Hydrogen production from sorption-enhanced steam methane reforming chemical-looping

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Abstract. Conventionally, hydrogen is produced from steam methane reforming of which methane is reformed into syngas (H2/CO) and carbon dioxide as a by-product. However, high energy requirement is a drawback of this technique. This work aims to improve hydrogen production efficiency by focusing on the development of intensified process, named sorption-enhanced steam methane reforming chemical looping. The use of mixed metal oxide, NiO/CuO, as oxygen carrier and calcium oxide as CO2 sorbent were examined with different amount usages. Process performances were studied through thermodynamic analysis via process simulation using Aspen Plus program. The results showed that the reforming temperature of 500-650°C provides a maximum hydrogen yield of 84% using NiO:CuO = 0.8:0.2.

1. Introduction

Greenhouse gas effect, a result of fossil burning, leads renewable energy to be more attractive for replacing of fossil fuels. Hydrogen energy is an interesting energy carrier as it provides only water as a by-product after combustion. Moreover, hydrogen can be used as raw material for chemical products such as ammonia and methanol.

Hydrogen can be produced from a variety of feedstocks, i.e., natural gas, oil, coal, or biomass. Hydrogen can be produced via steam reforming (SR), partial oxidation (POX), dry reforming (DR), or autothermal reforming (ATR). Among these, sorption enhanced chemical-looping steam reforming (SE-CLSR) is an attractive process as it can operate with less energy when compared with conventional steam reforming. One improved advantage of this technology is it can use metal oxide as oxygen carrier instead of oxygen gas, leading to the reduction of energy required for separation unit.

Mostly, SE-CLSR process is operated using metal oxide (MeO) as oxygen carrier instead of oxygen gas for autothermal reforming reaction and calcium oxide (CaO) is used as CO adsorbent to simultaneously remove a by-product CO2 from the process, leading the reaction to move forward. After reforming reaction, MeO is reduced to metal (Me) and CaO is converted into calcium carbonate (CaCO3), as a consequence, regeneration material is required. To recover MeO, oxygen is used as oxidizing agent and to regenerate CaO, heat is required to calcine CaCO3 into CaO. After that, the recovered MeO and CaO is fed back to the reforming reactor for repeated cycle.
Generally, iron, nickel, copper and manganese are the most promising oxygen carriers applied for SE-CLSR. NiO was found to show high selectivity towards hydrogen production and high stability of multiple cycles of oxidation/reduction [3]. However, it was found that high energy requirement for reformer is still required [1]. In this study, we are therefore interested in improving SE-CLSR system in term of minimization of energy consumption. CuO is found to be a good oxygen carrier as it is easy to regenerate and produces fewer carbon deposit when compared with other oxygen carriers. The reactions between oxidation and reduction of CuO are exothermic, which is beneficial to autothermal reforming. Therefore, development of the SE-CLSR system is focused on investigating the effect of the addition of CuO on hydrogen production and energy requirement.

2. Simulation

The thermodynamic analysis was studied by using Aspen plus 8.8 program. Physical properties were calculated using the Peng Robinson equation of state with the consideration of minimizing Gibbs free energy for all substances at the specific temperature and pressure using RGibbs reactor model. Reaction temperature was varied in the range of 400-900 °C, amount metal oxide to carbon molar ratio was varied between 0.1 to 1, and NiO:CuO molar ratio from 1:0 to 0:1 at atmospheric pressure. Performances of the process were determined in terms of methane conversion, hydrogen purity, and hydrogen yield (dry basis).

Figure 1 shows block flow diagram of sorption enhanced steam methane reforming chemical-looping process (SE-SMR-CL) adapted from Antzara et al. [1] and the modification to the SE-SMR-CL process, which provides a direct supply of NiO, CuO and CaO from the regeneration reactor to the reforming reactor. A schematic diagram of our modified sorption enhanced steam methane reforming chemical-looping process (SE-SMR-CL) process is shown in Figure 2.

**Figure 1:** H₂ production process with an integrated sorption-enhanced chemical looping steam reforming (SE-CLSR) from methane system.
Figure 2: Aspen Plus flow diagram of sorption-enhanced steam methane reforming chemical looping (SE-SMR-CL).

For the SE-SMR-CL process, methane and steam (FEEDHOT), metal oxide and calcium oxide (MEO-CaO) were fed into the reforming reactor (R1). Solids from the MEO-CaO stream are comprised of NiO, CuO and CaO. The reformer is operated at atmospheric pressure, where reduction of metal oxide and steam reforming reaction take place. Carbon dioxide in the system is adsorbed by CaO. After reaction completes, gases and solids are fed to the first cyclone (CY1) for solid-gas separation. The separated solids are thereafter fed into regeneration reactor (R2). Carbon dioxide is desorbed from the CaO adsorbent in the regeneration reactor (R2) with the supply of oxygen to oxidize metal into metal oxide. The regeneration reactor is operated under isothermal conditions, at a temperature of 855 °C and a pressure of 1 atm, where CaO can be completely regenerated. The obtained gases (CO and O) and solids (NiO, CuO and CaO) are fed to a cyclone (CY2) for gas-solid separation, and the separated solids are fed back to the reforming reactor for cycle operation. Reactions involve in both reactors are listed below:

Reforming reactor:

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\begin{align*}
\text{CH}_4(g) + H_2O(g) & \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H_{\text{rxn}} = +206 \text{ kJ/mol} \quad (1) \\
\text{CO}(g) + H_2O(g) & \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H_{\text{rxn}} = -41 \text{ kJ/mol} \quad (2) \\
\text{CH}_4(g) + CO_2(g) & \rightleftharpoons 2CO(g) + 2H_2(g) \quad \Delta H_{\text{rxn}} = +247 \text{ kJ/mol} \quad (3) \\
\text{CH}_4(g) & \rightleftharpoons C(s) + 2H_2(g) \quad \Delta H_{\text{rxn}} = +75 \text{ kJ/mol} \quad (4) \\
2\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(g) + C(s) \quad \Delta H_{\text{rxn}} = -172 \text{ kJ/mol} \quad (5) \\
\text{C}(s) + H_2O(g) & \rightleftharpoons \text{CO}_2(g) + H_2(g) \quad \Delta H_{\text{rxn}} = +131 \text{ kJ/mol} \quad (6) \\
\text{CaO}(s) + \text{CO}(g) & \rightleftharpoons \text{CaCO}_3(s) \quad \Delta H_{\text{rxn}} = -178.8 \text{ kJ/mol} \quad (7) \\
\text{CH}_4(g) + \text{NiO}(s) & \rightleftharpoons \text{CO}(g) + 2H_2(g) + \text{Ni}(s) \quad \Delta H_{\text{rxn}} = +203 \text{ kJ/mol} \quad (8) \\
\text{CH}_4(g) + 4\text{NiO}(s) & \rightarrow 4\text{Ni}(s) + \text{CO}_2(g) + 2\text{H}_2O(g) \quad \Delta H_{\text{rxn}} = +156 \text{kJ/mol} \quad (9) \\
\text{NiO}(s) + \text{H}_2(g) & \rightarrow \text{H}_2\text{O}(g) + \text{Ni}(s) \quad \Delta H_{\text{rxn}} = -0.21 \text{kJ/mol} \quad (10) \\
\text{NiO}(s) + \text{CO}_2(g) & \rightarrow \text{Ni}(s) + \text{CO}(g) \quad \Delta H_{\text{rxn}} = +43.3 \text{kJ/mol} \quad (11) \\
\text{CH}_4(g) + \text{CuO}(s) & \rightarrow \text{CO}_2(g) + 2\text{H}_2(g) + \text{Cu}(s) \quad \Delta H_{\text{rxn}} = -35.72 \text{kJ/mol} \quad (12) \\
\text{CH}_4(g) + 4\text{CuO}(s) & \rightarrow 4\text{Cu}(s) + \text{CO}_2(g) + 2\text{H}_2O(g) \quad \Delta H_{\text{rxn}} = -178 \text{kJ/mol} \quad (13) \\
\text{CuO}(s) + \text{CO}_2 & \rightarrow \text{Cu}(s) + \text{CO}(g) \quad \Delta H_{\text{rxn}} = -126.9 \text{kJ/mol} \quad (14)
\end{align*}
\]
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\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \quad \Delta H_{298K} = -85.5\text{kJ/mol} \quad (15)
\]

Regeneration reactor:
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\begin{align*}
2\text{Ni}_x + \text{O}_2 &\rightarrow 2\text{NiO}_x & \Delta H_{298K} = -479.4\text{ kJ/mol} & (16) \\
2\text{Cu}_x + \text{O}_2 &\rightarrow 2\text{CuO}_x & \Delta H_{298K} = -312.1\text{kJ/mol} & (17) \\
\text{CaCO}_3 &\rightleftharpoons \text{CaO} + \text{CO}_2 & \Delta H_{298K} = +179\text{ kJ/mol} & (18)
\end{align*}
\]

3. Results and discussion

3.1. Validation of the sorption enhanced chemical looping steam methane reforming (SE-CL-SMR)

Validation of a thermodynamic equilibrium simulation of the sorption enhanced chemical-looping reforming was performed by comparing with Antzara et al. [1], who carried out both experimental and simulation investigations for sorption enhanced steam methane reforming chemical-looping using NiO as the oxygen carrier and CaO as CO\(_2\) sorbent. Validation of our sorption enhanced chemical-looping reforming simulations was carried out by assuming thermodynamic equilibrium and isothermal conditions. The results show our model is valid with those reported by Antzara et al. [1].

![Figure 3: Results of our CH\(_4\) conversion (a), H\(_2\) yield (b), H\(_2\) purity (c) and CO\(_2\) capture efficiency (d) as a function of the reformer’s temperature for SE-SMR and SE-CL-SMR simulation validated with Antzara et al. (2015) [1]: operating pressure 1 atm, S/C = 3, NiO/CaO = 0.5, CaO/C = 1.](image)

3.2. Effect of reforming temperature

The effect of reforming temperature on gas composition, methane conversion, and hydrogen yield at atmospheric pressure and with a S/C to 3 are presented in Figure 4. The results show that high methane
conversion is found at temperatures above 650 °C because steam reforming is endothermic reaction (Eq. 1). In addition, high hydrogen yield and hydrogen purity can be obtained for the typical operating temperatures are about 500 to 650 °C due to favorable CO₂ sorption of calcium oxide sorbent (Eq.7) at atmospheric pressure.

Figure 4: Gas composition, CH₄ conversion and H₂ yield as a function of the reformer temperature for SE-CL-SMR (operating at pressure 1 atm, S/C = 3, CaO/C = 1, MeO/C = 0.5, NiO:CuO = 0.5:0.5).

3.3. Effect of amount metal oxide NiO:CuO molar ratio on hydrogen production

Figure 5 shows the result of hydrogen production from the SE-CL-SMR system using different molar ratios of NiO:CuO at atmospheric pressure, S/C to 3, CaO/C molar ratio 1 and with a MeO/C molar ratio of 0.5. The results show that increasing NiO:CuO to 0.2 provides the highest hydrogen yield. After that, increasing molar fraction of CuO leads to the decrease in hydrogen yield.

Figure 5: H₂ yield as a function of NiO:CuO molar ratio for SE-CL-SMR (operating at adiabatic, pressure 1 atm, S/C = 3, CaO/C = 1, MeO/C = 0.5).
3.4. Effect of amount metal oxide NiO:CuO molar ratio on energy requirement

The effect of adding CuO as co-oxygen carrier has been investigated in term of energy required for the SE-CL-SMR process as shown in Figure 6. The results show that addition of CuO leads temperature in the reforming reactor increases when compared with SE-SMR. This phenomenon is due to exothermic nature of CuO reduction by CH$_4$. For regeneration reactor, 50% less energy requirement is observed for SE-CL-SMR when compared with SE-SMR process. This result is due to exothermic oxidation reaction of both Ni and Cu.

![Figure 6: Energy required of regeneration as a function of NiO:CuO molar ratio for SE-CL-SMR (operating at adiabatic, pressure 1 atm, S/C = 3, CaO/C = 1, MeO/C = 0.5, NiO:CuO = 0.8:0.2).](image)

4. Conclusion

The addition of CuO into the SE-CL-SMR could provide heat transfer to endothermic sorption-enhanced steam methane reforming reaction and regeneration reactor as less energy requirement was observed. Typical operating temperatures are 500–650°C, with the addition of CuO not greater than 0.2 can increase H$_2$ yield and lower energy requirement of the SE-CL-SMR process.

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