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SYNERGISTIC EFFECT BETWEEN CO_2 AND H_2O ON BIOMASS CHEMICAL LOOPING GASIFICATION WITH HEMATITE AS OXYGEN CARRIER

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ABSTRACT

A computational fluid dynamic (CFD) model has been developed for the fuel reactor of a chemical looping gasification (CLG) system with biomass as fuel and natural hematite as oxygen carrier (OC). By coupling the fluid dynamics and the chemical kinetics, the multiphase continuum model is able to describe the motion of gas and solid phases and the heterogeneous reactions between them, which take place in a bubbling fluidized bed reactor. The simulated average concentrations of five gas species fit the experimental data provided in the literature quite well, with a deviation for each gas component lower than 2%. This verified model is then applied to investigate the effects of various gasifying agents on the compositions of syngas. The results show that the biomass CLG performance is significantly improved in the presence of CO_2/H_2O and their mixture. Furthermore, synergistic effect of CO_2/H_2O mixture can be observed based on the evolution of char mass within the reactor.

Keywords: biomass gasification, chemical looping, synergistic effect, gasification atmosphere

1. INTRODUCTION

As a renewable and carbon neutral energy source, biomass is regarded as one of the promising solutions to cope with fossil fuel depletion and global warming by mitigating the CO_2 emissions in the atmosphere [1]. Increasing attention has been paid to various energy conversion technologies for biomass, among which gasification is undoubtedly a favorable one that can convert the solid fuel into valuable synthesis gases, including H_2 and CO [2]. Moreover, researchers have found that gasification process will show better performance in the presence of H_2O/CO_2 or their mixture, which are excellent gasifying agents for producing high quality syngas [3].

The chemical looping method is considered as one of the clean energy conversion technologies and has been extensively studied in the fields of combustion and gasification with various kinds of fuels [4,5]. Unlike the traditional gasification technologies, a chemical looping gasification (CLG) system consisting of two reactors (air reactor and fuel reactor) adopts the circulating solids called oxygen carrier (OC) instead of air or pure O_2 to be the oxygen source and convert solid fuels into syngas. The application of two reactors avoids the direct contact between fuel and air, thus eliminating both the dilution of syngas by N_2 and the potential generation of NO_x. Previous research has experimentally proved that the presence of metal oxides can evidently promote the biomass conversion and obtain higher efficiency in comparison to the conventional gasification process [6].

Numerical simulation is a useful approach to analyze the interaction between hydrodynamics and chemical kinetics. Li et al. [7] conducted a numerical investigation of syngas production in a fixed bed reactor, where the effects of operating temperature and steam ratio were also evaluated in terms of gas yield and gasification efficiency. Despite the considerable impact of CO_2 on char conversion [3], there have been few reports on the modelling of CLG process with CO_2 as gasifying agent.

The objective of this study is to develop a CFD model to simulate a CLG fuel reactor with biomass as fuel. The model is validated by the experimental results, after which it is applied to examine the effects of H_2O, CO_2 and

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their mixture on the solids conversion as well as the gasification performance.

2. METHODOLOGY

2.1 CFD model

The multi-fluid model has been employed in the present work. The governing equations for mass, momentum, energy and species transport of the Eulerian approach are the same as those used in the published reference [8].

2.2 Chemical reaction kinetic model

The reaction mechanisms adopted for this study are shown in Table 1. The two-step pyrolysis model considering the biomass devolatilization and tar cracking [9] is utilized in this work, with a composition of various gas species determined by the ultimate and proximate analyses in the experimental study of Huang et al. [6]. The expressions and constants for the reaction rates of char gasification, WGS reaction and metal oxide reduction are basically provided in [8]. Partial oxidation of hydrocarbons by Fe_2O_3 is incorporated into the chemical reaction equation according to our previous study [7].

Table 1
Reaction mechanisms used in this model.

Description	Reaction equation	
Primary pyrolysis	Biomass → Char + Wood gas (CH_4, C_2H_4, CO, CO_2, H_2, H_2O) + Tar	(R1)
Secondary pyrolysis	Tar → Wood gas (CH_4, C_2H_4, CO, CO_2, H_2, H_2O) + Tar_{inert}	(R2)
Char gasification	$C + CO_2 \rightarrow 2CO$	(R3)
	$C + H_2O \rightarrow CO + H_2$	(R4)
Water-gas shift (WGS)	$CO + H_2O \rightarrow CO_2 + H_2$	(R5)
Metal oxide reduction	$CH_4 + 9.75Fe_2O_3 \rightarrow 0.25CO + 0.5H_2 + 0.75CO_2 + 1.5H_2O + 6.5Fe_3O_4$	(R6)
	$C_2H_4 + 12Fe_2O_3 \rightarrow CO + CO_2 + H_2 + H_2O + 8Fe_3O_4$	(R7)
	$CO + 3Fe_2O_3 \rightarrow CO_2 + 2Fe_3O_4$	(R8)
	$H_2 + 3Fe_2O_3 \rightarrow H_2O + 2Fe_3O_4$	(R9)

2.3 Initial and boundary conditions

Four cases with different gasification atmosphere are examined in this study, as shown in Table 2. Case 1 is to simulate the experiment of Huang et al. [6] and acts as the base case, in which the volumetric flow of Ar is 1500L/h. For case 2 and 3, the fluidizing gas is a mixture of steam/Ar and CO_2/Ar, respectively, with the same total volume flow rate. Both steam and CO_2 are introduced into the reactor to investigate the synergistic effect during chemical looping gasification in case 4. The natural hematite containing 90 wt.% of Fe_2O_3 is packed inside the reactor with the initial height of 26 mm. The sawdust is continuously fed into the reactor through a drop tube, whose bottom is 30 mm from the porous plate. The operating temperature is set at 840 ℃. More details of the experimental setup can be found in [6].

Table 2
Various atmosphere adopted in this study.

Case No.	Gasification atmosphere
1	100% Ar
2	50% H_2O + 50% Ar
3	50% CO_2 + 50% Ar
4	25% H_2O + 25% CO_2 + 50% Ar

3. RESULTS AND DISCUSSION

3.1 Model validation

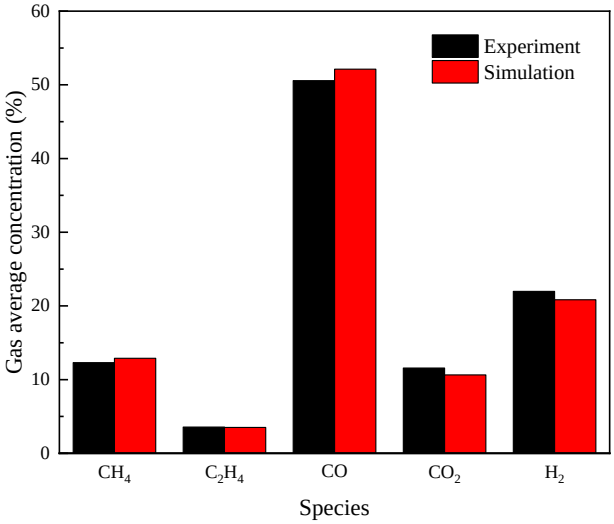
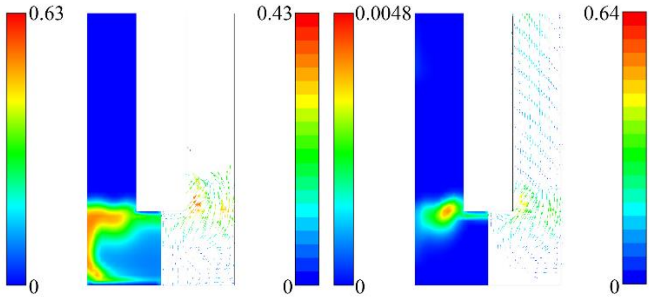


Fig. 1. Comparisons of gas average concentration between simulated results and experimental data.

In order to verify the numerical model, a comparison of the calculated concentration of five gas components and the experimental data is conducted [6], as shown in Fig. 1. It can be seen that a good agreement has been

reached, although the CO concentration is slightly overestimated by 1.6% due to a relatively higher reaction rate assumed for the Boudouard reaction R3, resulting in more CO_2 being converted to CO. Nonetheless, the discrepancy between simulated results and measured values is quite satisfactory, indicating that this model is capable of simulating the biomass CLG fuel reactor with the atmosphere of CO_2, H_2O and their mixture.

Fig. 2 shows the instantaneous contours of volume fractions and velocity vectors for both oxygen carries and biomass phases at approximately 10 min. It is observed that the biomass is mainly floating near the drop tube inlet due to its low density and the relatively high velocity of the rising gas stream, making this region the primary contact area between volatile gases and metal oxides.



(a) (b)

Fig. 2. Contours of volume fractions and velocity vectors (m/s) of oxygen carriers and biomass at *t* = 10 min. (a) Oxygen carriers and (b) Biomass.

3.2 Effects of gasifying agents

The biomass particles experience the thermal degradation once they enter the reactor, releasing the volatiles and producing char and tar. Simultaneously, char is gasified by CO_2 and H_2O via two main gasification reactions R3 and R4. During the simulation with various gasification atmosphere, the feeding rate of biomass and volume flow rate of fluidizing gas were kept constant. The time variation of total amount of char mass within the reactor for different cases (Fig. 3) demonstrates that the char mass of base case is around 3 times that of case 2 and 3, which proves that the addition of H_2O and CO_2 significantly promote the conversion of char into H_2 and CO. Moreover, case 4 displays the fastest consumption rate of char, suggesting the synergistic effect of CO_2/H_2O mixture in the gasification process. Similar results have been presented in literature [3,10]. In addition, char mass displays an increasing trend in all cases. This is because the mass fraction of Fe_2O_3 is descending, resulting in the decrease of the generation of gasifying agents from the metal oxide reduction reactions.

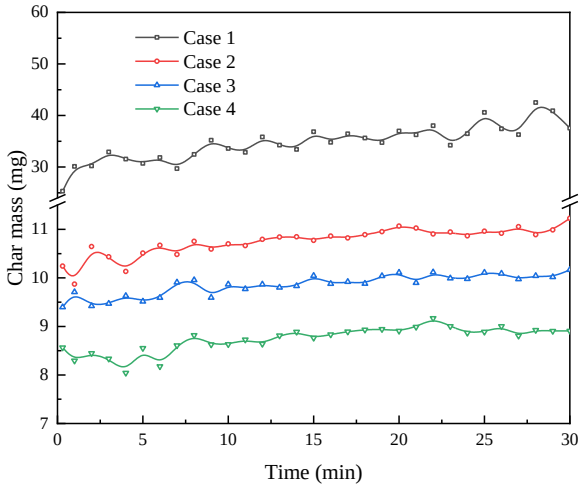


Fig. 3. Total amount of char mass within the reactor versus time for different cases.

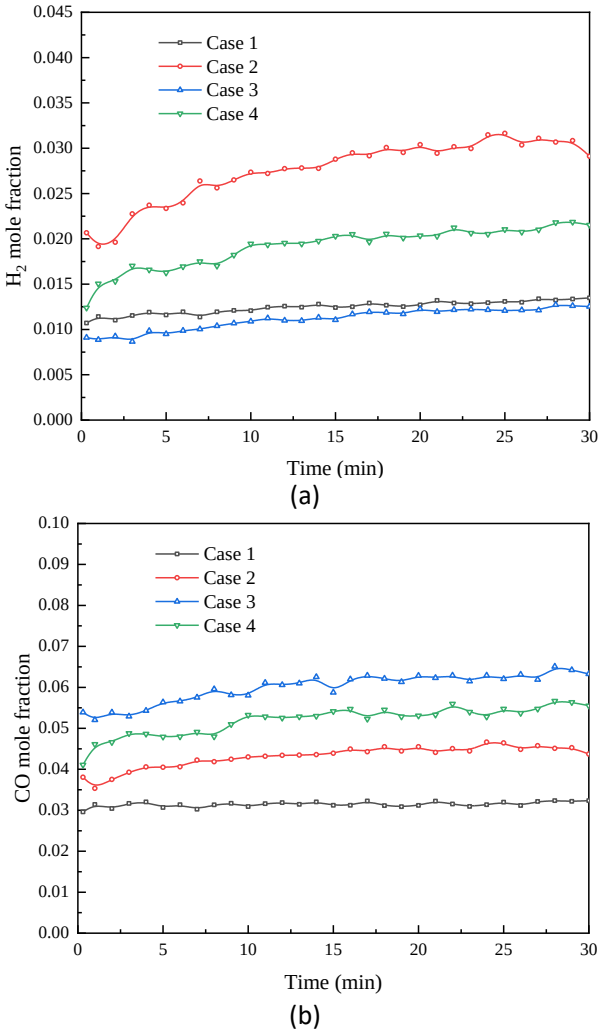


Fig. 4. Product gas mole fractions at the outlet of the reactor versus time for different cases. (a) H_2 and (b) CO.

CO and H_2 are two primary product gases in the gasification system. Fig. 4 shows the mole fractions of these two compositions at the outlet of the reactor as a function of time for different cases. The generation of both CO and H_2 are increased with the atmosphere containing H_2O (50% in case 2 and 25% in case 4), owing to the steam gasification reaction R4. However, the outlet mole fraction of H_2 is a bit lower in case 3 with the atmosphere of 50% CO_2 and 50% Ar than that in the base case with 100% Ar. This is attributed to the excessive CO_2 which is more conducive to the reverse reaction of R5, hence more H_2 is converted into H_2O in case 3. However, the total gas yield of CO and H_2 of case 2-4 are still significantly higher than that of the base case, as shown in Fig. 5. Both H_2 and CO production are elevated in the presence of steam while the CO_2 as the gasifying agent only enhances the conversion of char into CO but leads to a slight decrease of H_2 due to the reverse WGS reaction.

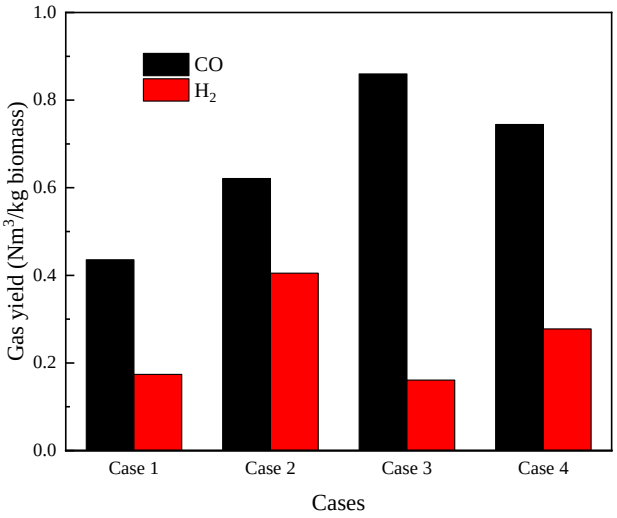


Fig. 5. Calculated gas yield generated from unit mass of biomass for different cases.

4. CONCLUSIONS

Several CFD simulations have been carried out to investigate the effects of various gasification atmosphere on the performance of a biomass CLG reactor based on the experimental study conducted by Huang et al. [6]. The developed model is able to accurately predict the gas concentration for the base case compared to the experimental values and clearly demonstrate the influences of H_2O/CO_2 and their mixture as gasifying agents in the other cases. The results show that the addition of H_2O/CO_2 has a remarkable enhancement on char gasification and indicate that their mixture has synergistic effects in the whole carbon conversion range. According to the outlet mole fractions and gas yields of the product gases, excess CO_2 has a negative effect on the H_2 production as the reverse WGS reaction is more favorable in such atmosphere.

ACKNOWLEDGEMENT

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