CFD modelling of CO_2 capture in the SE-SMR process in the fluidized bed reactors

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A three dimensional Eulerian two-fluid model with an in-house code was developed to simulate the gas-particle two phase flow in the fluidized bed reactors. The CO_2 capture with Ca-based sorbents in the steam methane reforming process was studied with such model incorporating the reaction kinetics. The sorption enhanced steam methane reforming (SE-SMR) process (i.e. SMR and adsorption of CO_2) and the regeneration process of sorbents were carried out in a bubbling fluidized bed reactor and a circulating fluidized bed reactor separately. The effects of pressure, temperature and inlet gas flow rate on the reactions were studied. The very high production of hydrogen in SE-SMR was obtained compared with the standard SMR process. It needs a rather long time to accomplish the sorbent regeneration.

1. Introduction

The hydrogen and CO_2 are main products in the steam methane reforming process. Hydrogen is an important material in the petroleum and chemical industries, and is considered to be a potential clean energy source. However, with the increasing impact of global warming caused mostly by increasing concentrations of greenhouse gases, the emission control of CO_2 as the most important greenhouse gas was concerned by many researchers. The process of sorption enhanced steam methane reforming (SE-SMR) is becoming an important topic due to its integration of hydrogen production and CO_2 separation. In this process, carbon dioxide is captured by an on-line sorbent, and the chemical equilibrium is shifted to the product side of the SMR reaction. Therefore, the higher hydrogen production may be obtained (Han and Harrison, 1994). The sorbent with the adsorbed carbon dioxide can be regenerated using the temperature or pressure swing desorption to release the CO_2 for storage or other treatment. The SE-SMR reactions can proceed at temperatures of about 200℃ lower than that for standard SMR process (Hufton et al., 1999).

Several researchers have reported the experimental work (Abanades et al., 2004; Hughes et al., 2004; Johnsen et al., 2006a) and theoritical studies (Prasad and Elnashaie, 2004; Johnsen et al., 2006b; Li and Cai, 2007; Lindborg and Jakobsen, 2009) on the SE-SMR process. A 3D numerical two-fluid model was developed in this paper. The

performances of the SE-SMR process with CaO sorbent and the regeneration of sorbent were studied in the fluidized bed reactors.

2. Numerical Models

2.1 Hydrodynamic models

A 3D non-axisymmetric two-fluid model has been developed for the simulation of the SE-SMR process in fluidized bed reactors. The kinetic theory of granular flow and the k-ε turbulence model are used to describe the particle-particle interactions and the gas phase turbulence quantities, respectively. The drag model presented by Benyahia et al. (2006) is used in this work to account for the gas-solid interactions. The detailed descriptions of the model and solution methods can be found in Lindborg et al. (2007), Lindborg and Jakobsen (2009).

2.2 Kinetic models

Three-reaction models for SMR reactions from Xu and Froment (1989) are used in our simulations for the following three reactions:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad \Delta H_{298} = 206 \text{ kJ/mol} \tag{11}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = \text{-41 kJ/mol} \tag{12}$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \qquad \Delta H_{298} = 165 \text{ kJ/mol} \tag{13}$$

The reactions for CO_2 adsorption by CaO and sorbent regeneration are as follows:

$$CaO + CO_2 \Leftrightarrow CaCO_3 \qquad \Delta H_{298} = \text{-178 kJ/mol} \tag{14}$$

$$CaCO_3 \Leftrightarrow CaO + CO_2 \qquad \Delta H_{298} = 178 \text{ kJ/mol} \tag{16}$$
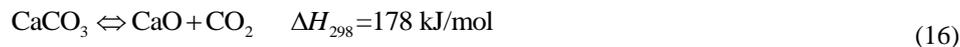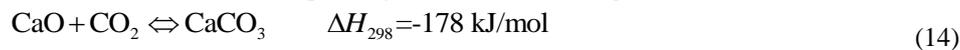
The rate equations for these two reactions are adopted from Sun et al. (2008) and Okunev et al. (2008) separately.

2. Results and Discussion

2.3 Hydrodynamic flow regimes

The catalytic steam methane reforming reactions and the CO_2 adsorption by sorbent take place simultaneously in a bubbling fluidized bed (BFB) reactor to provide sufficient residence time for the solid phase. The sorbent regeneration is considered to take place in a circulating fluidized bed (CFB) reactor with outside solid particle circulation. The solid particles have diameter of 500 μm and density of 1500 kg/m³. A schematic illustration of the reactors appears in Figure 1. The velocity profiles also display the heterogeneous structure of the bed and the non axial symmetric behavior of the solid flow.

2.4 Comparison between SE-SMR and standard SMR

Figure 2 shows the outlet hydrogen concentration for SMR and SE-SMR processes in the BFB reactor.
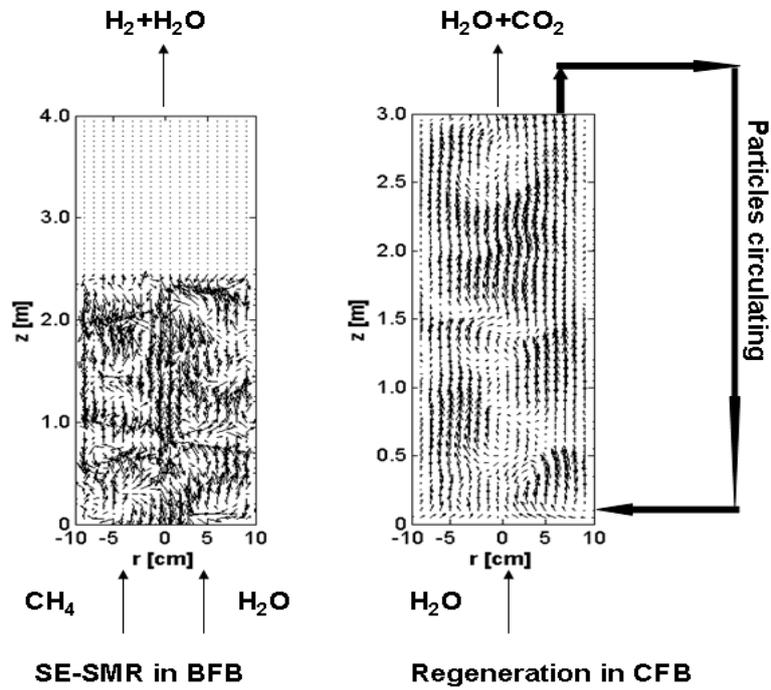
Figure 1: Schematic diagram of the reactors and velocity profiles in a vertical section.
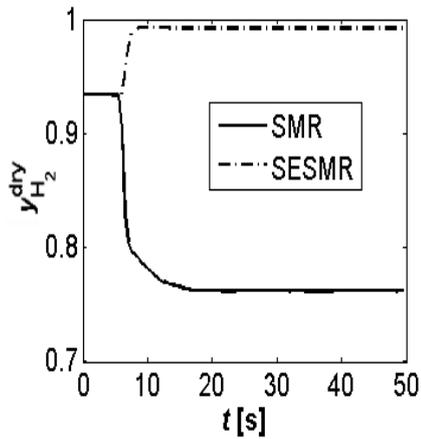
Figure 2: Average outlet concentration of hydrogen for SMR and SE-SMR ($u_0=0.3$ m/s, $T=848$ K, $r_{sc}=5:1$, $p=1$ bar)
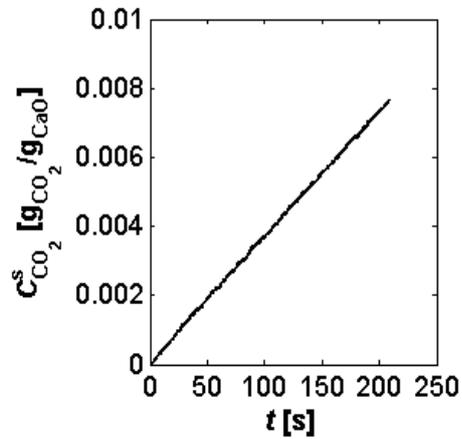
Figure 3 Average concentration of CO_2 in sorbents for SE-SMR. ($u_0=0.3$ m/s, $T=848$ K, $r_{sc}=5:1$, $p=1$ bar)

In the SMR results, the outlet concentration of H_2 is only 76%, and a lot of CO_2 and CH_4 are emitted out of the reactor. However in the simulations of SE-SMR process, both the conversion of methane and the adsorption of CO_2 are larger than 99%. In this

case the amount of CO_2 produced in methane reforming reactions can be considered to be adsorbed totally by the sorbent, the methane reforming and hydrogen production are greatly enhanced. Figure 3 shows that the adsorption rate of CO_2 by sorbents is constant until 210 s. The sorbent capacity is large enough for the simulated conditions.

2.5 Influence of pressure and inlet gas flow rate on CO_2 capture in SE-SMR
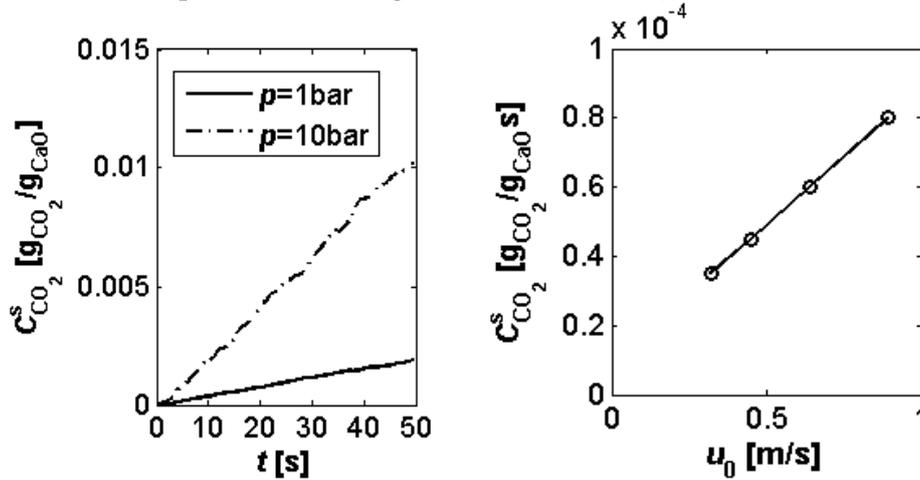
Figure 4 Average concentration of CO_2 in sorbents at different pressures(u_0=0.3 m/s, T=848 K, r_{sc}=5:1)

Figure 5 Average adsorption rate of CO_2 at different inlet gas flow rates(T=848 K, r_{sc}=5:1, p=1 bar)

Figure 4 shows that the adsorption rate of carbon dioxide by sorbents is higher at higher pressure. It is a natural result of the adsorption process. The CO_2 adsorption rate is increased as the gas flow rate increased (Fig. 5) and maintains constant with the time for the tested values of gas flow rate before the capacity of the sorbent was exhausted. The kinetic equation (17) for CO_2 desorption shows that the reaction rate of CO_2 adsorption depends on the partial pressure of CO_2 and the specific surface area of sorbent. At the reactor startup and at lower gas flow rates, the SMR CO_2 production rate is relatively low, thus the partial pressure of CO_2 in the gas phase is low and only a fraction of the surface area of the sorbent is occupied by CO_2. Under these SMR conditions the adsorption rate is low and far from its equilibrium. As a result, the adsorption rate will increase with the increase of partial pressure of CO_2 at the higher gas flow rates.

2.6 Sorbent Regeneration

In order to determine the time required for cleaning the CO_2 adsorbed in sorbents, the so-called self-circulation mode was simulated. In this mode, the amount of particles is fixed and equal to the initial amount of solids inside the reactor. The initial CO_2 mass fraction in carbonated sorbent was set to be 0.2 g (CO_2)/g (carbonated sorbent). In the process of sorbent regeneration, the particles with partly regeneration flowing out of the reactor outlet are re-entering into the reactor from the bottom. After such a re-circulation, the CO_2 fraction in the sorbent will be gradually decreased with time. The simulation results show that only 10% of the CO_2 content in the solid phase is released after 80s. It means that the kinetic rate of sorbent regeneration is not fast enough for

such kind of reactor and operation, or the initial fraction of CO_2 in sorbent was set too high compared to the residence time of solids in the CFB reactor.

The sorbent can be regenerated using the principles of temperature swing desorption or pressure swing desorption. Temperature swing desorption is easier to be carried out in CFBs. Figure 6 shows that the CO_2 concentrations in the gas phase are very different at different temperatures, but nearly constant over the reaction time. The CO_2 concentration in the gas phase increased very quickly at the beginning and then been kept to a constant value in the later period. The variation of CO_2 fraction in the sorbent with time is opposite to that of CO_2 concentrations in the gas phase. The difference of CO_2 fraction in the sorbent for different temperatures increases with the time. The reaction temperature has large effect on the desorption rate of CO_2.
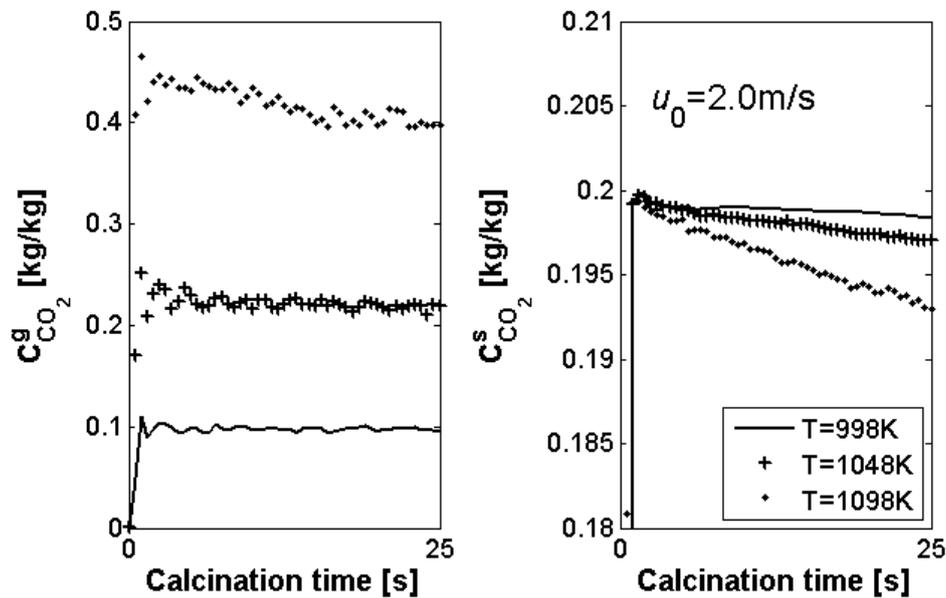
Figure 6: Variation of the outlet CO_2 concentration in gas and solid phase with time in the sorbent regeneration (p=1 bar, u_0=2.0 m/s).

3. Conclusions

The simulation results show that the integration of CO_2 sorption into the SMR process can increase the methane conversion to about 100% and produce higher amount of hydrogen in the bubbling fluidized bed reactor. The adsorption rate of CO_2 by the CaO sorbent is fast enough compared with the SMR rate. The sorbent can completely adsorb the CO_2 produced in the SE-SMR process at the gas flow rate up to 0.89 m/s for a long time. The adsorption rate of CO_2 is higher at higher gas flow rate and higher pressure.

Higher temperature can increase the desorption rate of CO_2 from sorbent. However, the reaction rate of CO_2 desorption from sorbent is still too slow in the circulating fluidized

bed reactor and the sorbent capacity is too large to complete the release of CO_2 under the continuous operating conditions of a CFB reactor with short residence time.

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