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Simulation And Optimization Of Hydrogen Production By Steam Reforming Of Natural Gas

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Abstract: Hydrogen (H_2) production through natural gas steam reforming is widely adopted due to its cost-effectiveness and energy efficiency. A simulation and optimization study was performed on an industrial natural gas steam reforming system using Aspen Hysys V12 software to optimize this process. The study focused on optimizing various parameters, including the Reformer Reactor, Water Gas Shift Reactor, and purification units such as the Separator and Pressure Swing Adsorption (PSA). The Reformer and Water Gas Shift reactors were set at 900 °C and 300 °C, respectively, to maximize hydrogen production. Under specific conditions of 5 atm pressure and a steam-to-carbon ratio (S/C) of 2.5, the process achieved a hydrogen production rate of 402.2 kg/h. The treatment zone effectively eliminated ~ 100% of undesirable CO_2 and CO gases, with only trace amounts of CH_4 and H_2 remaining in the waste gases. Additionally, the PSA unit efficiently removed ~ 100% of the water from the separator, ensuring water-free dry gases were sent to the PSA unit. The integration of heating and cooling heat exchange units reduced energy consumption by approximately 51.6%. After the removal of undesired gases in our PSA unit, the production yield for the final product (H_2, based on dry gas inlet to PSA) is 77.83%, resulting in 100% pure dry H_2. In the waste gas outlet (tail gas) of PSA a composition (22.17%), includes CO, CO, H_2O, and CH_4. Resulting high-quality hydrogen is well-suited for a wide range of applications, including fuel cells, petroleum refining, natural gas refineries, and petrochemical processes.

Keywords: Natural Gas Steam Reforming, Hydrogen Production Process Simulation, Process Optimization, Reformer, Water Gas Shift (WGS)

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1. INTRODUCTION

An increase in the global population of 7.98 billion in 2022 and in heavy industrialization of 3.217% in 2018, has been enormously rising energy demand. Thus, world energy consumption is expected to grow by nearly 50% by 2050, predisposing the world's economic and political stability into a precarious position. In this context, and as awareness increases, a growing coalition between governments and oil and gas giants, is seeking an advanced prospect of the hydrocarbon reserve that would be capable of powering complex industrial processes and growing population demands (El-Shafie et al., 2019). Therefore, according to the "The Future of Hydrogen" report, released by the international energy agency IEA in 2019, hydrogen got the world's attention due to its potent role. Its demand within various industrial sectors is now at the highest level in history. For instance, according to the U.S. Department of Energy, global hydrogen demand surpassed the threshold of 70 MMT in 2018. Hydrogen acts as an energy vector that can be transported, stored, and easily blended. Moreover, most of today's demand of 70 million tons of produced H_2 worldwide annually, is for chemical applications and the petrochemical industry. Therefore, these industries represent 63% of the total industrial hydrogen demand according to certify where, ammonia is by far the largest consumer in the chemical sector, ranging between 27 and 53% of the total demand. The methanol industry, accounting for 12% of the market share, is the second largest hydrogen consumer in the petrochemical sector. Moreover, the project hydrogen demand for ammonia and methanol is expected to reach 14 MT (H_2/Year) by 2030 (a 31% increase under existing policies for ammonia and methanol due to economic and population growth) (Alves et al., 2013). Accordingly, refineries represent the second largest consumer of hydrogen after the petrochemical industry segment, with a market share of 30%. And, hydrogen is used for the hydro-processing of crude oil and petroleum products involving sulfur, nitrogen, metal impurities removal, as well as for the production of lighter and more valuable products (Sarkarzadeh M, et al., 2019). A wide variety of technologies is currently used for hydrogen production, such as gasification, solar (or wind) water electrolysis, high-temperature electrolysis (HTE) water splitting, and natural gas steam reforming including steam methane reforming (SMR) (Goswami et al., 2003). On a commercial scale, SMR is considered the invaluable and the most practical technology to produce H_2, thus it is capable to produce high hydrogen yield efficiency of approximately 75% with an estimated cost of around 1.8 – 2.3 \$/kg versus an average between 3 and 5.80 \$/kg for the (HTE) and versus the incomparable highest production cost for wind and solar electrolysis (production cost >7 \$/kg H_2). SMR is relatively environmentally friendly in comparison with coal gasification technology. SMR will be a practical and brilliant idea to boost the petrochemical and refinery industries in the world (Lemus & Martínez Duart, 2010). This work covers a detailed analysis of a steady state simulation and optimization of an industrial natural gas steam reforming process capable of meeting the hydrogen demand of petrochemical-refining industries and fuel cell technology. In SMR high methane purity in natural gas is needed in order to save on the capital and operating cost of the system, by decreasing the load of the purification stage. An optimization of the operating conditions in the main units of the process was performed. The effect of, i) steam to carbon ratio (S/C), ii) pressure, and iii) temperature was conducted by Aspen HYSYS v12. Presently, the hydrogen demand around the globe is majorly met the steam methane reforming with the natural gas feedstock. Hydrogen (H_2) production through natural gas steam reforming is widely adopted due to its cost-effectiveness and energy efficiency. A simulation and optimization study was performed on an industrial natural gas steam reforming system using Aspen Hysys V12 software to optimize this process. The study focused on optimizing various parameters, including the Reformer Reactor, Water Gas Shift Reactor, and purification units such as the Separator and Pressure Swing Adsorption (PSA). The Reformer and Water Gas Shift reactors were set at 900 °C and 300 °C, respectively, to maximize hydrogen production.

2. MATERIALS AND METHODS

The adopted methodology in this study is summarized by the following three steps: i) calculation of a certain market need in hydrogen (MT/year); ii) simulation of a natural gas steam reforming process aiming to produce the required Hydrogen needs; iii) optimization of the adopted process in order to maximize hydrogen yield, to reduce energy consumption and to minimize the production of polluting gases. Simulation software was adopted to perform a steady-state study involving all the thermodynamic parameters and the simulator was the commonly used Aspen HYSYS. Finally, results were obtained from software and the calculation of hydrogen production. Hydrogen produced is mostly used by ammonia, petroleum refineries, and fertilizer-producing companies. A total of 99% of hydrogen comes from fossil fuel reforming, as it is the most conventional and cost-effective method, but it is not beneficial for the environment due to CO_2 emission. Hydrogen production goes through an unprecedented revolution under the net-zero emissions scenario. When the global output reaches 200 MT H_2 in 2030, low-carbon technologies will account for 70% of that production (electrolysis) (Ramachandran & Menon, 1998). By 2050, the amount of hydrogen produced will have increased to about 500 MT H_2, almost entirely due to low-carbon technologies. Different technologies will be needed to alter the energy system to achieve net-zero emissions by 2050. Energy efficiency, behavioral modification, electrification, renewable energy, hydrogen, and hydrogen-based fuels, and carbon capture utilization storage (CCUS) are likely to be the major pillars for decarbonizing the world's energy system. In the net zero emissions scenario, strong hydrogen demand growth and the adoption of cleaner technologies for its production will allow hydrogen and hydrogen-based fuels to prevent up to 60 gigatonnes (GT) of CO_2 emissions in 2021–2050 or 6.5% of all cumulative emissions reductions. Utilizing hydrogen fuel is especially important for cutting emissions in hard-to-decarbonize industries including heavy industries (especially steel and chemical) heavy-duty road transport, shipping, and aviation where direct electrification is challenging. Hydrogen Generation Market by Technology (SMR, POX, Coal Gasification, Electrolysis), Application (Refinery, Ammonia Production, Methanol Production, Transportation, Power Generation), Source (Blue, Green, Gray). The global hydrogen generation market is projected to reach USD 263.5 billion by 2027, at a compound annual growth rate (CAGR) of 10.5% between 2022 to 2027 ("Global Hydrogen Review"., 2021). The growing demand for hydrogen for fuel cell electric vehicles (FECV) and rockets in the aerospace industry is driving market growth. Utilization of hydrogen fuel cells in lightweight vehicles such as bicycles, cars, buses, trains, material handling equipment, boats, ships, commercial aircraft, auxiliary power units (APUs) of aircraft, marine vessels, and specialty vehicles such as forklifts are fostering the market growth in the transportation sector. In this regard, ammonia could be synthesized from a mixture of hydrogen and nitrogen gas via the process (Rn1), and methanol could be prepared from a syngas mixture which is the product of methane steam reforming process (CO & H_2 mixture or CO_2 & H_2 mixture). However, a one-pass methanol yield of nearly 55% can be obtained for pure CO, while pure CO_2 would only yield 18% of CH_3OH. This illustrates the possibility of a more effective methanol production via the hydrogenation of carbon monoxide (Rn2).

$$3H_2 + N_2 \leftrightarrow 2NH_3 \quad \text{(Rxn 1)}$$

$$2H_2 + CO \leftrightarrow CH_3OH \quad \text{(Rxn 2)}$$

In this respect, the mentioned quantities were calculated via stoichiometry co-efficient of (Rxn1&Rxn2) taking into account the imported amounts of methanol and ammonia fertilizers of the year 2019 (Leonzio G., 2018).

2.1. Natural gas feedstock requirement

Industrial steam reforming is a well-established process that reacts natural gas and steam in order to produce high-purity hydrogen, according to the following chemical reaction (Rxn3).

$$C_nH_m + n\ H_2O \leftrightarrow nCO + (0.5\ m + n)\ H_2 \quad \text{(Rxn 3)}$$

The heavier is the natural gas the lower is the H_2/CO ratio (Speight JG., 2011). In this sense, high ratios are favored by reacting almost pure methane pre-extracted via a cryogenic separation process natural gas with high methane content where CH_4 undergoes following steam reforming reaction (Rn4, Rn5) (Cherbanski R, & Molga E., 2018). where (Rn4) is the major steam reforming reaction instead of (R5).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2\ (\Delta H^\circ = 206\ \text{kJ/mol}\ CH_4) \quad \text{(Rxn 4)}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2\ (\Delta H^\circ = 165\ \text{kJ/mol}\ CH_4) \quad \text{(Rxn 5)}$$

Where ΔH^0 represents the standard enthalpy of the reaction. Because natural gas is expected to have a similar composition to raw gas with a high methane fraction of 99% as seen in Table 1, a natural gas stream could be directly fed into the process plant to undergo the principal reforming reactions (Rxn4), (Rxn6-Rxn12) and the water gas shift reaction (Rxn13). The purpose of this measure was to avoid the pre-purification step of the main stream hence, to save on the capital & operation costs. Moreover, the steam reforming reactions of all the natural gas components (Rxn6-Rxn12), were taken into consideration in the stoichiometric approach in order to maximize the calculation accuracy (Olateju et al., 2017). The average natural gas components in the hydrogen production unit plant layout are provided in Table 1.

$$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2 \quad \text{(Rxn 6)}$$

$$C_3H_8 + 3H_2O \leftrightarrow 3CO + 7H_2 \quad \text{(Rxn 7)}$$

$$i\text{-}C_4H_{10} + 4H_2 \leftrightarrow 4CO + 9H_2 \quad \text{(Rxn 8)}$$

$$n\text{-}C_4H_{10} + 4H_2O \leftrightarrow 4CO + 9H_2 \quad \text{(Rxn 9)}$$

$$i\text{-}C_5H_{12} + 5H_2O \leftrightarrow 5CO + 11H_2 \quad \text{(Rxn 10)}$$

Table 1: Natural gas composition.

Component	**Mole fraction (Xi)**
Methane	0.989
Ethane	0.003365
Propane	0.001631
i-butane	0.000421
n-butane	0.000421
i-pentane	0.000245
n-pentane	0.000096
C6+	0.001471
N_2	0.002146
CO_2	0.001192

$$n\text{-}C_5H_{12} + 5H_2O \leftrightarrow 5CO + 11H_2 \quad \text{(Rxn 11)}$$

$$C_6H_{14} + 6H_2O \leftrightarrow 6CO + 13H_2 \quad \text{(Rxn 12)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298}{}^0 = -41.1\ \text{kJ/mol} \quad \text{(Rxn 13)}$$

In this perspective, the stoichiometric natural gas quantity required to produce 3,524,275 MT/year and found to be 402.2 Kg/h. Based on pre-determined input stream parameters and the reformer and shift reactor operating conditions, the HYSYS simulator calculated the outlet compositions of the production zone and the purification zone units. In order to check the HYSYS accuracy in the production zone. Almost similar hydrogen molar flow rate was calculated by utilizing the Aspen HYSYS software 402.2 Kg/h respectively.

2.2. Optimization Of Steam Methane Reforming Process Aspen Hysys Simulation

The simulation and optimization study of hydrogen production through steam methane reforming, using Aspen HYSYS V12 software, has been conducted. Steam methane reforming is considered a cost-effective method for producing the majority of the world's hydrogen (H_2), considering product yield and energy consumption. In this study, the simulation and optimization of an industrial steam methane reforming process, using Aspen HYSYS V12 software, was performed. All parameters, including units in the hydrogen production area (reformer, water gas shift reactor), and purification area (separator and pressure swing adsorption), were simulated and optimized to execute a comprehensive process. Moreover, the study incorporated a detailed analysis of the economic viability of this method in comparison to other hydrogen production methods. The software's flexibility allowed for the simulation of multiple scenarios with varying parameters, therefore providing a more comprehensive understanding of the impact of different operational conditions on the process. Additionally, the study considered the environmental impact of the process, analyzing the carbon footprint and identifying possible opportunities for reducing emissions. All in all, this study provides a thorough evaluation of the steam methane reforming process for hydrogen production using Aspen HYSYS V12 software, with a focus on optimizing yield, energy consumption, and environmental impact. Typical industrial natural steam reforming processes are well known for involving a reaction zone to produce hydrogen gas (steam reformer with successive shift reactors) followed by a purification zone to get rid of carbon oxides CO_2 and CO. In this study, the simulation and optimization of an industrial steam methane reforming process, using Aspen HYSYS V12 software, was performed. All parameters, including units in the hydrogen production area (reformer, water gas shift reactor), and purification area (separator and pressure swing adsorption), were simulated and optimized to execute a comprehensive process. Moreover, the study incorporated a detailed analysis of the economic viability of this method in comparison to other hydrogen production methods. The software's flexibility allowed for the simulation of multiple scenarios with varying parameters, therefore providing a more comprehensive understanding of the impact of different operational conditions on the process. Additionally, the study considered the environmental impact of the process, analyzing the carbon footprint and identifying possible opportunities for reducing emissions. All in all, this study provides a thorough evaluation of the steam methane reforming process for hydrogen production using Aspen HYSYS V12 software, with a focus on optimizing yield, energy consumption, and environmental impact. Typical industrial natural steam reforming processes are well known for involving a reaction zone to produce hydrogen gas (steam reformer with successive shift reactors) followed by a purification zone to get rid of CO_2 and CO. Hence, a conceptual process was performed on Aspen HYSYS V12 as shown in Figure 1, simulating a steady-state model where the hydrogen production, the $CO_{2,}$ and CO removal were optimized in function of each unit operating parameters. Natural gas and steam were mixed and heated before being fed to a Gibbs reforming reactor. Conventional steam reforming reactors use Ni-based catalysts between 10 and 20 wt% on a-Al_2O_3, calcium, or magnesium aluminate with a typical lifetime of 3-5 years due to the low cost of nickel, its wide availability, and sufficient catalytic activity (Olateju, et al., 2017). Then, the head headstreams reformer is cooled down in cooler E-101 and fed to a water gas shift (WGS) Gibbs reactor generally operating with a copper-based catalyst (Vozniuk et al., 2019). The simulation process was performed after determining the operating conditions. Figure 1, illustrates the process model for hydrogen production. The simulation was conducted using the specified feed conditions, aiming to obtain highly efficient hydrogen production. The average natural gas components in the hydrogen production unit plant layout are provided in Table 1. Detailed reference supporting information is given for the description of the factory layout scheme. Natural gas feed is assumed to be approximately 100% methane.

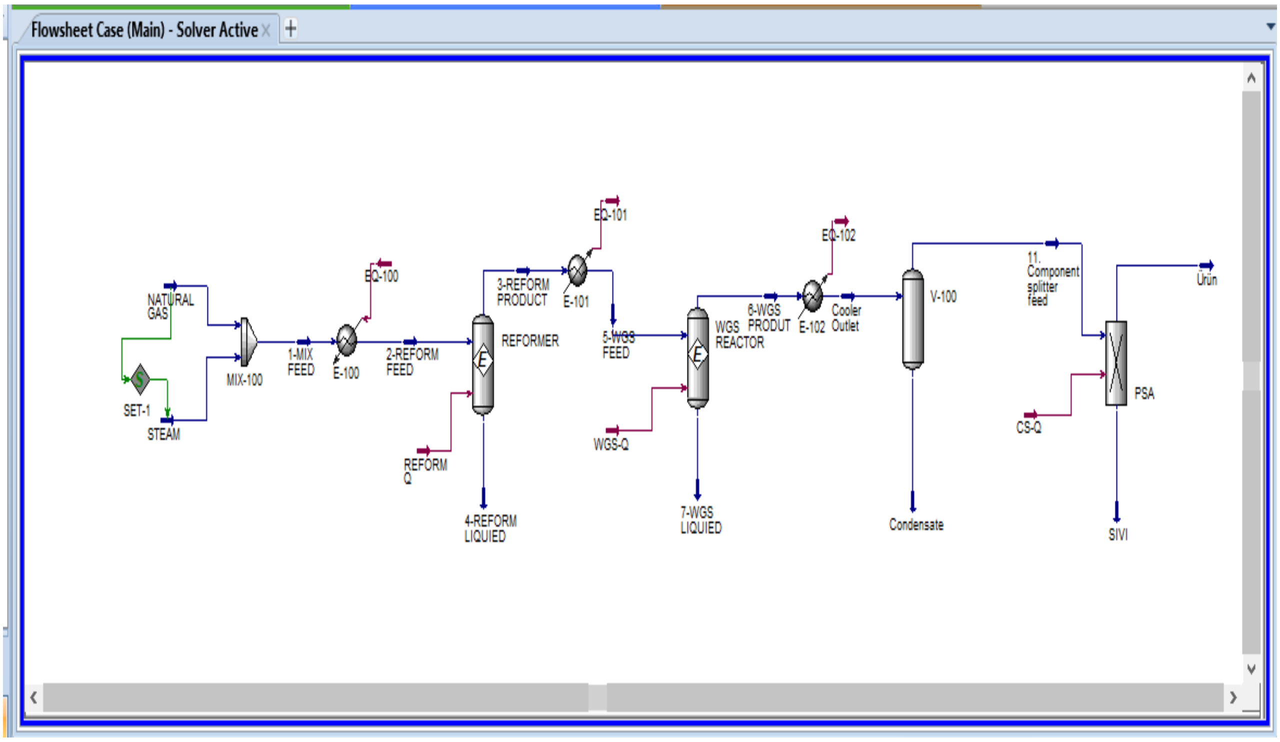

Figure 1: Steam methane reforming process Aspen HYSYS V12 simulation.

2.3. Choice of fluid packages and reactors

In order to optimize the process simulation in the reformer and water gas shift reactors, a Peng Robinson fluid package was selected (gas law shown in supporting information). This package could accurately predict the thermodynamic data (pressure & temperature) of light gases (CH_4, C_2H_6, C_3H_8, C_nH_m, CO_2, CO, H_2). In addition, the product yield and the consumption of the reactants were simulated by having Aspen HYSYS calculate the reaction equilibrium constant (Eq. 1) from the change in the Gibbs free energy at a specified temperature by taking into consideration the non-ideal behavior of the relatively light gases predicted by the thermo-package of Peng Robinson.

$$\ln K_{eq} = \frac{-\Delta G\, reaction}{RT} \qquad \text{(Eq. 1)}$$

Where **K_{eq}** **ΔG** reaction, **R**, and **T** are the reaction equilibrium constant, variation in Gibbs free energy, the universal gas constant, and the temperature respectively. In this context, a Gibbs reactor was chosen to model the following production units: Reformer and WGS.

2.4. Thermodynamic parameters optimization

After choosing the fluid packages and the convenient reactors for the steady state model, pressures (P), temperatures (T), and steam-to-carbon ratio (S/C) were optimized in the production zone (Reformer, WGS) in order to maximize the H_2 production. Moreover, the pressure, temperature, and purification zone in order to reach the highest CO_2 removal and CO conversion. In addition, the heat duty required to operate at optimum conditions was computed by the Aspen HYSYS simulator. The results are thus discussed in the following section. The optimization of reformer and water-gas shift (WGS) reactor temperatures is a crucial step for maximizing hydrogen production and optimizing energy consumption. In general, achieving high conversion and hydrogen yield is attainable at temperatures exceeding 700 °C. and literature suggests that reformer reactor temperatures should ideally range between 700 °C and 1000 °C. Furthermore, it is worth mentioning that temperatures exceeding 950 °C can result in coke formation on the catalyst. Therefore, the selection of 900 °C as the operating temperature is a deliberate choice to prevent coke formation and ensure a high hydrogen yield. It is important to note that the water gas shift reaction is slightly exothermic, while steam-reforming reactions are significantly endothermic, making it challenging to favor both reactions in a single reactor. Elevated reformer temperatures enhance hydrocarbon conversion rates, thus increasing hydrogen yield; however, excessively high temperatures can lead to catalyst deactivation and heightened energy costs. In contrast to the reformer, the WGS reactor operates at lower temperatures, which are conducive to carbon monoxide conversion into hydrogen. These distinct temperature conditions collectively impact overall hydrogen production, striking a balance between yield and energy efficiency within the process. Given that wgs reactors are exothermic, they are typically operated at lower temperatures, typically falling between 200 °c and 400 °c to optimize the conversion process (Dejong et al., 2009).

3. RESULTS AND DISCUSSION

3.1. Reformer

After defining the adequate fluid package and the reactor type, a balance between the effect of the operating parameters of each reactor, such as P, T, and S/C was tuned. This step is critical to overcoming the imposed thermodynamic limitation on the natural gas (NG) conversion due to the steam reforming and WGS reaction’s reversibility. For this purpose, reformer temperature and pressure were first adjusted at a stoichiometric S/C = 2.5. The reason behind adjusting the reformer pressure first relies on its designated purpose to favor the main steam reforming reactions (Rxn 4, Rxn6-Rxn12) that are strongly affected by the pressure variation, at the expense of the WGS reaction (Rxn13) that is pressure independent according to Peng-Robinson principle. Because, the water gas shift reaction is slightly exothermic, while the steam-reforming reactions are heavily endothermic, both reactions could not be favored in the same reactor. Hence, the H_2 molar flow rate was plotted at the reformer outlet in the function of the industrial scale pressure and temperature range of 1-20 atm and 700-1000 °C respectively, while S/C was fixed at its stoichiometric level of 2.5. As a result, it can be seen in Figure 2, that the thermodynamic response of the system of existing reactions turned out to be in conformity with the Peng-Robinson of the system of existing reactions turned out to be in conformity with the Peng-Robinson principle.

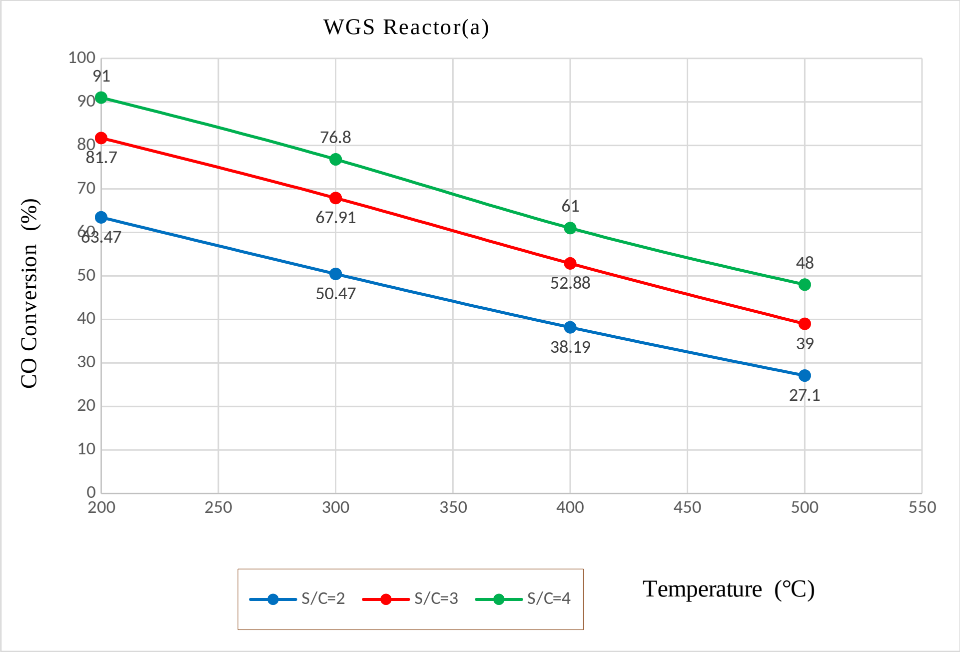

Figure 2: Hydrogen molar flow rate versus temperature and pressure variation at the stoichiometric S/C=2.5

A decrease in the operating pressure down to 1 atm was found sufficient enough to push the steam reforming reactions to a maximum H_2 molar flow rate of ~3807 kmol/h while still operating at a relatively moderate T= 900 °C. However, by increasing the pressure to 20 atm, a maximum molar flow rate of ~2700 kmol/h was only reached by raising the temperature to 900 °C. Such a notable difference in operating temperatures could be found in the thermodynamic behavior of the endothermic steam reforming reactions. Thus, very low pressure was sufficient to drastically move the reaction (Rxn 4, Rxn6-12) equilibrium to the right, translated into a high H_2 molar flow rate, yet, any increase in pressure from that level (shifting the equilibrium to the left) required higher operating temperature to restore back the equilibrium to a previous state. As a result, a low operating pressure of 1 atm and a relatively high temperature of 900 °C, would provide a maximum natural gas conversion and would save on the heater's and the compressor's duties (Vozniuk et al., 2019). Moreover, it is preferable to avoid harsh temperatures >950 °C because they could increase coke deposition on the Ni-based catalyst according to the side reaction (Rn14).

$$CH_4 \leftrightarrow C + 2H_2 \qquad \Delta H_{298}^{0} = +74.58\ \text{kJ/mol} \qquad \text{(Rxn14)}$$

However, in industrial natural gas steam reforming plants, such low pressure creates some limitations on the adsorption of the natural gas (NG) on the catalyst's surface, thus preventing the catalytic mechanism, lowering its efficiency, and creating low conversion kinetics (Mokheimer E, et al., 2015). For this specific reason, a pressure trade-off between high H_2 yield and enabling adsorption on the catalyst surface was made and a pressure of 5.2 atm was chosen for this case study. In addition, a temperature trade-off between high hydrogen yield and coke build-up was made and an operating temperature of 900 °C was also chosen. Another important parameter to be adjusted was the reformer inlet temperature. Hence, the non-uniform temperature distribution could result in carbon deposition at this reactor inlet where methane concentration is at the highest level. This carbon deposition contributes to the catalyst fouling and deactivation. However, experience has shown that a normal inlet temperature from 500 to 650 °C keeps coke formation at its lower level. For this reason, an inlet temperature of 550 °C was chosen. Consequently, the initial natural gas stream could be fed to the heater at any pressure >5 atm (in this case, P = 5.2 atm was chosen) to assure its natural circulation in the process and then mixed with the steam (also fed with P > 5 atm). This measure aimed to deliver a new stream of a temperature of 550 °C to the reformer inlet.

3.2. Water Gas Shift Reactors

Once the reformer pressure and temperature were adjusted, the WGS reactors' temperatures were tuned to favor the best conditions for the WGS reaction (Rxn 13) to take place. The operating pressure was preserved at 5 atm to limit the methanation reaction (Rxn15) (here hydrogen consumption) at this process stage.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H^{o}_{298} = -206\ \text{kJ/mol} \qquad \text{(Rxn15)}$$

As for the operating temperature, high CO conversion is favored at low temperatures (according to Peng Robinson's Principle), while higher temperatures kinetically increase the reaction rate. Therefore, in industrial plants, water gas shifting is performed in a reactor at temperature regimes, (between 200 and 330 °C). In this scope, a minimum temperature of 300 °C was chosen for the WGS reactor in order to reach a maximum CO conversion especially since lower temperatures than 300 °C would favor the undesired reaction (Rxn15). For the operating temperature, the approach was to accelerate the reaction and to reach a high CO conversion (remaining CO on a dry basis) within the industrial range of 3-5%. For this reason, the CO conversion was plotted in Figure 3 as a function of the operating temperature at different S/C ratios. According to Peng Robinson's Principle, it was observed that increasing the S/C from 2 to 4 consistently reduced the CO conversion as seen in Fig. 3a while rising the temperature from 200 to 500 °C had an opposite effect on it. In order to operate within the industrial range at a relatively convenient temperature condition, an S/C=4, and a temperature of 500 °C were chosen. Consequently, optimizing the WGS temperatures resulted in an overall CO conversion of ~99.86% measured at the end of the WGS zone as seen in Figure 3b. Thus the measured CO content on a dry basis at the WGS outlet was reduced to a relatively lower percentage (of ~0.14%) than the minimum required (0.3- 1%), resulting in an enhanced conversion of CO into H_2. In a hydrogen production process, the number of WGS (Water-Gas Shift) reactors required depends on the desired hydrogen-to-carbon monoxide (H_2/CO) ratio and the level of conversion needed. In this study, a single reactor was found to achieve the required conversion and ratio effectively, as indicated by Figure 4, where the co-conversion is 96.52%, CH_4-conversion is 96.52%, and H_2 yield is 70.2%. The highest conversion, particularly in the temperature range of 200 °C to 300 °C, is evident from Figures 3a and 3b. Consequently, a second WGS reactor was not deemed necessary in our simulation. The primary function of the WGS reactor is to adjust the ratio of hydrogen to carbon monoxide in the reformat gas by reacting carbon monoxide with water vapor. This adjustment is critical because downstream processes or applications often require a specific H_2/CO ratio. Following the WGS reaction, the gas mixture typically undergoes separation processes in a separation column to eliminate unwanted water through pressure swing adsorption (PSA). Subsequently, the gas is directed to PSA units to remove undesired CO and CO_2.

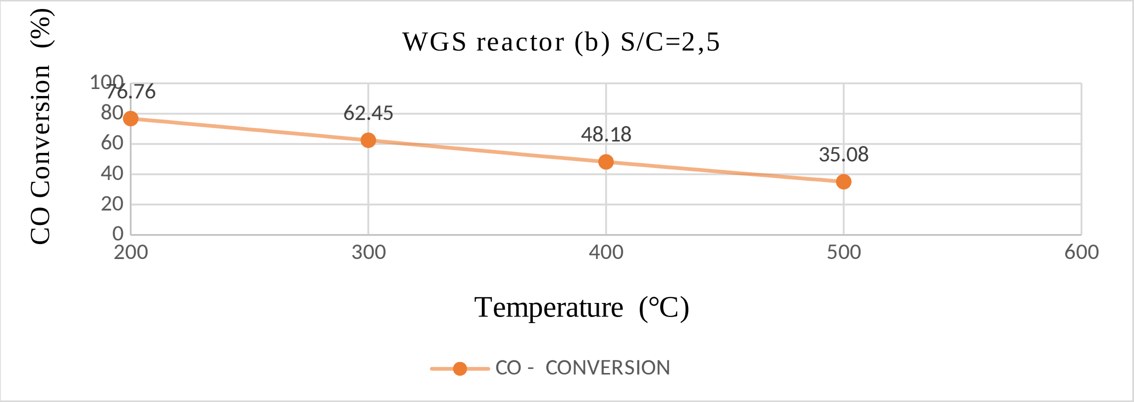

Figure 3: (a) CO conversion variation in the WGS reactor versus its operating temperature and S/C ratio

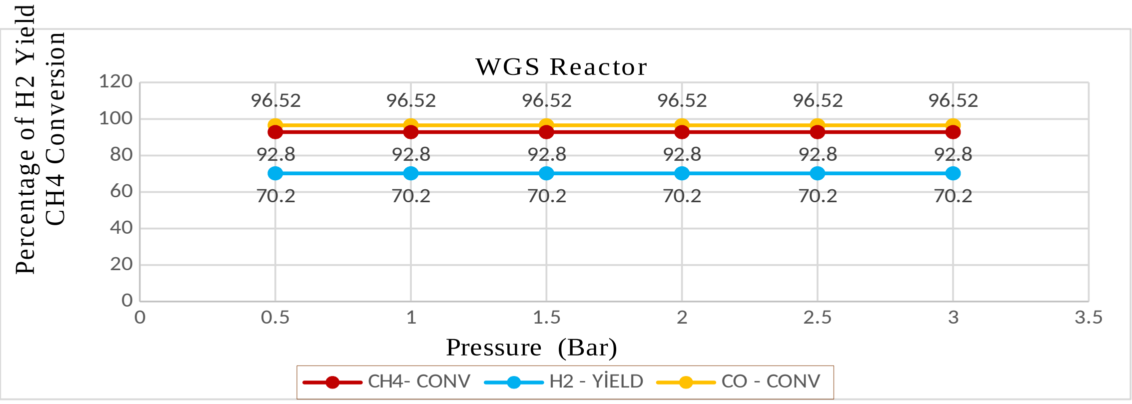

Figure 3 (b) Variation of the CO conversion at the WGS outlet in the function of the WGS temperature at S/C=2.5.

3.3. Effect Of Pressure on WGS Reaction Conversion and H_2 Yield

Pressure has a zero effect on the conversion in the WGS equilibrium reactor. This means that an increase or decrease in the pressure on the reactor has no effect on the conversion and ultimately on the yield of H_2 in the product stream. From the equation of (Rxn2), the number of moles on both sides of the equation is balanced. As a result, there is no net shift in the equilibrium of the system due to an increase or decrease in pressure shown in Figure 4.

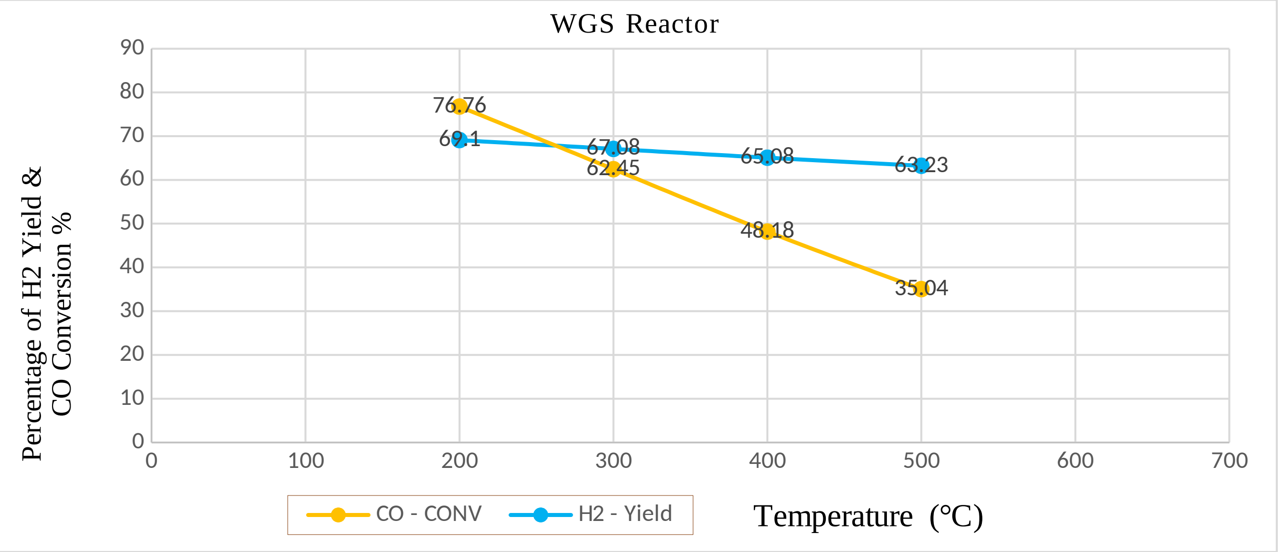

Figure 4: Effect of pressure on WGS reaction conversion and H_2 yield.

3.4. Effect Of Temperature on WGS Reaction Conversion and H_2 Yield

The water gas shift (WGS) reaction in the converter reactor is exothermic, and therefore, lower temperatures are preferred. As shown in Figure 5, at a temperature of 500 °C, the H_2 efficiency is 63.23%, at 400 °C it is 65.05%, and at 300 °C it is 67.08% for obtaining H_2 product. This indicates that the highest H_2 efficiency can be achieved at temperatures of 300 °C and below in the water gas shift reactor. In this simulation modeling, an H_2 efficiency of 67.08% was observed at a temperature of 300 °C in the converter reactor. The CO conversion and H_2 efficiency were not highly sensitive to temperature changes. However, with an increase in temperature, due to the adiabatic and exothermic nature of the water gas shift reactor (WGS), a significant decrease in H_2 efficiency and a rapid decrease in CO conversion were observed. As the temperature increased from 300 °C to 500 °C, the CO conversion decreased rapidly from 62.45% to 35.04%, while the H_2 efficiency decreased from 67.08% to 63.23%. This indicates the preference for operating an exothermic reactor at high temperatures.

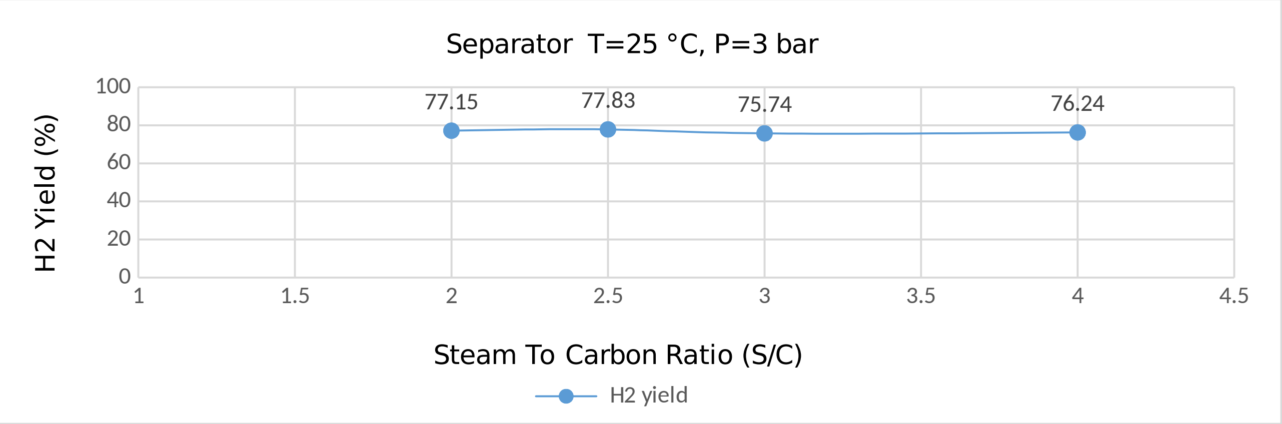

Figure 5: Effect of temperature on WGS reaction conversion and H_2 yield.

3.5. Separator and Pressure Swing Adsorption (PSA)

To achieve an almost pure hydrogen stream and minimize CO_2 and CO gas concentrations, our approach involved the simultaneous operation of two units. The parameters of these units, guided by the Peng Robinson fluid package's principles, were optimized. Initially, the separator was employed to eliminate excess H_2O, followed by the PSA unit, which effectively removed waste gases containing

CO, CO_2, minimal H_2O, and CH_4, resulting in the production of 100% pure H_2.

3.6. Separator

The first step that needs to be performed before sending the product from the WGS reactor to the PSA unit is the removal of unwanted water in the PSA unit. Accordingly, the product from the converter reactor is cooled down to atmospheric temperature in a cooler before being sent to the separator, where the water is completely separated and removed. The separator operates at 25 °C and 3 atm, and the results are presented in Table 2 and Figure 6.

Table 2: Separation of components in the Separator and removal of unwanted water.

Components	Separator feed	Condensate	PSA
CO	0.0527	0.0	0.0612
CO_2	0.1281	0.0002	0.1468
H_2O	0.1468	0.9998	0.0102
CH_4	0.0015	0.0	0.0017
H_2	0.6708	0.0	0.7783
	1	1	1

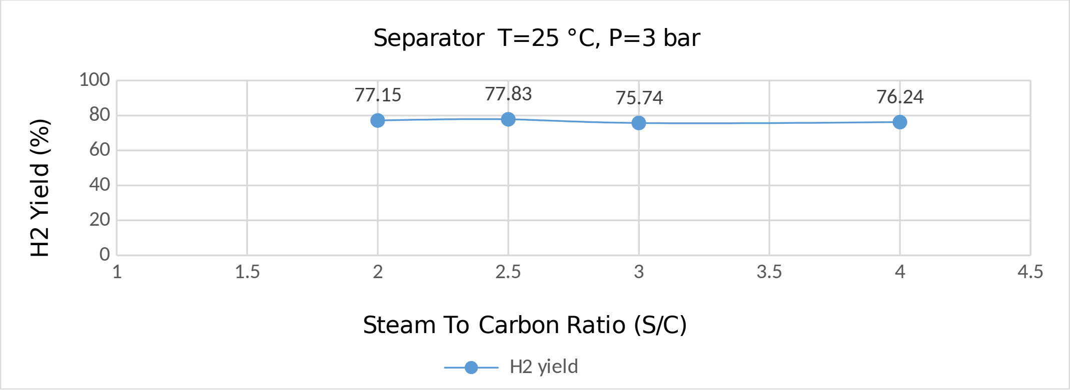

Figure 6: Product output in terms of the percentage of H_2 content after removing unwanted water in the separator for different steam-to-carbon ratios (S/C).

3.7. Pressure Swing Adsorption (PSA) Unit

Pressure Swing Adsorption (PSA) technology uses Carbon Molecular Sieve (CMS) columns to separate compressed air. The vessels operating on the principle of PSA are filled with CMS granules, which are a special adsorption material. In this case, a Component Splitter Reactor is used instead of PSA columns (simulated as continuous active operation in Aspen HYSYS V12 software) in various applications such as fuel cells, refineries involving hydrogenation (hydrocarbon cracking, petroleum gases, gasoline, jet fuel, gas oil, diesel, fuel oil, asphalt, etc.), petrochemicals (hydrocracking, steam reforming (pyrolysis), isomerization, hydrogenation, etc.). The main objective of this study, particularly, is to obtain 100% pure hydrogen for use in fuel cells. The results, as provided in Table 2 show the processed gas that has been converted and separated from water entering the PSA unit. The outcome of the process is illustrated in Figure 7. In this unit, as shown in Figure 8, non-hydrogen gases (H_2O, CO, CO_2, and CH_4) present in the process gas are separated to purify hydrogen. Output data from the PSA unit obtained through the simulation is shown in Table 2. The PSA unit operates at 25°C, 3 bar, and in an adiabatic condition.

Table 2: Output data from the PSA unit obtained through Aspen HYSYS v12 simulation.

Components	**Feed (PSA)**	**PSA (tail gases**	**PSA (product)**
CO	0.0612	0.1894	0.0
CO_2	0.1468	0.4603	0.0
H_2O	0.0102	0.0317	0.0
CH_4	0.0017	0.0052	0.0
H_2	0.7783	0.3133	1.0
Total	1	1	1

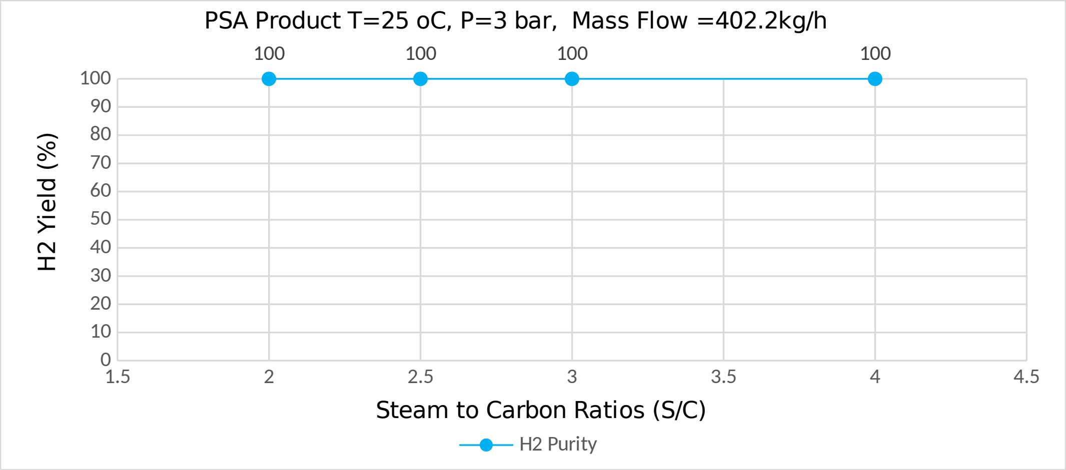

Figure 7: PSA unit product output and purity of the product (100% pure H_2) for different steam-to-carbon ratios (S/C).

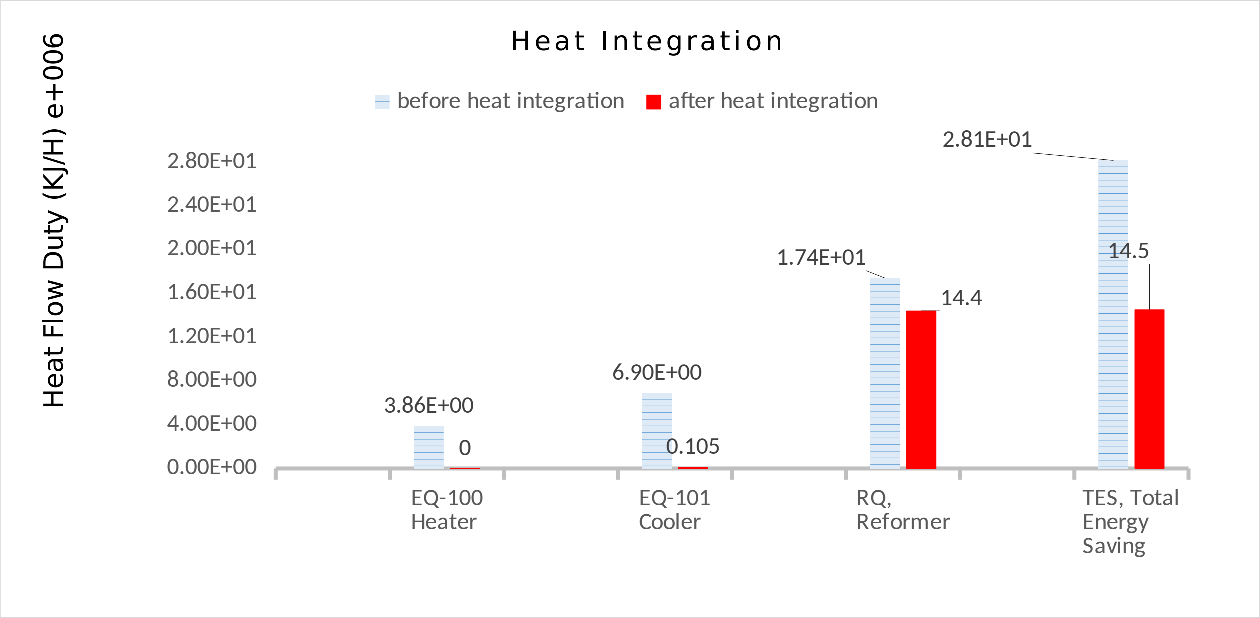

Figure 8: Tail gas output from the PSA unit for different steam-to-carbon ratios (S/C) (tail gas content).

3.8. Process Heat Duty And Cooling Cost Optimization

The reactors and miscellaneous heat duty were calculated through HYSYS by fixing as input parameters the working temperatures in the reactors and the output stream temperatures of the coolers and the heater. The obtained results are shown in Table 3.

Cooling and heating capacity play a significant role in the operational cost of this system. Therefore, it would be beneficial to save on these high-cost expenses by optimizing heat consumption or reducing cooling capacity.

3.9. Heat Integration

In this context, an improved process was developed in Aspen HYSYS v12 as shown in Figure 9, and certain heat exchangers were placed at key points. As a result, the waste heat exiting the reformer in heat exchanger 1 was recovered by replacing the heater with an exchanger (UA = 3.855e+06 kJ/h). The feed going to the reformer was heated by exchanging heat in heat exchanger 1, resulting in significant energy savings. At the outlet of heat exchanger 1 (E-100), the feed was cooled down to 310°C in heat exchanger 2 (UA = 3.147e+05 kJ/h) and then sent to the E-101 cooler. In the E-101 cooler, the feed for the WGS reactor was further cooled down to 300°C. The results of this optimization are shown in Figure 9, Table 4, Table 5, and Figure 10.

Table 3: Hysys simulation heat duties for reactors, cooler, and heaters.

Unit	Energy stream	Duty (kJ/h)
Heater	EQ-100	3.855e + 006
Reformer	Reformer Q	1.738e +007
Cooler	EQ-101	6.895e +006
WGS	WGS -Q	0.0 (adiabatic)
Cooler	EQ-102	6.336e + 006
PSA	CS- Q	0.0

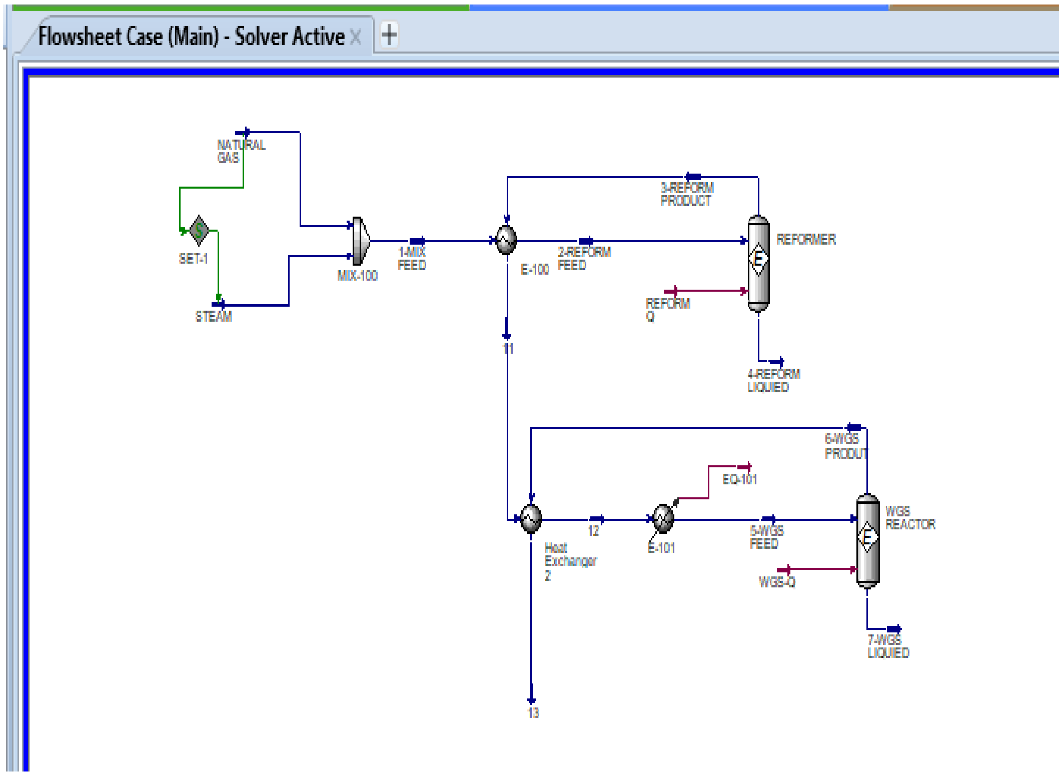

Figure 9: Steam methane reforming process Aspen HYSYS V12 simulation after heat integration.

Table 4: Heat flows for the cooler, heater, and reactors in Aspen HYSYS simulation (before heat integration).

Units	Energy stream	Heat Duty (kJ/h)
Heart	EQ-100	3.855e+006
Reformer	R- Q	1.738e+007
Cooler	EQ-101	6.895e+006
WGS	WGS-Q	0.0

Table 5: Heat flows for the cooler, heater, and reactors in Aspen HYSYS simulation (after heat integration).

Units	Energy stream	Heat Duty (kJ/h)
Heater	EQ-100	0.0
Reformer	R-Q	1.414e+007
Cooler	EQ-101	0.105e+006
WGS	WGS-Q	0.0

The important parameters; temperature, pressure, and hydrogen production yield in this study was compared with a similar study and was shown in Table 6:

Table 6: Comparison of similar works and this study.

Parameter	**Our study**	**Similar Study**
Temperature (°C)	Reformer: 900°C WGS Reactor: 300°C	Reformer: 800°C WGS Reactor: 200°C
Pressure	Pressure (atm):5	Pressure (atm):3
Hydrogen Production Yield Waste gas	77.83% 100% pure H_2 22.17% H_2 CH_4 CO CO_2 H_2O	product and waste parts are not specified H_2: 98.719% CH_4:0.185% CO:0.212% H_2O:0.884%
Using area	fuel cells, petroleum refining, natural gas refineries, and petrochemical processes.	PEMFC
Reference		(Ihoeghian et al., n.d.)

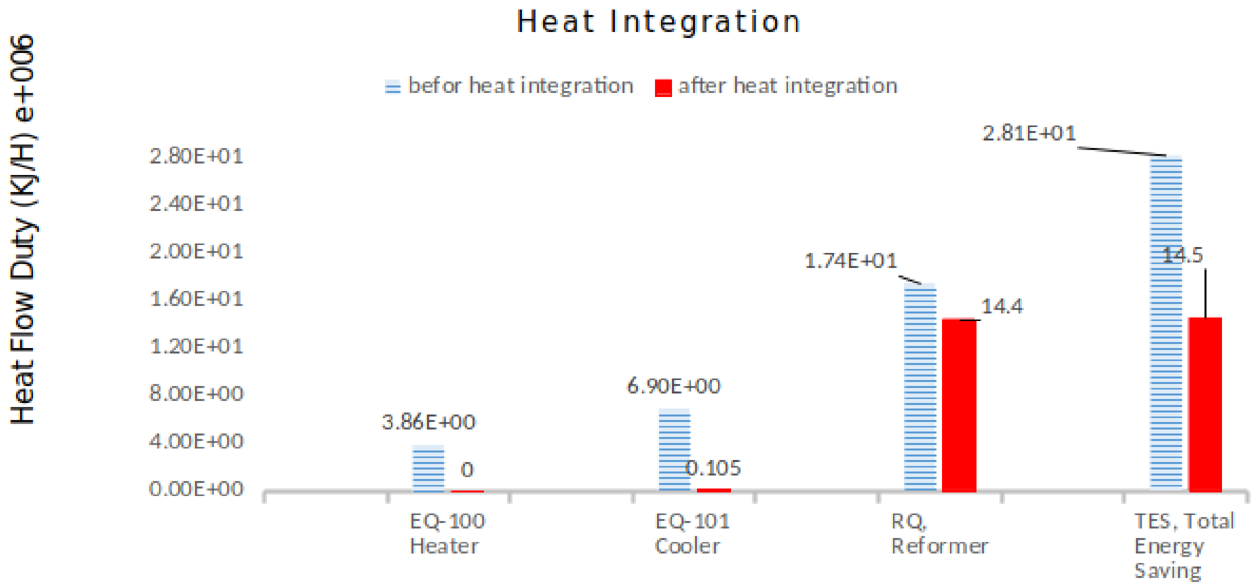

Figure 10: Aspen HYSYS simulation of the heat integration before and after the integration of the heater and cooler heat exchangers (achieving 51.6% energy savings after integration). Total Energy Savings (TES).

4. CONCLUSION

A simulation and optimization study of an industrial natural gas steam reforming process was conducted to meet the high-purity H_2 production requirements for various applications such as fuel cells, petrochemicals, refineries, and many other industrial applications. All parameters were optimized to successfully operate the complete process, including hydrogen production units (reformer, water gas shift reactor) and purification units (separator and PSA). An optimization study was performed to control the steam reforming conversion process, aiming to control the final hydrogen yield and purity. The hydrogen molar flow rate was calculated using Aspen HYSYS V12 software. Furthermore, at the end of the process, the product efficiency was 77.83%, and 402.2 kg/h of 100% pure hydrogen was obtained, equivalent to 3,523.272 MT/year. Some of the hydrogen quantities from the production area and at the end of the process were mixed with other gases in the waste gas outlet of the PSA unit. It is beneficial to recover and separate hydrogen from waste gases, as it has high energy and economic value. As a result of the careful optimization of process parameters, a significant amount of 402.2 kg/h of 100% pure hydrogen was achieved, and there was a 51.6% energy savings in the heating and cooling units of the process. In conclusion, this study successfully conducted a simulation of a natural gas reforming system design capable of economically producing high-purity hydrogen for use in fuel cells. The produced hydrogen can also be utilized in various industrial applications. Similar studies present a simulation and optimization study of an industrial natural gas steam reforming process for hydrogen production to meet the refinery and petrochemical demands in Lebanon, using Aspen HYSYS software (Madon et al., 2015). All parameters were optimized to successfully operate the complete process, including hydrogen production units (reformer reactor, high-temperature shift reactor HTS, and low-temperature shift reactor LTS) and purification units (absorber and methanation) (Riachi, 2021). Optimum hydrogen production (87.404 MT/year) was achieved and fixed. The temperatures in the reformer and shift reactors (HTS & LTS) were maintained at 900 °C, 500 °C, and 7 atm pressure, with a steam-to-carbon ratio (S/C) of 4. Furthermore, approximately 99% of the unwanted CO_2 and CO gases were removed in the purification process, resulting in a hydrogen purity of 98%. When used as a combustion fuel, hydrogen reduces greenhouse gas emissions. This study encompasses the steady-state simulation and optimization of steam methane reforming for hydrogen production from natural gas (methane) using Aspen HYSYS v8.6. With a steam/methane flow ratio of 2.5, the reformer temperature and pressure were set at 800 °C and 3 bar, respectively. The water gas shift reactor temperature was 200 °C, and the hydrogen purity achieved was 97% (Ding & Alpay, 2000). To conclude the cost-effectiveness and energy efficiency of the Steam Methane Reforming (SMR) process by natural gas compared to alternative hydrogen production methods, such as electrolysis or solar-based approaches, can vary depending on several factors. However, according to the International Energy Agency (IEA), the levelized cost of hydrogen production by energy source and technology in 2019 and 2050. The efficiency of SMR without carbon capture and storage (CCS) is estimated to be 76% in 2019 and 2050. The levelized cost of hydrogen production using SMR without CCS is projected to be USD 910/kW H_2 in 2019 and 2050. The efficiency of electrolysis using low-carbon electricity is estimated to be 64% in

2019 and 74% in 2050. The levelized cost of hydrogen production using electrolysis is projected to be USD 872/kW in 2019 and USD 269/kW in 2050 (iea.org, nrel.com). Solar-based approaches hydrogen production methods, such as solar water splitting or photoelectrochemical (PEC) cells, are highly dependent on location and available sunlight. Initial capital costs can be high, but operational costs can be low if abundant sunlight is available. These approaches can be energy-efficient when ample solar energy is harnessed. Efficiency can vary depending on the specific technology and system design. It’s important to note that these figures are global averages and can vary depending on regional factors, technological advancements, and economies of scale. Additionally, the cost-effectiveness and energy efficiency of different hydrogen production methods can be influenced by factors such as the availability and cost of natural gas, renewable energy sources, carbon capture technologies, and government policies.

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