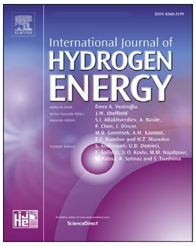
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Enhancement of membrane hydrogen separation on glycerol steam reforming in a fluidized bed reactor

Xuesong Yang, Shuai Wang*, Zhenjie Li, Kai Zhang, Bowen Li

School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China

ARTICLE INFO

Article history:
Received 5 July 2018
Received in revised form
4 August 2018
Accepted 9 August 2018
Available online xxx

Keywords:
Glycerol steam reforming
Membrane separation
Fluidized bed
Numerical simulation
Hydrogen

ABSTRACT

Membrane hydrogen separation can effectively promote fuel conversion and hydrogen yield by means of altering chemical equilibrium of reforming reactions. In this work, the enhancing process of glycerol steam reforming via a fluidized bed membrane reactor is numerically investigated. Under the framework of the Euler-Euler method, chemical kinetic model is implemented and the reforming performance with and without membrane separation is compared. The effect of densified zones caused by membrane separation is examined. Meanwhile, the impacts of operating parameters including hydrogen partial pressure on the permeate side and fuel gas velocity on densified zones and hydrogen yield are evaluated. The results demonstrate that the excessive reduction of hydrogen partial pressure on the permeate side and the increase of feed gas velocity are detrimental to fuel conversion and hydrogen yield.

Introduction

Hydrogen is regard as an environmentally friendly energy source owing to its clean and renewable characteristic [1,2]. Most of hydrogen production methods come from fossil-fuel-based thermo-catalytic reactions. Among them, th reforming technology has become a main approach to produce hydrogen from natural gas [3]. Crude glycerol as a byproduct in biodiesel production process provides a promising way for hydrogen production as a result of its renewability [4,5], which is also a potentially important way to the utilization of biomass resources.

The catalytic steam reforming technology establishes a bridge between glycerol utilization and hydrogen production, which has attracted more and more concerns [6–8]. However, a majority of researches concentrate on the glycerol reforming performance in a fixed bed reactor by means of experimental methods and thermodynamic analysis. The carbon deposition on the catalyst surface caused by the reforming process in a fixed bed will lead to the deactivation or descending capacity of catalyst. In addition, there is a poor uniformity of temperature distribution. A fluidized bed reactor has its excellent potential in solving the above mentioned problems owing to a good interphase heat transfer under the fluidization state. Moreover, it provides a possibility of continuous operation and catalyst regeneration. Remón et al. [9] conducted an experimental study of crude glycerol reforming in a fluidized bed reactor and discussed the dependence of glycerol conversion and carbon formation on operating parameters. It was

---

* *Corresponding author.*
E-mail address: shuaiwang@hit.edu.cn (S. Wang).

https://doi.org/10.1016/j.ijhydene.2018.08.069

Please cite this article in press as: Yang X, et al., Enhancement of membrane hydrogen separation on glycerol steam reforming in a fluidized bed reactor, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.08.069

pointed out that high hydrogen selectivity could be achieved under a reasonable temperature range, which was also limited by glycerol concentration. Dou et al. [10] conducted a two-dimensional simulation to investigate the glycerol steam reforming performance in a fluidized bed. The model was further verified by the experimental data. Wang et al. [11] employed CaO-based sorbents and simulated the sorption-enhancing reforming process in a fluidized bed reactor, where the bubble-based drag model was implemented to consider bubble effects on interphase force. The predicted results demonstrated that the CO_2 absorption process could provide the required heat of glycerol reforming process so as to attain the auto-thermal condition of the system.

The hydrogen production via the reforming technology is restricted by chemical equilibrium. The development of enhancing methods is essential for the increase of hydrogen yield. The hydrogen separation via the membrane can shift chemical equilibrium into the direction that favors hydrogen production [12,13]. Wang et al. [14] carried out a thermodynamic analysis of glycerol steam reforming with hydrogen separation and discussed the influence of operating parameters on hydrogen yield and carbon formation under different hydrogen removal extents. It was found that the increase of hydrogen separation fraction could restrict carbon formation. Leal et al. [15] further discussed the auto-thermal reforming process of crude glycerol via CO_2 removal and hydrogen separation. It was concluded that hydrogen separation via membrane reformers could achieve the maximum hydrogen yield at a low temperature. With regards to the fluidized bed membrane reactor, Mahecha-Botero et al. [16] developed a comprehensive reactor model where the multiple phases and regions were taken into account. Mass transfer and fluidization hydrodynamics along the reactor were discussed. Marín et al. [17] employed a fluidized bed as the air feeding system into the internal fixed bed reactor via the membrane. By comparing with the traditional fixed bed, it was emphasized that the propagation of flames could be avoided via the fluidized bed membrane reactor. Tan et al. [18] performed a discrete particle simulation to investigate the impact of H_2 extraction via membranes. The results revealed that densified zones had a negligible influence on mass transfer resistance. Lu et al. [19] developed a three-phase phenomenological model to investigate the auto-thermal methane reforming in a fluidized bed reactor with O_2 permeable membranes. It was found that the performance could be promoted via membrane reactors with a small amount of catalysts load. From the above mentioned, there are less reports about dynamic behaviors for the reforming process in a fluidized bed membrane reactor.

In this paper, the glycerol steam reforming process in a fluidized bed membrane reactor is numerically studied where membrane hydrogen separation is employed as the enhancing reforming approach. Based on the Euler-Euler framework, chemical kinetic model is implemented and the glycerol reforming performance with and without hydrogen separation are compared. Particle volume fraction and gas component distribution are predicted. The effects of hydrogen membrane separation on fuel conversion and hydrogen yield under different operating conditions are investigated.

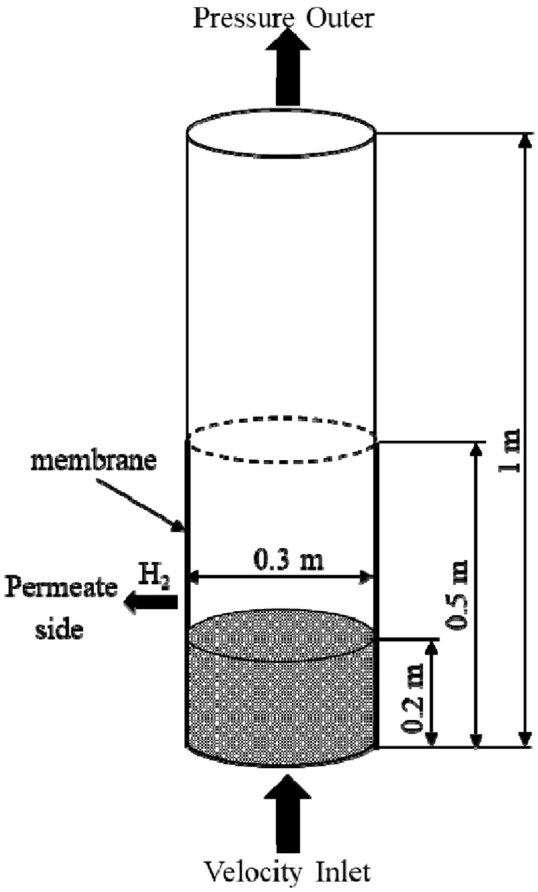


Fig. 1 – **Sketch of glycerol reforming system with membrane separation.**

Mathematic model

Governing equations

To model flow behaviors in a fluidized bed reactor, the Euler-Euler model is used where the solid phase is assumed to be spherical with a uniform size. The main governing equations comprise continuity equations, conservation equations of momentum and energy, species transportation equation and

Table 1 – **Main operating parameters in the simulation.**

Description	Simulation	Unit
Reactor height	1.0	m
Reactor diameter	0.3	m
Particle diameter	87.5	μm
Particle density	2650	kg/m^3
Initial solid height	0.2	m
Membrane height	0.5	m
Initial solid volume fraction	0.53	–
Inlet gas velocity	0.5–0.7	m/s
Inlet gas composition ($C_3H_8O_3/H_2O/N_2$)	0.02:0.12:0.86	–
Inlet temperature	873	K
Pressure outlet	0.1	MPa
H_2 partial pressure on permeate side	0.0001–0.0013	MPa

Please cite this article in press as: Yang X, et al., Enhancement of membrane hydrogen separation on glycerol steam reforming in a fluidized bed reactor, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.08.069