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Simulation of Hydrogen Production with In Situ CO_2 Removal Using Aspen Plus

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In this work, the sorption-enhanced steam methane reforming (SE-SMR) in which the integration of steam reforming reaction and carbon dioxide removal can be carried out in a single step was investigated in the thermodynamics aspects by using AspenPlus^{TM}. Thermodynamics analysis was performed on both conventional steam methane reforming (SMR) and sorption-enhanced steam methane reforming processes based on minimization of Gibbs free energy method to determine the favorable operating conditions of each process. The effects of operating conditions (i.e., pressure, temperature and steam to carbon ratio) on hydrogen production were examined. The simulation results show that the optimal steam to carbon ratio is 6 and 5 for SMR and SE-SMR process, respectively. For SMR process, the maximum hydrogen purity of 78 % (dry basis) can be obtained at 950 K. While, the SE-SMR process offers two advantages over SMR process: (1) higher purity of hydrogen product can be achieved to 99 % (dry basis) and (2) required operating temperature is lower in the range of 700-850 K which is 100-150 K lower than SMR process, indicating that the SE-SMR process is less requirement of energy consumption.

1. Introduction

Presently, hydrogen plays an important role in many industries. Chemical industry uses hydrogen as a raw material for chemical synthesis and production, such as ammonia production from hydrogen and nitrogen via hydrogenation process. In petrochemical industry, hydrogen is required in hydrodesulphurization process for removing sulphur from the natural gas feedstock. More importantly, hydrogen is one of the alternative fuels for the future. It can be used in internal combustion devices or fuel cell without pollution emissions since its by-products are only water and heat and thus, hydrogen is regarded as a clean energy. With the aforementioned usefulness of hydrogen, the demand of hydrogen trends to be increased continuously. As a consequence, there are many researchers being pursued in the development of hydrogen production process. Steam methane reforming (SMR) which is traditional process for producing hydrogen has been received interest in the industrial scale and extensively studied in recent years (Caravella et al., 2009. However, the steam reforming retains some limitations that are main obstruction for hydrogen production. Due to its highly endothermic reaction, this process is carried out under high temperature operation and thus, the external heat source is required. In addition, the alloy-based reformer must be used to tolerate the severe conditions which are expensive. The most important constraint is that the reaction is limited by thermodynamics equilibrium of reversible reaction, higher operating temperature is required to achieve high production of hydrogen. When the hydrogen production is limited, the content of carbon dioxide always presents in gaseous product. This leads to the requirement of separation unit to purify hydrogen. Collodi et al. (2010) reported that 1 t of hydrogen produced will also produce 9 to 12 t of CO_2.

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One approach to improve the hydrogen production process is through simultaneous separation of carbon dioxide during the steam reforming reaction (Ochoa-Fernández et al., 2009). This approach can be performed by adding a carbon dioxide sorbent (such as calcium oxide) into the reformer (Liu et al., 2013). When carbon dioxide is produced from steam reforming reaction, it will be adsorbed into adsorbent. Removal of carbon dioxide causes a shift in equilibrium; and this leads to the achievement in hydrogen production. This process is called “sorption-enhanced steam methane reforming (SE-SMR)”. Due to the fact that the adsorption reaction is exothermic, overall reaction temperature can be reduced, resulting in a decrease in energy consumptions (Dou et al., 2014). The combination of production and purification processes results in the lower capital costs. In addition, the carbon dioxide capture on adsorbent can eliminate the emission carbon dioxide into the atmosphere as the most important greenhouse gas.

Chen et al. (2009) presented a non-stoichiometric thermodynamic analysis of the sorption enhanced steam reforming of glycerol. Non-linear equations were simultaneously solved to determine the equilibrium gas composition. In the same way, Wang et al., 2011 studied the sorption enhanced steam reforming of propane by using the thermodynamic approach. However, the design and development of this process in AspenPlus^{TM} has not been reported. The advantage of using Aspen Plus is that it is easily accessible to design engineers in industry. This work aims to investigate a hydrogen production from the SE-SMR process based on thermodynamics aspect, which is useful for providing the appropriate operating condition for this process. The equilibrium composition of the gaseous product can be calculated based on the minimization of Gibbs free energy method through the use of AspenPlus^{TM}. Effect of the operating parameters (i.e., pressure, temperature and steam to carbon ratio) on hydrogen production is also examined. Thermodynamics calculation of both conventional SMR and SE-SMR processes are determined to define the most favorable operating condition of each process

2. Methodology

In this work, methane (CH_4) and steam are main reactants for hydrogen production process. In general, methane is main composition in natural gas along with other impurities. However, it is noted that in this work, pure methane is used to minimize the negative impact and side reactions. For CO_2 adsorption, calcium oxide (CaO) is utilized as CO_2 sorbents because it’s inexpensive, easy to find and considered as high adsorption ability. The thermodynamics calculation is performed by using AspenPlus^{TM}. By giving the operating condition, the equilibrium compositions in the product from reformer can be calculated by using the minimization of Gibbs free energy method. The physical property method for thermodynamics calculation is based on the Soave-Redlich-Kwong (SRK). In addition, the sensitivity analysis function integrated in AspenPlus^{TM} will be used to examine the effect of operating conditions.

3. Process description

Figure 1 illustrates the flowsheet of the sorption-enhanced steam methane reforming process. The process begin with the mixture of pure methane (METHANE) and steam (STEAM) obtained from mixer (MIXER) is fed through compressor (COMP) and heater (HEATER) to reach the specified reformer operating condition. Then, the gas mixture is fed to reformer (REFORMER) along with the CO_2 sorbents (SORB-IN).

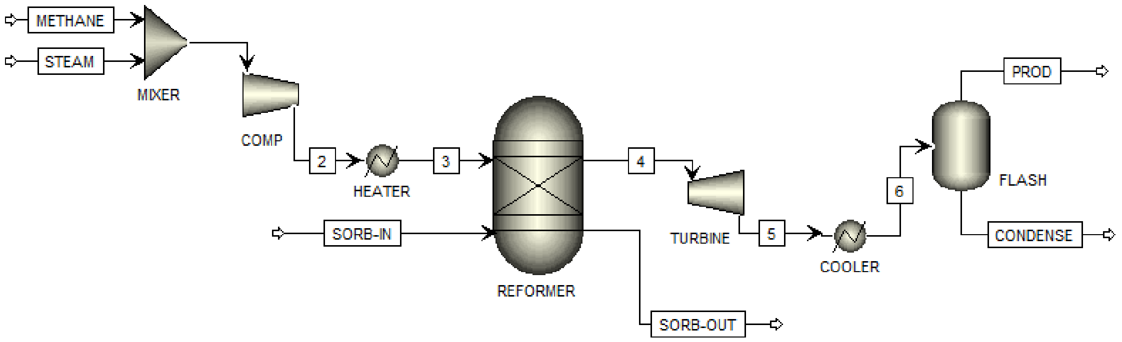

Figure 1: Flowsheet of the sorption-enhanced steam methane reforming process

Table 1: Possible reactions in sorption-enhanced steam methane reforming process

Steam methane reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H^0_{298} = +206$ kJ/mol	(1)
Water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H^0_{298} = -41$ kJ/mol	(2)
CO_2 adsorption	$CaO + CO_2 \leftrightarrow CaCO_3$	$\Delta H^0_{298} = -178$ kJ/mol	(3)

Table 2: Specification detail of each unit models in sorption-enhanced steam methane reforming

Name	Unit model	Initial condition	
		Temperature (K)	Pressure (bar)
MIXER	Mixer	-	-
COMP	Compr	-	1
HEATER	Heater	900	1
REFORMER	RGibbs	900	1
TURBINE	Compr	-	1
COOLER	Cooler	323.15	1
FLASH	Flash2	323.15	1

Here the steam reforming and CO_2 adsorption reaction is carried out in this reactor. To calculate the product composition at the equilibrium, RGibbs model reactor is utilized. The possible species in the process are CH_4, H_2O, CO, CO_2, CaO, $CaCO_3$ and H_2. In order to condense steam from the gas mixture, the effluent from reformer (Stream 4) is reduced pressure and temperature by turbine (TURBINE) and cooler (COOLER), respectively. The flash drum (FLASH) is further used to separate liquid condensates from the gaseous phase. The possible reactions in sorption-enhanced steam methane reforming process are shown in Table 1 whereas Table 2 lists a specification detail of each unit models in the process. The initial flow rate of methane and steam is set respectively to be 1 kmol/h and 3 kmol/h and thus, the steam to carbon (S/C) ratio is equal to 3. The CO_2 sorbent or CaO feed rate is 1 kmol/h which equal to the stoichiometric value of CO_2 produced from water-gas shift reaction (Eq(2)). For the simulation of the conventional SMR process, the CaO feed rate is set to be 0 for omitting the CO_2 adsorption reaction.

4. Model Validation

The simulation results from AspenPlus^{TM} are compared with the experimental results of Balasubramanian et al. (1999) to ensure model validation. Under same operating conditions, SMR process provides 94 % H_2 and 5 % CH_4 whereas the gas composition of 95 % H_2 and 4.7 % CH_4 can be obtained in SE-SMR process. It is found that the model validation shows a good agreement with the experimental data

5. Results and Discussion

Thermodynamics calculation is performed on both SMR and SE-SMR processes in which the equilibrium composition of the gaseous product and the molar flow rate of each component are determined. The effect of operating parameters, i.e., pressure, temperature and S/C ratio are investigated by using sensitivity analysis function in AspenPlus^{TM}. Under the standard conditions as shown in Table 2, the SMR process provides a gas product consisting of 75.23 % H_2, 9.31 % CO, 11.82 % CO_2 and 3.64 % CH_4 (dry basis), the molar flow rate of H_2 is 3.04 kmol/h and the methane conversion undergoes 85.34 %. For the SE-SMR process, the gas mixture of 95.42 % H_2, 1.54 % CO, 1.17 % CO_2 and 1.87 % CH_4 (dry basis) can be obtained whereas the molar flow rate of H_2 and methane conversion are 3.65 kmol/h and 92.86 %, respectively. From the simulation results, it can be seen that molar flow rate of H_2 obtained from SE-SMR process can be achieved close to its stoichiometric value (4 kmol H_2/1 kmol of CH_4).

5.1 Effect of operating pressure in both SMR and SE-SMR process

Figure 2 presents the molar flow rate of product composition as a function of different operating pressure (1-21 bar) at temperature of 900 K and S/C ratio of 3. From the simulation result, it is found that the low operating pressure is favoured to the hydrogen production for both processes and the maximum molar flow rate of H_2 can be obtained when the reformer operates at 1 bar. This is due to the fact that the total moles of product are higher than those of reactant according to Eq(1)-(3). As a result, increasing of operating pressure will shift the equilibrium backward to the reactant side. The simulation results indicate that the low pressure is suitable operation for both processes.

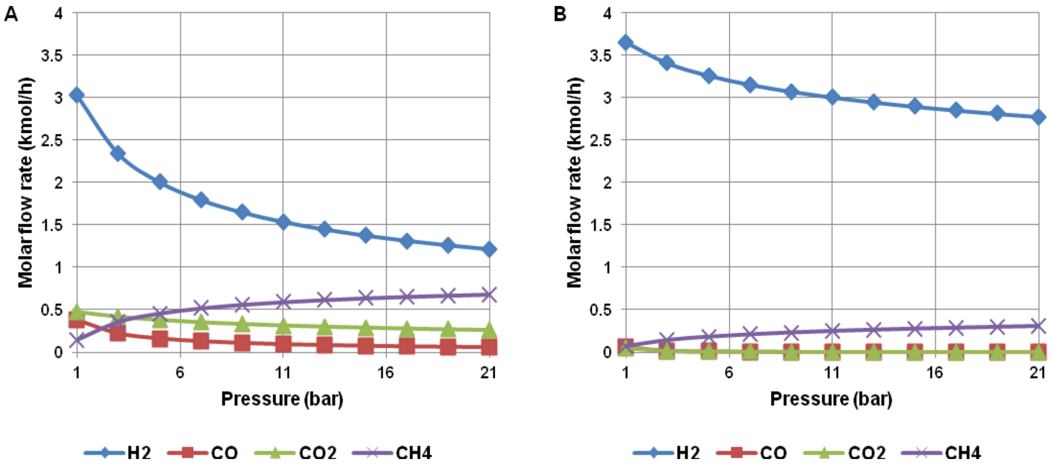

Figure 2: Molar flow rate of each components as a function of operating pressure at 900 K and S/C = 3: SMR (A) and SE-SMR (B)

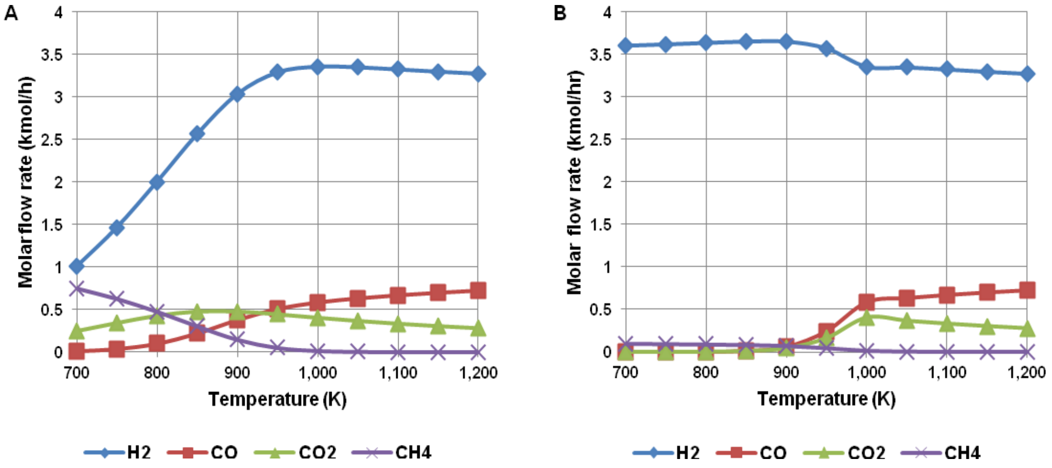

Figure 3: Molar flow rate of each component as a function of operating temperature at 1 bar and S/C = 3: SMR (A) and SE-SMR (B)

5.2 Effect of operating temperature in both SMR and SE-SMR process

Figure 3 represents the effect of operating temperature in the reformer (REFORMER) on molar flow rate of each component at the equilibrium state. The operating temperature is varied from 700 to 1,200 K while the operating pressure and S/C ratio are kept constant at 1 bar and 3, respectively. For SMR process, operating temperature has a great impact on molar flow rate of produced H_2, as illustrated in Figure 2A. The molar flow rate of H_2 is increased with an increase in the operating temperature. Since steam methane reforming reaction (Eq(1)) is endothermic, higher operating temperature can shift equilibrium to the product side, therefore; higher H_2 can be obtained. The maximum molar flow rate of H_2 is 3.36 kmol/h at 1,000 K. When the operating temperature is further increased, it is found that the molar flow rate of H_2 decreases. This is because high temperature is not favorable to the exothermic water-gas shift reaction (Eq(2), leading to inhibiting the additional H_2 production. The increasing in CO flow rate confirms the diminishing of water-gas shift reaction. In the SE-SMR process, the molar flow rate of H_2 is steadily increased between 700 and 850 K. As shown in Figure 2B, it can be seen that the molar flow rate of CO_2 is in the trace amount and $CaCO_3$ was formed (result not shown). Maximum H_2 produced from this process is 3.66 kmol/h at 850 K. When the operating temperature is further increased, the H_2 molar flow rate becomes decrease. This can be explained that high temperature operation inhibits the adsorption of CaO. The increment of CO_2 molar flow rate indicates the deactivation of the sorbents.

5.3 Effect of S/C ratio in both SMR and SE-SMR process

The effect of S/C ratio (1-12) on H_2 production is represented in Figure 4. For both SMR and SE-SMR processes, the simulation results show that the H_2 molar flow rate is increased as the S/C ratio increases. This is due to the equilibrium shift of the reaction from the increment of reactants (steam). The H_2 production rate in SMR is increased rapidly with increase of S/C ratio from 1 to 6 and steadily increased afterwards. For SE-SMR process, when S/C is increased in range between 1 and 5, the H_2 molar flow rate increases significantly and relatively stable afterwards. In this process, the H_2 molar flow rate is close to 4 kmol/h and this indicates that the theoretical value of reforming reaction can be achieved in SE-SMR process.

Although high S/C ratio can enhance both SMR and SE-SMR process significantly, it is known that higher S/C will require more reactor volume due to higher steam volumetric flow. In addition, the heat duty input is also increased because higher vaporization for steam is needed. From the simulation results, it is suggested that the optimal S/C ratio for SMR and SE-SMR process is 6 and 5, respectively. Since increases in S/C ratio more than these values are slight influences on H_2 production

5.4 Purity of H_2 produced from both SMR and SE-SMR process

One of the advantages of SE-SMR over SMR process is that higher purity of the H_2 products can be obtained. As illustrated in Figure 5, the purity of H_2 produced by SE-SMR process at 1 bar and S/C = 5 is close to 100 % (dry basis) when the operating temperatures are between 700 and 850 K. However, when operating temperature is higher than 850 K, will cause the reduction of H_2 purity because high temperature inhibit the CO_2 adsorption reaction of CaO. As seen in Figure.5B, when the operating temperature is higher than 900 K,

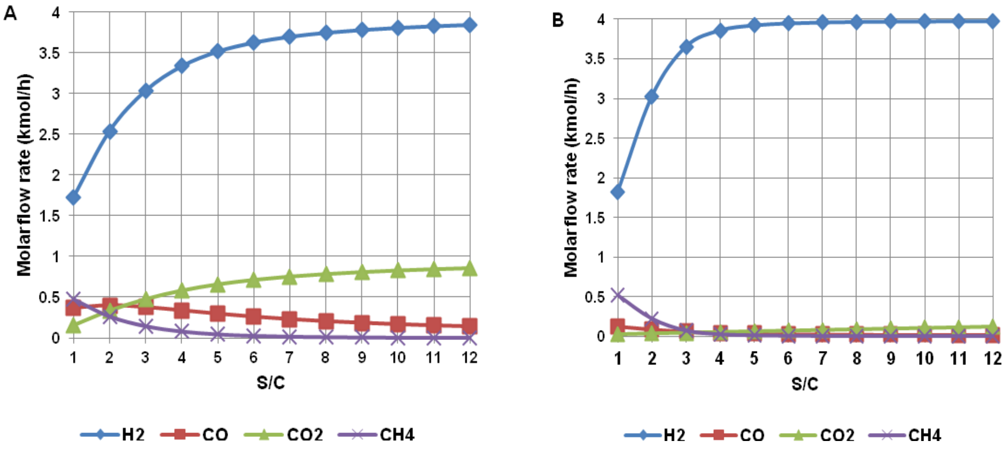

Figure 4: Molar flow rate of each components as a function of S/C at 900 K and 1 bar: SMR (A) and SE-SMR (B)

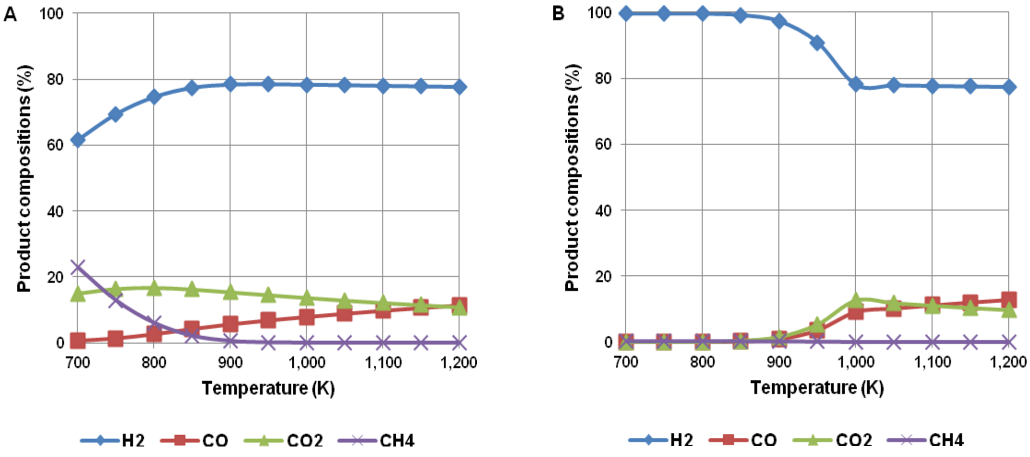

Figure 5: Product compositions as a function of operating temperature at 1 bar: SMR with S/C = 6 (A) and SE-SMR with S/C = 5 (B)

the CO_2 concentration is increased which in turn is no CO_2 adsorption. For SMR process, the maximum H2 purity achievable is 78 % (dry basis) at 950 K which is far lower than SE-SMR process and need to purify. Therefore, the purification unit is required for SMR process, and this leads to an increase in cost of production compared with SE-SMR process.

5.5 Effect of CaO molar flow rate of SE-SMR process

In this section, the impact of CaO molar flow rate on H_2 production in SE-SMR process is investigated. The CaO molar flow rate is varied in range of 0.1 to 1.5. The simulation results reveal that increasing CaO molar flow rate can provide higher amount of H_2. However, increasing CaO molar flow rate more than 1 kmol/h isn't impact on H_2 production. This is mainly since the CaO molar flow rate of 1 kmol/h is stoichiometric value of Eq(2) and (3) and thus, no CO_2 adsorption is occurred when CaO molar flow rate is more than this value.

6. Conclusions

The thermodynamics analysis of both SMR and SE-SMR processes has been examined with the minimization of Gibbs free energy method by using AspenPlusTM. The effect of operating parameters was investigated to find the favourable operating conditions of each process. The simulation results indicate that low pressure operation is feasible for both SMR and SE-SMR processes. The most favourable operating temperature for SMR process is 950-1,000 K which capable of producing maximum H_2. While, the optimal operating temperature for SE-SMR process is 950 K which is 100-150 K lower than SMR process. The most appropriate S/C ratio is 6 and 5 for SMR and SE-SMR process, respectively. From the simulation results, it was found that the addition of CaO as a CO_2 sorbent into the reformer can greatly enhance the H_2 production compared with SMR process in which nearly 4 kmol/h (stoichiometric value) can be produced at lower temperature (700 – 850 K). In addition, the purity of H_2 produced from SE-SMR is over 99 % (dry basis) below 850 K which is very high compared with SMR process which can only achieve 78 % (dry basis) at 950 K. All results indicate that improving hydrogen production process can be achieved with sorption-enhaced process.

Acknowledgement

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