Optimization of hydrogen production from a sorption-enhanced steam reforming process

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Abstract:
The sorption-enhanced steam reforming is considered to be a suitable process for hydrogen production. By adding solid calcium oxide (CaO) to a reformer, carbon dioxide (CO_2) is removed via a carbonation reaction and the yield of hydrogen is improved. The aim of this study is to find the optimal operating conditions of the sorption-enhanced steam reforming process using methanol as a hydrogen source. The fixed-bed reactor model in flowsheet simulator is applied to explain the sorption-enhanced steam reforming based on the kinetics of methanol steam reforming, methanol decomposition, water gas shift reaction and carbonation reaction. The sensitivity analyses of primary parameters of the sorption-enhanced steam reformer were performed and the obtained results were used for the optimization task with the aim to find its optimal operating conditions to maximize hydrogen yield with the presence of CO in the hydrogen product below 10 ppm. It was founded that the sorption-enhanced steam reformer should be run at the temperature of 347ºC and steam-to-carbon feed ratio of 1.78. The maximum hydrogen yield of 3 mole hydrogen per mole methanol used is achieved and the CO content in the hydrogen product is less than 10 ppm. However, the net heat input required for the sorption-enhanced steam reforming process is about 52% higher than a conventional steam reforming process due to the combustion unit for CaO regeneration.

Keywords: *Sorption-enhanced steam reforming; Methanol; Hydrogen production; Simulation; Optimization*

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1. Introduction

Hydrogen is considered as clean energy and important chemical in many chemical and petro-chemical industries. In addition, it can be used as a fuel supply to fuel cells for power generation. Because hydrogen is not readily available, it is necessary to produce it from other sources. Many studies on hydrogen production from various non-renewable and renewable fuel sources, such as natural gas, ethanol, methanol and biogas, have been conducted.

For hydrogen production, the reformation of fuels is one of the main steps. There are several thermochemical methods to produce hydrogen from gas and liquid hydrocarbons, such as steam reforming, partial oxidation and autothermal reforming which combines steam reforming and partial oxidation in a single unit. In general, steam reforming results in a 20% higher H_2 yield compared to autothermal reforming because, in autothermal reforming, a portion of the fuel feed is consumed by the combustion reaction to supply heat to the system. However, the steam reforming process requires high external energy input to maintain the reformer operation at the desired temperature. The hydrogen-rich gas derived from the reforming process is generally composed of H_2, CO, CO_2 and CH_4. To make a pure hydrogen, the reformate gas must therefore be further treated and this causes a complicated hydrogen production and purification processes.

One of the most serious obstacles to the operation of conventional fuel processors is caused by the thermodynamic equilibrium of reversible reforming reactions. For conventional reformers, high reaction temperatures are required to achieve completed fuel conversion; however, such operating conditions favor the formation of carbon, which leads to the deactivation of the reforming catalysts. Several approaches have been proposed to improve the performance and reduce the complexity of the fuel processor. The coupling of reaction and separation systems can improve reactant conversion or product selectivity. This coupling results in a lower operating temperature compared to that required for a conventional reforming process. The selection of different components in the fuel

processor significantly affects the efficiency and the cost of the fuel processor.

A membrane reactor is an attractive technology for hydrogen purification. During the reforming of fuel, hydrogen is continually removed from the reaction zone; consequently, the equilibrium-limited reforming reaction is shifted forward to the product side. However, the cost of membrane and high energy consumption are the limitations of the membrane reactor. Alternatively, the sorption-enhanced steam reforming process has been proposed to minimize the complexity of the fuel processor. In the sorption-enhanced steam reforming, calcium oxide (CaO) sorbent is added to the steam reformer to adsorb generated CO_2 via a carbonation reaction. The removal of CO_2 causes the reforming equilibrium shift toward the hydrogen production. Hence, high purity of hydrogen product is achieved in a single reformer. However, the sorption-enhanced steam reforming system requires high energy input caused by a regeneration unit of the spent CaO sorbent.

The objective of this study is to improve the performance of the sorption-enhanced steam reforming process to produce hydrogen. Methanol is used as the fuel supply due to its low reforming temperatures and high hydrogen-to-carbon ratio. The sensitivity analyses of primary design parameters on the sorption-enhanced steam reforming process are first performed. The optimization of such a process is then carried out to determine their optimal values.

2. Process description

The sorption-enhanced steam reforming and conventional steam reforming processes were theoretically studied using Aspen Plus simulator. The RPlug model based on the methanol reforming reactions, i.e., methanol steam reforming, methanol decomposition, water gas shift reaction and carbonation (Eqs. (1)-(4)) was used to simulate the reformer. The kinetic models of the reactions (1)-(3) developed by Peppley et al. (1999) using $Cu/ZnO/Al_2O_3$ catalysts were used, whereas the carbonation reaction (reaction (4)) was based on the intrinsic rate of the CaO-CO_2 reaction improved by Sanchez et al. (2012). The CaO-CO_2 reaction was based on Arctic Dolomite (CaO-based sorbent) and its kinetic constant developed by Sun et al. (2008) was employed. Fresh CaO sorbent is assumed to be continuously fed to the reformer while the spent sorbent is removed to the regeneration unit. This looping of operation can be controlled by a level control and a hopper. Thus, a fixed volume of the sorbent in the reformer can be assumed and used as a reference for modeling. The specific surface area of the Arctic Dolomite is kept constant as the fresh sorbent is assumed throughout the reforming operation.

Sensitivity analyses of key operating parameters of the sorption-enhanced steam reformer were performed at the temperature of 200-400 °C, steam-to-carbon (S/C) feed ratio of 1.25 to 6 and sorbent-to-catalyst volume ratio (λ) of 0.15 to 0.90. Results from the sensitivity analyses were used to perform the optimization of the reforming process. The aim was to find the optimal operating conditions of the reformer, maximizing H_2 yield with a constraint on the amount of CO in the hydrogen product stream below 10 ppm. This produced hydrogen can be used in fuel cells without the poisoning of anodic catalyst (Martinez et al., 2013). The bed length of the CaO sorbent and reforming catalysts is varied between 11.26 and 18.61 cm. The internal diameter of the bed is 2.5 cm.

Methanol Steam Reforming

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \Delta H_{R,25} = 49 \frac{kJ}{mol} \quad (1)$$

Methanol Decomposition

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H_{R,25} = 90.1 \frac{kJ}{mol} \quad (2)$$

Water Gas Shift Reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{R,25} = -41.2 \frac{kJ}{mol} \quad (3)$$

Carbonation

$$CaO + CO_2 \leftrightarrow CaCO_3 \quad \Delta H_{R,25} = -178.8 \frac{kJ}{mol} \quad (4)$$

3. Results and discussion

The sensitivity analyses of the sorption-enhanced steam reforming process are performed. Figs. 1-2 show the effect of sorbent-to-catalyst volume ratio (λ) in the reformer, which is operated at

temperature of 200-400°C, S/C feed ratio of 2 and methanol feed flow rate of 2.5 mol/h, on the contents of H_2 and CO in the reformate gas. The concentration of H_2 increases with the increased sorbent-to-catalyst volume ratio at all temperature ranges. The removal of CO_2 by CaO sorbent causes the equilibrium of the steam reforming and water gas shift reactions shift to the hydrogen product side. The CO concentration in the reformate gas is always less than 10 ppm when the reformer is designed with λ of higher than 0.75. The reformer with lower value of λ must be operated at high temperatures to obtain high pure hydrogen. Because the performance of the used $Cu/ZnO/Al_2O_3$ catalysts can be degraded at temperatures higher than 350°C (Choi and Stenger, 2005), the reformer with λ of 0.6 will be used for further study.

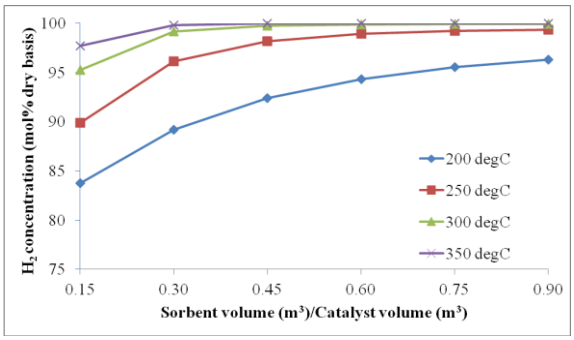

Fig. 1 – H_2 concentration (mol% dry basis) as a function of sorbent-to-catalyst volume ratio (λ) (Temperature = 200-350°C, S/C = 2, CH_3OH = 2.5 mol/h)

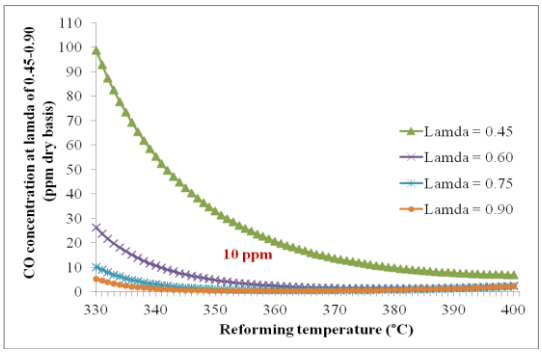

Fig. 2 – CO concentration (ppm dry basis) as a function of λ and reforming temperature (Temperature =330-400°C, S/C = 2, CH3OH = 2.5 mol/h, λ = 0.45-0.90)

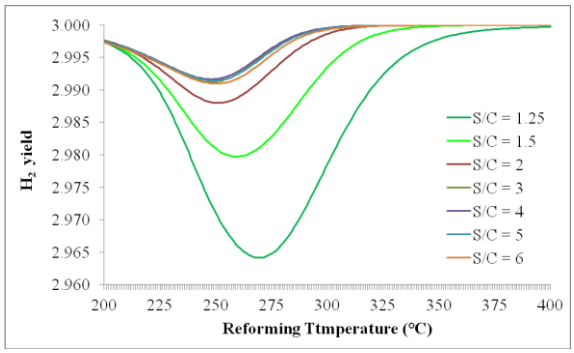

Fig. 3 H_2 yield as a function of reforming temperature and S/C feed ratio (Temperature = 200-400°C, S/C = 1.25-6, CH_3OH = 2.5 mol/h, λ = 0.60).

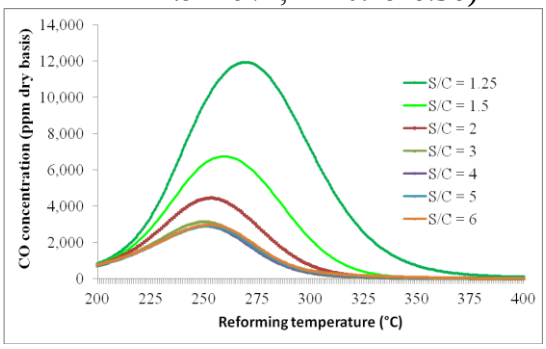

Fig. 4 CO concentration as a function of reforming temperature and S/C feed ratio (Temperature = 200-400°C, S/C = 1.25-6, CH_3OH = 2.5 mol/h, λ = 0.60).

Figs. 3-4 show the effect of reforming temperatures and S/C feed ratio to H_2 yield and CO concentration in the reformate gas. The H_2 yield initially decreases with the increased temperatures and then increases to its maximum of 3 mole H_2 per mole CH_3OH used. A decrease in H_2 results from the increased CO; the methanol decomposition is more pronounced than the methanol steam reforming, whereas the water gas shift reaction is used to explain the reduction of CO. At the temperature range of 250-265°C, methanol is completely converted, but the CaO-CO_2 reaction is still carried on over the methanol decomposition resulting in the continuous removal of CO_2. The removal of CO_2 raises the water gas shift reaction and thus, the CO concentration is decreased.

An optimization of the sorption-enhanced steam methanol reforming (SE-SMR) is studied with the aim to determine optimal design parameters for maximizing the H_2 yield. The optimization problem is formulated with a constraint on the amount of CO below 10 ppm and solved by the sequential quadratic programming method in Aspen Plus. Both the SE-SMR and conventional SMR are

considered. The results are summarized in Table 1. The maximum H_2 yields of the SE-SMR and SMR are 3 and 2.98 mole H_2 per mole CH_3OH used, respectively. The SE-SMR process needs the feed with higher S/C ratio. The net heat duty required for the SE-SMR process is higher than the SMR process about 52%. This is mainly caused by the combustion unit used to regenerate CaO.

Table 1 The optimization results of the SE-SMR and SMR processes

	SMR	**SE-SMR**
Methanol feed inlet (mol/h)	2.50	2.50
Steam feed inlet (mol/h)	2.28	4.44
S/C feed ratio	1.10	1.78
Total steam feed inlet comparing to SMR process (%)	-	+ 95
Reformer operating temperature (°C)	240	347
Reformer heat duty (kJ/h)	+ 153.12	- 289.13
Water gas shift reactor heat duty (kJ/h)	- 7.90	-
PROX reactor heat duty (kJ/h)	- 10.56	-
Regenerator heat duty (kJ/h)	-	+ 430.11
Net heat duty (kJ/h)	+ 357.30	+ 543.69
Net heat duty comparing to SMR process (%)	-	+ 52
Methanol conversion (%)	98.74	100
H_2 yield	2.98	3.00
H_2 purity in outlet product of the reformer (% dry basis)	74.20	99.99
H_2 purity in final product (% dry basis)	74.90	99.99
CO content (ppm dry basis)	0.00	8.68

4. Conclusion

In this study, the analyses and optimization of the sorption-enhanced steam methanol reforming (SE-SMR) over $Cu/ZnO/Al_2O_3$ catalysts were performed. The results showed that the product distribution of the SE-SMR is greatly affected by the sorbent-to-catalyst volume ratio (λ), steam-to-carbon (S/C) feed ratio and reforming temperatures. To achieve high H_2 purity with low CO content (less than 10 ppm), the sorbent-to-catalyst volume ratio should be 0.60 to avoid the degradation of the used catalyst. By performing the optimization of the SE-SMR process, it was found that the optimal operating conditions of the SE-SMR is at the temperature of 347°C with S/C feed ratio of 1.78 and the maximum H_2 yield for the SE-SMR is 3 mole H_2 per mole CH_3OH used.

5. Acknowledgement

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