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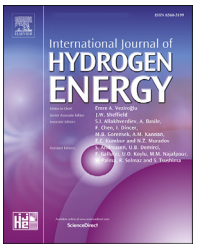

Assessment of sorption-enhanced crude glycerol steam reforming process via CFD simulation

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ABSTRACT

The sorption-enhanced glycerol reforming performance in a fluidized bed reactor is numerically studied with CaO and Li_4SiO_4 as CO_2 sorbents, where the multi-fluid model with the kinetic theory of granular flow is employed to carry out three-dimensional simulations. The ethanol is treated as the impurity in the crude glycerol and its effect on the reforming performance is evaluated. It is found that the hydrogen yield is higher using the crude glycerol with the ethanol owing to a greater reaction rate of the ethanol. An increase of the temperature is beneficial to the glycerol conversion and hydrogen production. Meanwhile, the enhancing effect on the reforming performance of CaO and Li_4SiO_4 is compared. The result demonstrates that the enhancing reforming effect of the Li_4SiO_4-based sorbent is similar to that of the CaO-based sorbent. At a high temperature, the CaO-based sorbent has a better performance.

Introduction

Hydrogen, as a clean and renewable fuel, is a promising candidate for replacing fossil fuels and avoiding environment pollution in the future, which has attracted more and more concerns [1–3]. Glycerol steam reforming as the utilization of biodiesel byproduct provides an effective way for hydrogen production industry owing to its renewable characteristic and low price [4–8]. The conventional glycerol steam reforming produces the hydrogen with the release of carbon dioxide, which results in environmental concern. The sorption-enhanced reforming via in-situ CO_2 removal can reduce the CO_2 emission and promote the fuel conversion via altering the reaction equilibrium limit [9,10]. Li et al. [11] conducted a thermodynamic evaluation of glycerol steam reforming with CO_2 adsorption and discussed the effects of different parameters on coke formation and energy efficiency. The results revealed that the CO_2 separation can reduce coke formation and promote the energy efficiency. A continuous sorption-enhanced glycerol steam reforming was experimentally investigated [12]. It was concluded that there was no significant change of activity for continuous reaction-regeneration of catalyst and sorbent. Wang et al. [13] synthesized a multi-functional catalysts for the sorption-enhanced steam reforming of glycerol with CO_2 removal and conducted an experimental evaluation. It was pointed out that the catalyst activity determined the multi-cycles performance for the high-purity hydrogen production.

Most researches about the sorption-enhanced glycerol reforming process have focused on fixed bed reactors [14–16]. Compared to fixed bed reactors, fluidized bed reactors have better capabilities in heat transfer and mass transfer. In addition, continuous regeneration of sorbent and catalyst can be achieved in a fluidized bed reactor to meet the need of looping operation [17]. Dou et al. [18] and Shuai et al. [19] implemented the two-fluid model to study the glycerol

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reforming process in a fluidized bed reactor and assessed the influence of operating parameters. It was demonstrated that operating parameters greatly influenced the hydrogen yield and fuel conversion in a fluidized bed reactor. Carlo et al. [20] investigated the sorption enhanced methane steam reforming performance via CFD approaches and analyzed the dependence of the hydrogen yield on the conversion and ageing of bed material. However, there are few literatures about the sorption-enhanced glycerol reforming process in a fluidized bed reactor.

During the sorption-enhanced reforming process, the sorption process is restricted by the sorbent type. Different sorbents have their separate suitable operating range. He et al. [21] analyzed the effect of integration of CO_2 removal by means of a thermodynamic analysis and an experimental assessment using CaO-based sorbents at 500–750 °C. It was found that the CO_2 absorption with CaO-based sorbents could reduce the reaction temperature and restrict the catalyst coked. Ni et al. [22] used Li_2ZrO_3 as CO_2 sorbents to experimentally study the hydrogen production process in a sorption enhanced chemical looping glycerol reforming system. The results revealed that the activity of the potassium promoted Li_2ZrO_3 sorbent was good in the sorption enhanced process. Chen et al. [23] compared different sorbents (HTC and Li_2ZrO_3) on sorption-enhanced reforming processes at low temperatures through numerical simulations. It was pointed out that the impact of operating parameters depended on the sorbent type.

In the biodiesel production process, crude glycerol consists of many impurities which affect the conversion rate of glycerol and hydrogen selectivity in the glycerol reforming process. Remón et al. [24] investigated the effect of acetic acid, methanol and potassium hydroxide on crude glycerol reforming processes by means of experimental methods. It was found that the impact of impurities on liquid composition was more significant. Leal et al. [25] discussed the impurity effect on sorption-enhanced reforming performance on the basis of the Gibbs free energy minimization method. The results indicated that the amount of sorbents to achieve energetically neutral condition depended on the impurity fraction in the crude glycerol. Seretis et al. [26] conducted experiments to analyze the impact of crude glycerol concentration on the product selectivity. The results exhibited that the presence of the impurity could hinder the hydrogenolysis of crude glycerol.

In this work, a three-dimensional CFD simulation is carried out to investigate the sorption-enhanced crude glycerol reforming performance in a fluidized bed reactor where the multi-fluid model is employed with the bubble-based drag model to describe the meso-scale structure effect. The ethanol effect on the sorption-enhanced glycerol reforming process is assessed. Meanwhile, the performance of different sorbents with crude glycerol is compared.

Mathematical model

Based on the framework of the multi-fluid model, a bubble-based drag model is employed to reflect the bubble impact on interphase force in a binary mixture system. The kinetic theory of polydisperse particles is used to describe the interaction between catalyst and sorbent [27]. The reactive kinetic model is incorporated to characterize the sorption-enhanced glycerol reforming reaction process. The detailed model descriptions are summarized in the following section.

Governing equations

In the multi-fluid model, each solid phase is assumed to have a mean diameter and density. The governing equations consist of continuity and momentum balance equations, energy balance equations, species transportation equation. The detailed expressions can be listed in Table 1.

In the momentum balance equations, β represents interphase drag coefficient. A great deal of researchers have developed different drag models to characterize this important parameter. The energy minimization multi-scale (EMMS) model considering the mesoscale effect has been successfully applied in the simulations of gas-fluidized beds [28]. Here, a bubble-based multi-scale drag model is adopted [29,30]. The expression of the drag coefficient is written as follows:

$$\beta_{\text{bubble-EMMS}} = \frac{\varepsilon_g^2 \boldsymbol{F}_{\text{gs}}}{\boldsymbol{U}_{\text{slip}}} = \frac{\varepsilon_g^2}{\boldsymbol{U}_{\text{slip}}}[(1-\delta_b)n_e\boldsymbol{F}_{\text{de}} + \delta_b n_b \boldsymbol{F}_{\text{db}}] \quad (1)$$

The local structural parameters can be solved via a series of nonlinear equations to calculate the above multi-scale drag coefficient. The detailed solution can be found in Wang et al. [31].

In order to characterize the fluctuating behaviors of particles in a binary-mixture system, the granular temperature transportation equation is introduced, as shown in Eq. (T1-9). The constitutive correlations are required as the closure of the

Table 1 – Governing equations in the multi-fluid model.

1. Continuity equations

$$\frac{\partial}{\partial t}(\varepsilon_g\rho_g) + \frac{\partial}{\partial x_i}(\varepsilon_g\rho_g u_g) = S_g \quad \text{(T1-1)}$$

$$\frac{\partial}{\partial t}(\varepsilon_m\rho_m) + \frac{\partial}{\partial x_i}(\varepsilon_m\rho_m u_{mi}) = S_m \quad \text{(T1-2)}$$

2. Momentum conservation equations

$$\left[\frac{\partial}{\partial t}(\varepsilon_g\rho_g u_{gi}) + \frac{\partial}{\partial x_j}(\varepsilon_g\rho_g u_{gj}u_{gi})\right] = -\varepsilon_g\frac{\partial P_g}{\partial x_j} + \frac{\partial \tau_{gij}}{\partial x_j} + \varepsilon_g\rho_g g_i - \beta(u_{gi} - u_{mi}) + S_g u_{gi} \quad \text{(T1-3)}$$

$$\left[\frac{\partial}{\partial t}(\varepsilon_m\rho_m u_{mi}) + \frac{\partial}{\partial x_j}(\varepsilon_m\rho_m u_{mj}u_{mi})\right] = -\varepsilon_m\frac{\partial P_g}{\partial x_j} + \frac{\partial \tau_{mij}}{\partial x_j} + \varepsilon_m\rho_m g_i - \nabla p_m + \beta(u_{gi} - u_{mi}) + S_m u_{mi} \quad \text{(T1-4)}$$

3. Energy conservation equations

$$\varepsilon_g\rho_g C_{pg}\left(\frac{\partial T_g}{\partial t} + U_{gj}\cdot\frac{\partial T_g}{\partial x_j}\right) = -\frac{\partial q_{gi}}{\partial x_i} + \sum_{m=1}^{M}\gamma_{gm}(T_m - T_g) - \Delta H_g \quad \text{(T1-5)}$$

$$\varepsilon_m\rho_m C_{pm}\left(\frac{\partial T_m}{\partial t} + U_{mj}\cdot\frac{\partial T_m}{\partial x_j}\right) = -\frac{\partial q_{mi}}{\partial x_i} - \gamma_{gm}(T_m - T_g) - \Delta H_m \quad \text{(T1-6)}$$

4. Species transportation equations

$$\frac{\partial}{\partial t}(\varepsilon_g\rho_g X_{gn}) + \frac{\partial}{\partial x_i}(\varepsilon_g\rho_g X_{gn}U_{gi}) = \frac{\partial}{\partial x_i}\left(D_{gn}\frac{\partial X_{gn}}{\partial x_i}\right) + S_{g,n} \quad \text{(T1-7)}$$

$$\frac{\partial}{\partial t}(\varepsilon_m\rho_m X_{mn}) + \frac{\partial}{\partial x_i}(\varepsilon_m\rho_m X_{mn}U_{mi}) = \frac{\partial}{\partial x_i}\left(D_{mn}\frac{\partial X_{mn}}{\partial x_i}\right) + S_{m,n} \quad \text{(T1-8)}$$

5. Granular temperature transportation equation

$$\frac{3}{2}\varepsilon_m\rho_m\left[\frac{\partial \Theta_m}{\partial t} + U_{mj}\frac{\partial \Theta_m}{\partial x_j}\right] = \frac{\partial}{\partial x_j}\left(\kappa_m\frac{\partial \Theta_m}{\partial x_j}\right) + \tau_{mij}\frac{\partial U_{mi}}{\partial x_j} + \prod_m - \gamma \quad \text{(T1-9)}$$

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