2$ emitted from the plant could offer significant impact due to the large production scale.

## 6. Conclusions

A complete model of an ammonia plant based on the Haber-Bosch process was successfully built in Aspen Plus and validated using industrial data. Based on the validated model, a sensitivity study was performed with variable natural gas composition for the studied ammonia plant, where key operational parameters were maintained on-spec. Ammonia production was observed to be the most affected parameter with the average fall of 2.86% for each ±4% increase of methane content in natural gas due to lower hydrogen equivalent. In addition, an average rise of specific natural gas process and natural gas fuel consumption in $Nm^3$ (tonne $NH_3$)$^{-1}$ at 2.52% was recorded as natural gas shifted to lean gas, implying a critical impact if the ammonia production was to be maintained (as larger NG flowrate was needed). The limitation would be the design capacity of the individual equipment that contributes to the overall overdesign of the plant. It is expected that no capital costs are required for the ammonia production to be sustained if the increasing natural gas flowrate is well below the plant's overdesign allowance. Consequently, a further study to investigate the threshold of the methane content increase in natural gas becomes very important. Finally, introducing green hydrogen to substitute the additional NG flowrate may be beneficial and improve the sustainability aspect of the process, although the economic viability should be carefully considered.

Several key parameters such as process steam intensity and energy intensity in terms of NG process and NG fuel in MJ (tonne $NH_3$)$^{-1}$ were managed to be sustained due to maintained key operating parameters. Despite decreasing VHP steam production as NG shifted towards lean gas, the steam requirement of the energy users demonstrated a similar trend, sustaining the studied ammonia plant as an independent unit in providing steam required. This suggests the ability of the studied ammonia plant (a conventional ammonia process) to adapt with a drastic change of its feedstock and main energy source (NG). In terms of sustainability, although fossil-based feedstocks and energy source (NG) is still in use, positive impacts have been recorded in terms of raw material intensity and $CO_2$ emissions as NG composition shifted towards lean gas, with an average reduction of 1.17% and 1.79%, respectively.

## Author statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication.

## CRediT authorship contribution statement

**Erna Rokhayati:** Conceptualization, Methodology, Software, Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Anton A. Kiss:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Visualization, Validation, Supervision, Project administration, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

## Acknowledgments

ER gratefully acknowledges the financial support of PT Pupuk Kalimantan Timur (Indonesia) by awarding the scholarship to accomplish the master degree at The University of Manchester and to conduct this research study. AAK gratefully acknowledges the Royal Society Wolfson Research Merit Award (No. WM170003).

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.compchemeng.2022.107951.

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