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Research article

Investigation into enhancing reforming of biomass-derived glycerol in a membrane reactor with hydrogen separation

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ABSTRACT

In order to investigate the hydrogen separation enhancing effect on glycerol steam reforming performance, the simulation is carried out via a packed bed membrane reactor, where the porous media model is employed to model the distribution of catalyst and the non-isothermal environment in the reactor is considered. The reforming performances with and without membranes are compared. The results indicate that the membrane separation can promote the hydrogen production at a low temperature. The impacts of operating parameters including catalyst load, fuel gas temperature, sweep gas velocity and sweep gas temperature on the enhancement of the reforming performance are analyzed. The results reveal that the membrane separation is very sensitive to the temperature variation under different operating conditions. It is essential to properly control the operating parameter so as to achieve the promotion of hydrogen yield with low cost of energy.

1. Introduction

Crude glycerol as a by-product during the biodiesel production process is an excellent alternative to methane, which has been applied to the hydrogen production industry via reforming methods [1, 2]. In order to improve the fuel conversion and the hydrogen yield, it is necessary to develop the enhanced methods for glycerol steam reforming [3]. Dou et al. [4] performed an experimental study on the sorption-enhanced glycerol steam reforming process in a fixed bed using CaO as sorbents. It was pointed out that the hydrogen yield could be increased by the CO_2 removal, which was restricted by the reactivity of sorbents. In addition, Dou et al. [5, 6] took the advantage of bifunctional oxygen carriers for catalytic and redox reactions and introduced the chemical looping system to investigate the sorption-enhanced hydrogen production with the CO_2 removal. The results revealed that the combination of the oxygen carriers and the sorbents in a low-energy chemical looping process could achieve the high-purity hydrogen production. Meanwhile, the capacity of catalysts and sorbents could be retained for multiple cycles. Wess et al. [7] evaluated the capacity of CaO-based sorbents on the basis of a thermodynamic analysis and emphasized that the sorption-enhanced performance depended on the presence of Ca$(OH)_2$. As mentioned above, the sorption-enhanced method can improve the hydrogen production. However, it is hindered owing to the formation of Ca$(OH)_2$ at a low temperature. The dependence of sorbent reactivity on operating temperature is significant.

The hydrogen separation technology via membrane reactors is another effective enhanced method for reforming reactions, which has attracted more and more concerns [8]. Spallina et al. [9] experimentally investigated the ethanol auto-thermal reforming performance in a fluidized bed reactor with the Pd-based membrane for hydrogen separation and examined the influence of the operating conditions. Wu et al. [10] integrated the two methods of H_2 membrane separation and CO_2 sorption to analyze the dual-enhanced steam methane reforming performance by means of thermodynamic calculations and experiments. It was found that the reaction temperature could be reduced with a high fuel conversion. In recent years, the application of hydrogen separation in the glycerol steam reforming process has been studied. Wang et al. [11] evaluated the glycerol steam reforming with hydrogen separation and analyzed the impacts of the operating parameters on the basis of Gibbs free energy minimization. It was pointed out that the hydrogen removal could greatly reduce the reaction temperature with a high hydrogen yield. Leal et al. [12] and Wang et al. [13] conducted thermodynamic studies of crude glycerol autothermal reforming with hydrogen separation. It was found that the hydrogen removal was not beneficial to achieve the autothermal process. Although there have been some reports on the glycerol reforming with hydrogen separation, the non-uniform distribution of local temperatures caused by the reactions has not been considered.

Numerical simulation is an important tool to get a deep insight into the reaction performance inside the reactor [14]. Ma et al. [15] numerically studied the ethanol steam reforming performance in a catalytic membrane reactor. The model prediction was consistent with

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experimental data. The results revealed that the hydrogen yield was dependent on the membrane permeance. Sajjadi et al. [16] conducted a three-dimensional simulation to study the convection and diffusion in a packed membrane reactor for biodiesel production. It was found that the diffusion was more obvious at the membrane wall. The convection was influenced by the fluid velocity and the component concentration. Moreover, Marın et al. [17] carried out an evaluation of the butane partial oxidation process in a fluidized bed membrane reactor. The results indicated that the membrane reactor could give a better performance with a higher selectivity than the traditional reactor. Meanwhile, the fuel could be avoided mixing with air at the entrance, which reduced the flammability risk. Although some numerical investigations have been conducted on the membrane reactors, there are few numerical studies on the glycerol reforming performance in membrane reactors.

This paper aims to evaluate the enhancing effect of hydrogen removal in the glycerol steam reforming process via the membrane reactor in the form of a packed bed by means of numerical methods, which provides the possibility for the design and optimization of the reactors and operating conditions. The local temperature variation is taken into account by the implementation of the non-isothermal process. The packed bed is modeled using a porous media model and the local temperature variation caused by reactions in a reactor is taken into account. Besides, the gas composition distributions with and without hydrogen removal are compared. Meanwhile, the sensitivity of the enhanced reforming reaction in a packed bed reactor to operating parameters is conducted.

2. Computational theory

2.1. Governing equations

In the present work, the enhancing effect of hydrogen separation on the glycerol reforming process via membrane reactors is investigated. The assumption is made that the flow is laminar and the gas component obeys the ideal gas law. The membrane separates the reactor into two parts: the retentate side and the permeate side. The main governing equations are summarized as follows [15, 18]:

The momentum balance equation of the permeate side is written as follows:

$$\rho(\vec{u}\cdot\nabla)\vec{u} = \nabla\cdot[-pI + \mu(\nabla\vec{u} + (\nabla\vec{u})^T)] + F \quad (1)$$

For the retentate side, the porous media model is employed to model the packed catalyst layer in a fixed bed reactor. The momentum balance equation is expressed as below:

$$\frac{\rho}{\varepsilon_p}(\vec{u}\cdot\nabla)\vec{u}\frac{1}{\varepsilon_p} = \nabla\cdot[-pI + \mu/\varepsilon_p(\nabla\vec{u} + (\nabla\vec{u})^T)] - (\mu k^{-1} + \beta_F|\vec{u}|)\vec{u} + F \quad (2)$$

where ε_p is the porosity of the catalytic bed and β_F is the Forchheimer coefficient.

The energy balance equation and the species transportation equation are expressed as below:

$$\rho C_p\vec{u}\cdot\nabla T = \nabla\cdot(\kappa\nabla T) + Q \quad (3)$$

$$\nabla\cdot\left(-\rho w_i\sum_k D_{ik}\left(\nabla x_k + (x_k - w_k)\frac{\nabla p}{p}\right) + \rho w_i\vec{u}\right) = R_i \quad (4)$$

where Q and R_i are the heat and mass source terms owing to chemical reactions. The glycerol steam reforming reactions are considered to mainly include the glycerol decomposition reaction and the water-gas-shift reaction, which are expressed as follows:

$$C_3H_8O_3 \leftrightarrow 4H_2 + 3CO \qquad \Delta H_{r1} = 251.18\ \text{kJ/mol} \quad (R1)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta H_{r2} = -41.0\ \text{kJ/mol} \quad (R2)$$

Table 1
Kinetic parameters in glycerol steam reforming reaction [19].

Component	A (mol m^{-2} s^{-1} kP$^{a-(\beta+\gamma)}$)	E_a (kJ/mol)	β	γ
$C_3H_8O_3$	0.036	63.3	0.253	0.358
H_2	0.468	67.28	0.253	0.274
CO_2	0.074	64.06	0.281	0.403
CO	0.062	61.73	0.308	−0.065
CH_4	0.555	100.9	0.601	0.393

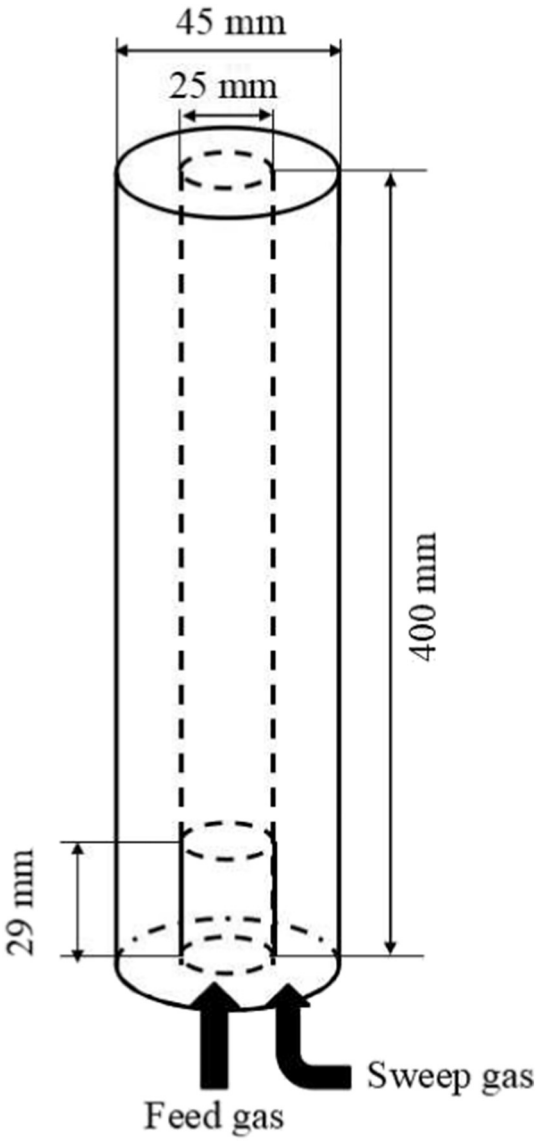

Fig. 1. Sketch of glycerol reforming system with membrane separation.

In addition, some side reactions may occur. Here, the methane production reactions are taken into account, which are expressed as below:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_{r3} = -206.0\ \text{kJ/mol} \quad (R3)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H_{r4} = -164.9\ \text{kJ/mol} \quad (R4)$$

From the analysis of Wang et al. [11], a high steam to glycerol feed ratio can avoid the carbon formation. In this work, the steam to glycerol feed ratio is 9.0. Hence, the carbon deposition reactions are assumed to be negligible [11]. A power law-type kinetic model is used to calculate the reaction rate of glycerol decomposition according to Cheng et al. [19]: