Low Temperature Solar-driven Biogas Steam Reforming in a Membrane Reactor

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Abstract. A prototype for a low temperature solar-driven biogas steam reforming process was designed by coupling a hydrogen selective membrane reactor and linear Fresnel collector technology. To verify the prototype, the membrane reactor model was established by using ASPEN Plus and was studied using a modelled biogas in the temperature range 450 to 500 °C. The methane conversion was significantly enhanced by applying the H_2 selective membrane. Based on the actual Direct Normal Irradiation in South Africa, the capability of linear Fresnel collector was verified for the required heat duty in this study, which varying from 90.1 to 366.4 kW/m². This novel work constitutes a reference study for new developments with reactor designs and solar energy application in biogas steam reforming processes.

1. Introduction

There is growing interest in hydrogen as a promising energy carrier, because of its high calorific value and pollution-free character as fuel. [1] One of the synthesis routes of hydrogen production is steam reforming using natural gas, alcohols, biogas, etc. as feedstock. [2] Biogas is produced in anaerobic digesters and normally consists of 50-75% of CH_4 in mole, 25-45% of CO_2 in mole and tiny amount of H_2O, N_2, H_2, O_2, H_2S. [3] Compared to other raw materials, biogas is regarded as a renewable and sustainable energy resource. Its application contributes to reducing the emission of one of the Greenhouse Gases (i.e. methane) indirectly, which is in accordance with the requirements for responding to the crisis of global warming. [4,5] Biogas steam reforming is a catalytic process that mainly includes steam reforming and dry reforming. The associated reactions are as follows: [6]

$$CH_4+H_2O=CO+3H_2 \quad \Delta H=206kJ/mol \quad (1)$$
$$CO+H_2O=CO_2+H_2 \quad \Delta H=-41kJ/mol \quad (2)$$
$$CH_4+CO_2=2CO+2H_2 \quad \Delta H=247kJ/mol \quad (3)$$

Because of its strongly endothermic nature, the route using solar radiation as the energy source for biogas steam reforming is considered promising. [7,8] The abundant supply of solar radiation can be concentrated and absorbed by solar collectors. Various types of solar collectors, including the flat-plat collector, the parabolic trough collector, the linear Fresnel collector (LFC), et al, were developed for different applications. [9]

Conventionally, steam reforming of biogas was carried out at a high temperature range of 600 to1000 °C. However, the activity and stability of the catalysts are easier to decline at higher temperatures owing to the accelerated coke formation on the catalyst surface. [10]

The technical requirements for solar collectors at a high temperature are more stringent and, in consequence, its capital cost may dramatically increase. Thus, biogas steam reforming at a lower operating temperature can benefit from both technical and financial aspects.

Low temperature steam methane reforming conducted below 500 °C using nickel-based catalyst has been reported. According to Nieva's study [11], methane steam reforming was conducted stably at a low temperature, as sintering on the catalyst surface was not found. However, it cannot be overlooked that the methane conversion and the reaction rate declined with a decrease of operating temperature. It has been shown that a membrane reactor (MR), which separates hydrogen in situ of a hydrogen generation reaction by a hydrogen-selective membrane, can distinguishably enhance the hydrogen yield and reactor efficiency. [12] Compared to other membrane materials, Pd-based membranes perform better in terms of hydrogen permeation and selectivity. [13] Herein, the MR is advised to the low temperature biogas steam reforming process.

However, the LFC technology, which was employed in this study, was capable to heat the tubular receiver to the designed operating temperature of 500 °C. The application of LFC also benefitted from considerable design freedom and the relatively low acquisition cost. [14] The LFC assembly involves an array of primary reflectors at a low position, an optional secondary reflector at the top position, and a fixed receiver on the linear focus. [15] The concentration ratio of LFC is more flexible as the primary reflector can be increased without causing a rise in wind load when compared to the parabolic trough collectors and the central-receiver system with large-size heliostat mirrors. [16] Thus,

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integration of the LFC and the MR holds promising route for the application of solar-driven biogas steam reforming.

In this study, a low temperature solar-driven biogas steam reforming process was designed and conducted in a prototype apparatus that integrated the LFC with the MR. The feasibility and performance of this novel process was discussed and verified by means of a simulation study done using ASPEN Plus.

2. Prototype description and modelling

A cross-section view of the prototype is shown in **Fig.1.** It contains three parts, namely a primary reflector array, a secondary reflector and a receiver. The tubular receiver was designed as a tube-shell structure with catalyst bed packed on the shell side and sweeping gas on the tube side. The hydrogen selective membrane was installed to separate the tube side and the shell side. The concentrated solar radiation that penetrated through the transparent outer wall was absorbed by the catalyst bed and gaseous mixture in the annular catalytic reactor. The biogas steam reforming was conducted on the shell side of the receiver, while the generated H_2 permeated through the membrane to the sweeping gas side simultaneously. In this study, the prototype was designed to be 10 m in length, 300 mm in receiver shell diameter and 100 mm in membrane tube diameter.
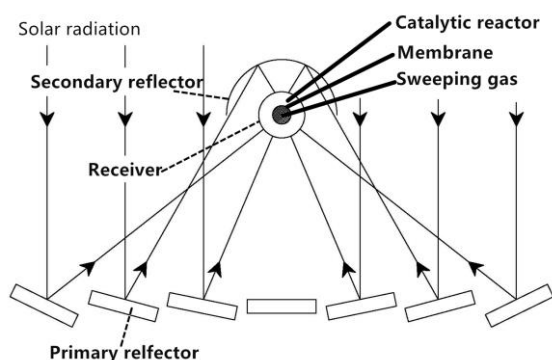

Fig.1. Schematic diagram of the designed steam methane reforming process

Assuming that the heat duty of the concentrated solar energy on the receiver outer wall was uniform and steady, the prototype can be considered to be as simple as a membrane catalytic reactor with a constant heat supply. Herein, ASPEN Plus is an important and reliable process simulator in chemical research, and was used to develop the MR model. To simplify the simulation process, assumptions were made as: there was uniform temperature in the reactor; pressure gradients can be ignored on both axial and radial directions in the reactor; the biogas steam reforming reactions can reach the thermodynamic equilibrium very quickly; the hydrogen partial pressure gradient in axial direction could be ignorable.

Since the steam reforming reactions and H_2 permeation were conducted simultaneously, no built-in reactor model in ASPEN Plus is suitable. Thus, the sequential modular approach in which the reactor is divided into a series of virtual axial distributed sub-reactors was implemented. [17] The sequential modular simulation diagram of this membrane catalytic reactor is shown in **Fig.2**. In each sub-reactor, the Gibbs reactor (GR) model (which simulates the steam reforming reactions) and the membrane model (which separates the hydrogen with local permeation rate) were conducted in sequence. The results were then passed to the next sub-reactor.

In the GR model, the composition of the outlet stream was determined by minimizing the Gibbs energy in the system. [18] The species involved in the equilibrium system were methane, CO_2, CO, H_2 and H_2O. The membrane model was established by using the Excel built-in subroutine in ASPEN Plus. The hydrogen flux on the membrane was evaluated according to Sievert's law: [19]

$$Q_{H2} = \eta * k * A_M * exp(-E_P/RT) * (P_{RH2}^{0.5} - P_{MH2}^{0.5})/Th \quad (4)$$

where Q_{H2} is the hydrogen permeation rate, $kmol*h^{-1}$; η indicates the permeation effective factor and equals 1 in this study; k is the pre-exponential factor, $mol*m^{-1}*h^{-1}*Pa^{-0.5}$; A_M and Th indicate the area (m^2) and thickness (m) of the membrane respectively; E_P is the permeation active energy, $J*mol^{-1}$; P_{RH2} and P_{MH2} are the H_2 partial pressures on the reactor side and the membrane side respectively, MPa.
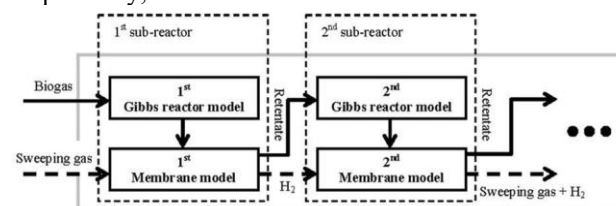

Fig.2. Sequential modular simulation diagram of the membrane catalytic reactor

A Pd-based membrane was implemented in this study and the parameters of the membrane were as cited in Brunetti's study. [20] Thus, the Th of the membrane was 50 μm; the k and E_P were 25.76 kJ/mol and 9.7×10^{-7} $mol*m^{-1}*s^{-1}*Pa^{-0.5}$ respectively. [21] The number of sub-reactors should be adequate so that the H_2 permeation is well described. In this study, the prototype was divided into 10 sub-reactors.

3. Results and discussion

In this study, a model biogas (which consists of only methane and CO_2 with a volumetric ratio of 1.5) was used in the simulation. The biogas steam reforming reactions were conducted under typical experimental conditions with the presence of Ni-based catalyst in the temperature range of 450~500 °C. Part of the inlet conditions were listed in **Table 1**.

To demonstrate the superior performance of the H_2-selective membrane, the simulation results from the MR model were compared with that from the GR model under the following conditions: 500 °C and 20 bar. The methane conversions (X_{CH4}) and the product compositions in dry-based from GR and MR respectively are listed in **Table 2**. The methane

conversion increased from 11.9% to 45.0% when the membrane reactor was applied to replace the conventional tubular reactor. Additionally, the molar composition of H_2 in dry-base increased from 21.4% to 51.6%, because the selective permeation of hydrogen contributed the equilibrium to the H_2 production. Therefore the utilization of the hydrogen selective membrane can effectively improve methane conversion as well as H_2 productivity.

Table 1. Conditions of reactant flow

Parameter	Value	Unit
CH_4/CO_2 ratio	1.5	-
Steam/CH_4 ratio	3.5	-
CH_4	19.4	% (mol)
CO_2	12.9	% (mol)
H_2O(g)	67.7	% (mol)
Space velocity	30	$m^3/(kg*h)$
Flow rate	1.69×10^4	m^3/h

Table 2. Simulation result comparison of GR and MR

	GR	MR
X_{CH4}/%	11.9	45.0
CO%	1.0	0.7
CO_2%	36.0	31.7
H_2%	21.4	51.6
CH_4%	41.6	16.0

Based on the membrane reactor model, a sensitivity analysis of the temperature was conducted. The effects of temperature on X_{CH4} and the required heat duty were shown in **Fig.3**. The X_{CH4} increased linearly from 11.1% to 45.0% with increasing the temperature. Furthermore, the required heat duty of membrane reactor for biogas steam reforming was increased from 90.1 to 366.4 kW/m^2 with increasing the temperature from 450 to 500 °C.
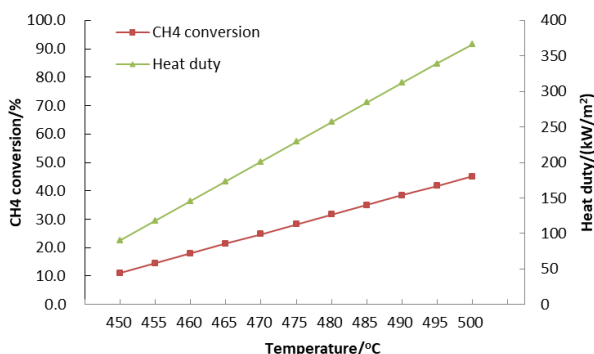

Fig.3. Effects of temperature on X_{CH4} and heat duty

As indicated above, this heat duty was supplied by the solar energy. South Africa can be used as an example: the country's long-term average Direct Normal Irradiation per day varies from 4.5 to 9 kW/m^2 in most regions of the nationwide according to the solar resource maps provided by World Bank Group (shown in **Fig.4**). [22] The concentration ratio of LFC (which is calculated as the ratio of the effective area of the reflector to that of the absorber) varies from 25 to 100. However, the

efficiency of the LFC (which is depending on the nature of the receiver, the working temperature, the concentration ratio, et al) was difficult to determine. Singh et al reported that the efficiency of a LFC with a round pipe absorber varied from 25.7% to 71.2%. [23] If we introduced those efficiency values reported by Singh et al. [23], the range of heat flux that supplied from the LFC may change from 28.9 kW/m^2 to 640.8 kW/m^2. These results indicate that the LFC technology may be capable to supply the required energy for the biogas steam reforming process.

Therefore, it was verified that the prototype equipment built couples the linear Fresnel collector and tubular membrane reactor for the solar-driven biogas steam reforming process at a low temperature.
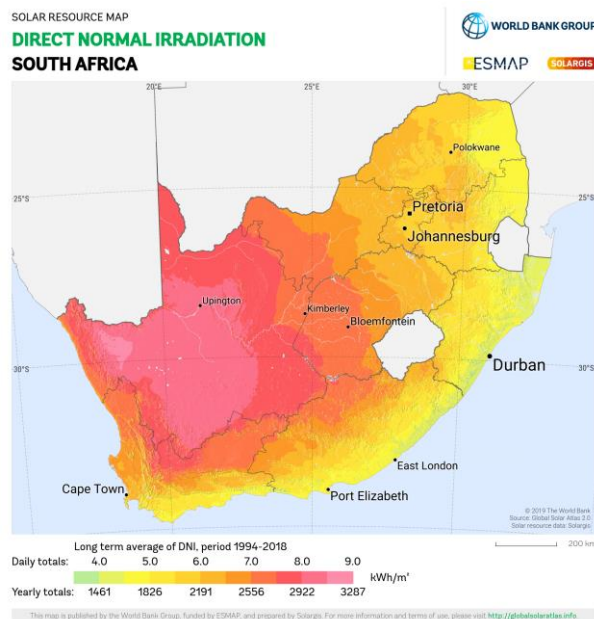

Fig.4 Solar resource maps of South Africa [22]

4. Conclusion

A configuration by integrating the LFC and the membrane reactor was designed for a prototype of a low temperature solar-driven biogas steam reforming process. A membrane reactor simulation model was built by ASPEN plus and conducted for biogas steam reforming under low temperatures (450 to 500 °C). Comparing to the simulation results obtained by a conventional tubular reactor, both methane conversion and H_2 productivity were significantly increased by using a H_2 selective membrane reactor even at relative low operating temperatures. The simulation data proved that the LFC afforded to supply the heat duty required by the membrane reactor. The current simulation work could have implications for the development of a low-cost solar-driven biogas steam reforming technology.

Acknowledgement

References

1. F. Wang, J. Tan, L. Ma, Y. Leng, Effects of key factors on solar aided methane steam reforming in porous medium thermochemical reactor, Energy Convers. Manag. 103 (2015) 419–430. doi:10.1016/j.enconman.2015.06.049.

2. D.G. Avraam, T.I. Halkides, D.K. Liguras, O.A. Bereketidou, M.A. Goula, An experimental and theoretical approach for the biogas steam reforming reaction, Int. J. Hydrogen Energy. 35 (2010) 9818–9827. doi:10.1016/j.ijhydene.2010.05.106.

3. M. Ashrafi, C. Pfeifer, T. Pröll, H. Hofbauer, Experimental study of model biogas catalytic steam reforming: 2. Impact of sulfur on the deactivation and regeneration of Ni-based catalysts, Energy and Fuels. 22 (2008) 4190–4195. doi:10.1021/ef8000828.

4. L.B. Braga, J.L. Silveira, M.E. Da Silva, C.E. Tuna, E.B. Machin, D.T. Pedroso, Hydrogen production by biogas steam reforming: A technical, economic and ecological analysis, Renew. Sustain. Energy Rev. 28 (2013) 166–173. doi:10.1016/j.rser.2013.07.060.

5. A. Iulianelli, S. Liguori, Y. Huang, A. Basile, Model biogas steam reforming in a thin Pd-supported membrane reactor to generate clean hydrogen for fuel cells, J. Power Sources. 273 (2015) 25–32. doi:10.1016/j.jpowsour.2014.09.058.

6. P. Kolbitsch, C. Pfeifer, H. Hofbauer, Catalytic steam reforming of model biogas, Fuel. 87 (2008) 701–706. doi:10.1016/j.fuel.2007.06.002.

7. R. Gu, J. Ding, Y. Wang, Q. Yuan, W. Wang, J. Lu, Heat transfer and storage performance of steam methane reforming in tubular reactor with focused solar simulator, Appl. Energy. 233–234 (2019) 789–801. doi:10.1016/j.apenergy.2018.10.072.

8. M. Böhmer, U. Langnickel, M. Sanchez, Solar steam reforming of methane, Sol. Energy Mater. 24 (1991) 441–448. doi:10.1016/0165-1633(91)90081-U.

9. V.K. Jebasingh, G.M.J. Herbert, A review of solar parabolic trough collector, Renew. Sustain. Energy Rev. 54 (2016) 1085–1091. doi:10.1016/j.rser.2015.10.043.

10. H.J. Alves, C. Bley Junior, R.R. Niklevicz, E.P. Frigo, M.S. Frigo, C.H. Coimbra-Araújo, Overview of hydrogen production technologies from biogas and the applications in fuel cells, Int. J. Hydrogen Energy. 38 (2013) 5215–5225. doi:10.1016/j.ijhydene.2013.02.057.

11. M.A. Nieva, M.M. Villaverde, A. Monzón, T.F. Garetto, A.J. Marchi, Steam-methane reforming at low temperature on nickel-based catalysts, Chem. Eng. J. 235 (2014) 158–166. doi:10.1016/j.cej.2013.09.030.

12. G. Di Marcoberardino, S. Foresti, M. Binotti, G. Manzolini, Potentiality of a biogas membrane reformer for decentralized hydrogen production, Chem. Eng. Process. Process Intensif. 129 (2018) 131–141. doi:10.1016/j.cep.2018.04.023.

13. E. Fernandez, A. Helmi, J.A. Medrano, K. Coenen, A. Arratibel, Palladium based membranes and membrane reactors for hydrogen production and purification : An overview of research activities at Tecnalia and TU / e, Int. J. Hydrogen Energy. 2 (2017) 13763–13776. doi:10.1016/j.ijhydene.2017.03.067.

14. N. El Gharbi, H. Derbal, S. Bouaichaoui, N. Said, A comparative study between parabolic trough collector and linear Fresnel reflector technologies, Energy Procedia. 6 (2011) 565–572. doi:10.1016/j.egypro.2011.05.065.

15. A. Rovira, R. Barbero, M. José, R. Abbas, F. Varela, Analysis and comparison of Integrated Solar Combined Cycles using parabolic troughs and linear Fresnel reflectors as concentrating systems, Appl. Energy. 162 (2016) 990–1000. doi:10.1016/j.apenergy.2015.11.001.

16. G. Zhu, T. Wendelin, M.J. Wagner, C. Kutscher, History , current state , and future of linear Fresnel concentrating solar collectors, Sol. Energy. 103 (2014) 639–652. doi:10.1016/j.solener.2013.05.021.

17. Y. Jin, Z. Rui, Y. Tian, Y. Lin, Y. Li, Sequential simulation of dense oxygen permeation membrane reactor for hydrogen production from oxidative steam reforming of ethanol with ASPEN PLUS, Int. J. Hydrogen Energy. 35 (2010) 6691–6698. doi:10.1016/j.ijhydene.2010.04.042.

18. F. Gallucci, L. Paturzo, A. Basile, Hydrogen Recovery from Methanol Steam Reforming in a Dense Membrane Reactor : Simulation Study, Ind. Eng. Chem. Res. 43 (2004) 2420–2432.

19. G. Ye, D. Xie, W. Qiao, J.R. Grace, C.J. Lim, Modeling of fluidized bed membrane reactors for hydrogen production from steam methane reforming with Aspen Plus, Int. J. Hydrogen Energy. 34 (2009) 4755–4762. doi:10.1016/j.ijhydene.2009.03.047.

20. A. Brunetti, A. Caravella, G. Barbieri, E. Drioli, Simulation study of water gas shift reaction in a membrane reactor, J. Memb. Sci. 306 (2007) 329–340. doi:10.1016/j.memsci.2007.09.009.

21. W.H. Chen, W.Z. Syu, C.I. Hung, Numerical characterization on concentration polarization of hydrogen permeation in a Pd-based membrane tube, Int. J. Hydrogen Energy. 36 (2011) 14734–14744. doi:10.1016/j.ijhydene.2011.08.043.

22. SOLSRGIS, Solar resource maps and GIS data for 180+ countries | Solargis, Solargis. (2019) All. https://solargis.com/maps-and-gis-data/download/zimbabwe.

23. P.L. Singh, R.M. Sarviya, J.L. Bhagoria, Thermal performance of linear Fresnel reflecting solar concentrator with trapezoidal cavity absorbers, Appl. Energy. 87 (2010) 541–550. doi:10.1016/j.apenergy.2009.08.019.