

# DESIGN AND COMPARISON OF PURE HYDROGEN PRODUCTION SYSTEM VIA STEAM METHANE REFORMING COUPLED WITH PSA PROCESS

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**Abstract:** Steam Methane Reforming (SMR) coupled with Pressure Swing Adsorption (PSA) is the most common process to produce pure hydrogen. This paper presents a simulation and energy evaluation of hydrogen production system. In this simulation, the energy released in exothermic adsorption reaction, is recovered to increase the latent and sensible heat of water. Required energy for desorption reaction is provided from recovered heat of SMR process. Since the rate of the saved energy is not significant enough, the temperature of the reformer is being increased. The simulation results are compared to conventional and heat integrated hydrogen production system. Generally, the modified design reduces the total energy consumption in 66.2% compared to conventional process and 14.32% compared to heat integrated process.

**Keywords:** Steam Reforming, PSA, Hydrogen Production, Energy consumption.

## 1 Introduction

Hydrogen is a clean and environmental friendly fuel which can be considered as an alternative for future. Although it is newly getting started in the market as a transportation fuel, the industry is working toward clean, economical, and safe hydrogen production. Hydrogen can be supplied from two sources: renewable (biomass and water) and non-renewable (natural gas and heavy hydrocarbons) (Holladay et al. (2009), Kapdan et al. (2006)).

The most common technology to produce hydrogen in large scale is steam reforming, which almost 50% of hydrogen production is via steam methane reforming (SMR) (R. Soltani et al. (2014), Metz et al. (2005)). SMR consists of two stages: reforming and water gas shift (WGS) reactions (Park et al. (2008), Martínez et al. (2014)). Reforming reaction happens in high temperature (700°C to 900°C) in order to produce syngas. While, WGS reaction takes place in two stages to have a higher hydrogen yield. The first WGS stage works at high temperature (350°C–510°C) and the second one works at lower temperature (180°C - 310°C). In addition, it is more economically beneficial to perform SMR process at high pressure (1500 Kpa-3000 Kpa), despite of its negative effects on the rate of methane conversion (Rostrup-Nielsen et al. (2002), Johnsena (2006)). Since there is a need for pure hydrogen in the industry, CO<sub>2</sub> in the syngas needs to be removed completely. The most common technologies used to separate impurities from hydrogen with high purity degree, are membrane and pressure swing adsorption (PSA) (Steven F. Rice, Ding (2002)). In the PSA process used in this study, there are different sorbents available to adsorb carbon dioxide (Fausto Gallucci et al. (2013), Liu et al. (2010)). Calcium oxide (CaO) is the most used CO<sub>2</sub> sorbent available in nature. CaO has broadly attracted the attention due to low cost as well as high capacity of CO<sub>2</sub> adsorption (Barelli et al. (2008), Yancheshmeh (2016)).

Although the SMR coupled with PSA process is the best way to produce hydrogen, it is not an efficient process due to high energy consumption (Boyano et al. (2011)). Various studies were performed on different aspects of SMR process to make it more efficient. For instance, in 2012, Hajjaji et al. performed an analysis on energy consumption in hydrogen production based on SMR process, in which heat exchangers were used to recover the waste heat so as to enhance the thermal efficiency. Wu et al. in 2013 dealt with improvement of heat regeneration using a heat exchanger network for the hybrid process of steam methane and dry reforming.

In 2015, Lin Zhu et al. worked on Calcium based sorption enhanced steam methane reforming (SE-SMR) to reduce the energy penalty for capturing CO<sub>2</sub> from combustion flue gas. They were able to increase exergy efficiency by 14.39%.

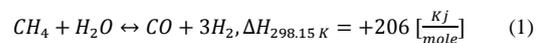
Furthermore, Guoqing Li et al. (2016) proposed a new design of SMR process which recovers heat and pressure energy via a gas turbine at the outlet of the reforming furnace. The energy consumption in this design was reduced by 2.5%.

In this work, both processes are studied to determine the possibility of reducing the energy consumption further. The simulation of this process is done via PRO/II v9.4 simulator. In the simulation, a network of heat exchangers are used to recover the waste heat of both processes. Also, temperature of reformer is being increased to obtain better results in energy recovery and hydrogen production rate. At the end, the energy consumption of the design will be compared to the design of Chunfeng Song et al. (2015).

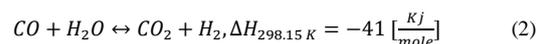
## 2 The governing equation

Hydrogen production system consists of the following reactions:

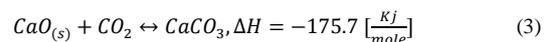
1. Steam Methane Reforming reaction :



2. Water Gas Shift (WGS) reaction:



3. CO<sub>2</sub> adsorption and desorption reaction:



Considering the exothermic reaction 1 and endothermic reaction 2, the above processes require a source of energy supply (Liu et al. (2010)). Reaction rate constants have been proposed by Xu & Froment and are used to determine the kinetics of these two equations. Equations 4 to 6 are the Rate equations for reactions 1 and 2 which are based on LHHW (Langmuir–Hinshelwood–Hougen–Watson Rate Equations) expression.

Rate equation of steam methane reforming reaction:

$$r_1 = \frac{k_1 \left( p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{eq,I}} \right)}{DEN^2} \left[ \frac{K mole}{Kg_{cat}.h} \right] \quad (4)$$

Rate equation of water gas shift reaction:

$$r_2 = \frac{k_{II} \left( p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{eq,II}} \right)}{DEN^2} \left[ \frac{K mole}{Kg_{cat}.h} \right] \quad (5)$$

DEN term is defined as below:

$$DEN = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \quad (6)$$

Where,  $r_i$  are the reaction rates  $i$  ( $i = 1, 2$ ), respectively;  $k_i$  are the reaction rate constants  $i$ , respectively;  $K_i$  are the adsorption constant of chemical species  $i$  ( $i = CH_4, CO, H_2$ ), respectively;  $p_i$  is the partial pressure of the chemical species  $i$  in the shell side (reaction part) ( $i = CH_4, H_2O, H_2, CO, CO_2$ ) (Silva J.D et al. (2016), Sánchez et al. (2012), Baek et al. (2014)).

In rate equations, pressure unit is in bars, energy unit in rate constant equations is in Kj/mole and temperature unit is in Kelvins. Equilibrium, rate, and adsorption constants are all included in equations 7 to 14 (Baek et al. (2014)).

$$k_I = 4.23 \times 10^{15} \times \exp\left(\frac{-240}{RT}\right) \tag{7}$$

$$k_{II} = 2.00 \times 10^6 \times \exp\left(\frac{-67.1}{RT}\right) \tag{8}$$

$$K_{EQ,I} = \exp\left(\frac{-26830}{T+30.114}\right) \tag{9}$$

$$K_{EQ,II} = \exp\left(\frac{4400}{T-4.036}\right) \tag{10}$$

$$K_{CH_4} = 6.65 \times 10^{-4} \times \exp\left(\frac{38.28}{RT}\right) \tag{11}$$

$$K_{H_2O} = 1.77 \times 10^5 \times \exp\left(\frac{-88.68}{RT}\right) \tag{12}$$

$$K_{H_2} = 6.12 \times 10^{-9} \times \exp\left(\frac{82.90}{RT}\right) \tag{13}$$

$$K_{CO} = 8.23 \times 10^{-5} \times \exp\left(\frac{70.65}{RT}\right) \tag{14}$$

**3 Process description**

**3.1 Hydrogen production process**

Generally, hydrogen production includes two major processes: steam methane reforming (SMR) and pressure swing adsorption (PSA). SMR and PSA processes can be categorized into six stages which are shown in Fig1.

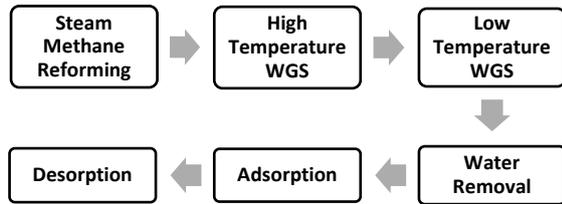


Figure 1: Overall scheme of hydrogen production system

In Figure 2, the hydrogen production system, which includes SMR and PSA processes, is shown. After the temperature and pressure of S1 and S13 increased to 700°C and 1010 Kpa, the feed mixture enters the reformer which the reaction 1 takes place. Then, in order to have a higher hydrogen production rate, the syngas (S6) is transferred to water gas shift process (WGS). It includes the high and low temperature reactors (1010 Kpa, 350°C and 200°C). In water removal stage, the S11 is cooled down to condensate the water. The water is separated from syngas in three stages.

In the next step, syngas (S35) is transferred to the PSA process for purification which the reaction 3 takes place. In the PSA process, Calcium Oxide (CaO) sorbent is utilized to adsorb CO2. Therefore, pure hydrogen is separated in the flash tank. Finally, CO2-enriched sorbent is sent to desorption column. Heat exchangers 09 and 10 are used to calculate the heat of adsorption and desorption reactions.

**3.2 Simulation model**

The SMR process is simulated using the commercial simulator software PRO/II v9.4. In this simulation, Peng-Robinson equation of state is used as the thermodynamic method for fluid properties computations. Reformer and WGS reactors are assumed as conversion reactors in which the rate of conversion is determined via Equations 4 to 6. Heat exchangers are counter-current type, and formulated using the pinch analysis and specified minimum temperature approach. It is also assumed that there is no heat loss within the heat exchangers. Minimum temperature difference in all heat exchangers is set at 10° C. The isentropic efficiency of the pump and compressor are set at 85%.

In addition, pressure drop in the adsorption and desorption columns is neglected. Since PSA columns operate at near-adiabatic conditions, they are assumed as a single column for simplification. In this section, conversion reactors are used instead of adsorption columns; hence, additional heater and cooler are used for computing the adsorption and desorption heats during the process.

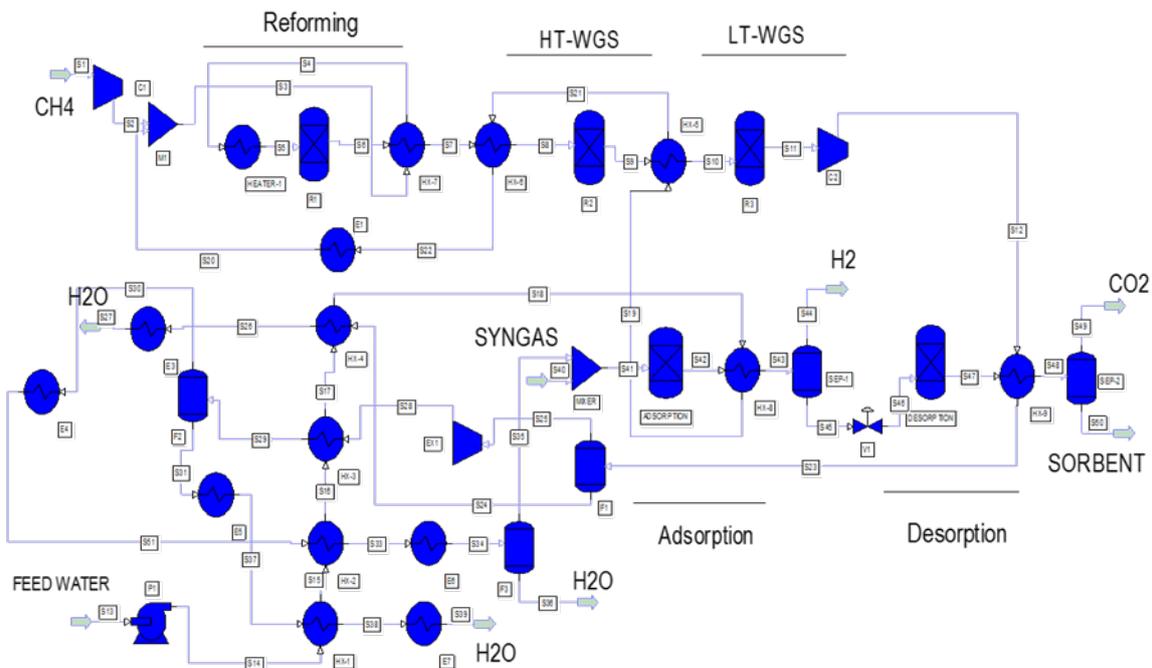


Figure 2: Steam methane reforming coupled with pressure swing adsorption process

#### 4 Results and discussion

A modified design of hydrogen production system is studied and compared to the design of the Chunfeng Song et al. (2015) that used heat integration technology to reduce the energy consumption. In the original design eight heat exchangers were used in the SMR process to recover energy and evaporate water feedstock. Also, the outlet stream of LT-WGS reactor was compressed to establish an optimal heat pairing between the cold and hot streams. To optimize the PSA process, a heat pump was used to recover the heat released from adsorption column and reused it for sorbent regeneration.

In this study, the energy required for desorption column is obtained by SMR process. Moreover, the energy released in the adsorption column is used to increase the latent and the sensible heat of the water feedstock in the SMR process. The S1 and S13 are pressurized up to 1010 Kpa which is done via compressor (0.241 MW) and pump (1.61 KW). Similar to Chunfeng Song et al. (2015) simulation, heat exchangers of 1 and 4 (0.16 MW and 0.003 MW) use the energy of extracted H<sub>2</sub>O from syngas to increase water feed temperature. The HX-2 (0.341 MW), HX-3 (0.113 MW), HX-5 (0.81 MW) and HX-6 (0.94 MW) are recovering the syngas heat to increase the latent and sensible heat of water feed stream. The mixture of vapor and methane is preheated to reach the right temperature for the reforming reaction. Therefore, HX-7 recovers 0.97 MW from the reformers outlet flow and heater-1 consumes 1.52 MW to heat S4 up to 700°C.

While the heat pump is omitted in the new design of the PSA process, adsorption heat is recovered via a heat exchanger (HX-8) to prevent the heat loss in the conventional PSA process. Therefore, HX-8 transfers the heat of adsorption to S18 to increase the sensible and the latent heat of the water. The recovered heat is around 0.98 MW. The saved energy used by heat pump in the heat integrated PSA process in the Chunfeng Song et al. (2015) design, is 0.36 MW. However, a small difference in the amount of the recovered heat can be observed between the HX-8 in this design and the HX-5 in the Chunfeng Song et al. (2015) design. The difference causes an increase in the total consumed energy of Heater 1 and 2. It rises from 2 MW to 2.23 MW. Moreover, S12 provides the energy demands of the desorption column, which HX-9 transfers 0.98 MW energy from S12 to S47.

The percentage of the saved energy in the new design, does not meet the eye. Thus, to have a more energy efficient process, temperature of reformer in the SMR process is increased from 700°C to 750°C. The temperature rise effects not only conversion of methane in reformer but also heat recovery of HX-7. While the HX-7 recovers more energy to preheat the feed for reformer, the energy load for the Heaters 1 and 2 decreases. Meaning, Heaters 1 and 2 consume less energy (1.32 MW, 0.5 MW).

Figure 3 shows the minimum temperature difference in the heat-integrated SMR process. It can be seen that the hot and cold stream lines are almost parallel which indicates that there is hot and cold streams are well paired. Also, there is a curve in the lines that shows the minimum temperature difference between the hot and cold streams. Figure 4 illustrates the pairing of the hot and cold streams in the new hydrogen production process.

Generally, it can be observed that there is no energy loss or consumption in proposed PSA process. Whereas in conventional PSA process (9.71 KJ/mole H<sub>2</sub>) and heat integrated PSA process (3.7 KJ/mole H<sub>2</sub>) more energy were wasted or consumed. Furthermore, the energy consumption of the new SMR process is 34.55 KJ/mole H<sub>2</sub>, while in the conventional process and heat integrated process was 92.4 KJ/mole H<sub>2</sub> and 36.63 KJ/mole H<sub>2</sub>, respectively.

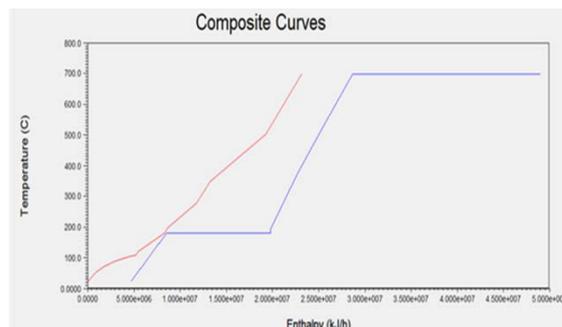


Figure 3: Temperature – enthalpy diagram for the heat exchangers of proposed process

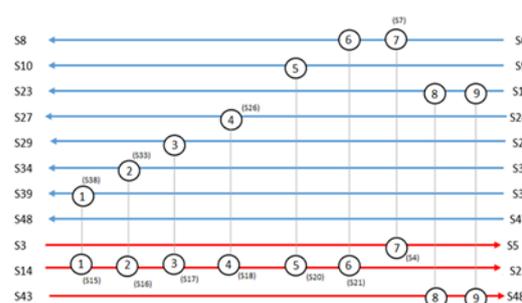


Figure 4: Schematic diagram of cold and hot streams in proposed process

#### 4 Sensitivity analysis

Reaction conditions are regarded as the key factors since their effect on the process performance is significant. The most relevant parameters are temperature and Steam/Carbon ratio (S/C) which crucially affect the process.

Figure 5.A shows the variation of the hydrogen composition versus temperature. It can be observed that the composition of the outlet hydrogen stream increases while the temperature rises. Since steam methane reforming reaction is endothermic, a rise in temperature causes the reaction to move toward producing more hydrogen.

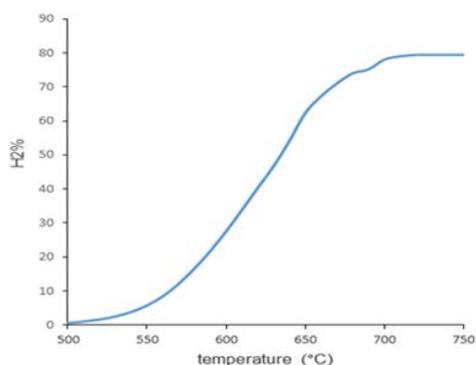


Figure 5

A) Diagram of hydrogen composition-temperature in heat-integrated SMR process where the temperature of the H-WGS and L-WGS reactors are constant at 350°C and 200°C, respectively, S/C ratio is constant at 3 and pressure (1010 Kpa) is constant through the whole process.

In Figure 5.B, the effects of the steam to carbon (S/C) ratio are analyzed. Based on the stoichiometry of the SMR and WGS reactions, increasing the steam will cause the reaction 1 to move further to the right side. Also, it causes methane in reaction 1

and CO in reaction 2 to convert further. Nonetheless, generation of large amount of steam at high pressure for reaching to the level of complete conversion of methane and CO requires a great deal of energy. In addition, it decreases the process efficiency drastically and increases the total energy demand. However, moderate steam-to-carbon ratio is used to optimize the process.

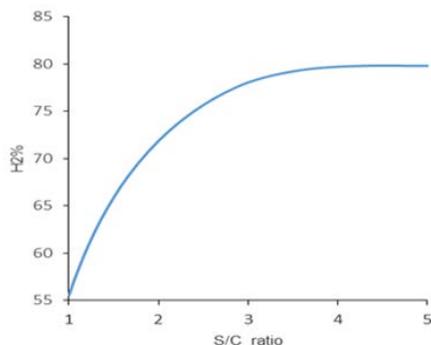


Figure 5

B) Diagram of hydrogen composition-S/C ratio in heat-integrated SMR process where the temperature of the H-WGS and L-WGS reactors are constant at 350°C and 200°C, respectively, temperature is constant at 700°C and pressure (1010 Kpa) is constant through the whole process.

## 5 Conclusions

In this study, a simulation of hydrogen production system via SMR and PSA processes was discussed and compared with previous works. In proposed process, a network of nine heat exchangers was used to reduce energy consumption. Eight heat exchangers recovered the heat loss of SMR process and one heat exchanger recovered the heat loss of PSA process. A part of the recovered heat in the SMR process was used to provide energy for endothermic desorption reaction. Similarly, heat of exothermic adsorption reaction was used to increase the sensible and latent heat of water feed stream. In addition, to reduce energy consumption and energy recovery, the temperature of reformer was increased. Compared to Chunfeng Song et al. (2015) design, the energy consumption was reduced to zero in the proposed PSA process, while in the conventional process 9.71 KJ/mole H<sub>2</sub> and in the heat integrated PSA process 3.7 KJ/mole H<sub>2</sub> energy was consumed, respectively. On the other hand, in the SMR process, the energy consumption of the new design was less than conventional and heat integrated process which is 34.55 KJ/mole H<sub>2</sub>, whereas the amount of energy consumption in conventional and heat integrated SMR process was 92.4 KJ/mole H<sub>2</sub> and 36.63 KJ/mole H<sub>2</sub>, respectively. In conclusion, the total energy consumption in the proposed design was reduced by 66.2% compared to conventional hydrogen production system and 14.32% in comparison to heat integrated hydrogen production system.

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