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Simulation study on the gasification process of Ningdong coal with iron-based oxygen carrier

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ABSTRACT

Chemical looping gasification (CLG) of Ningdong coal by using Fe₂O₃ as the oxygen carriers (OCs) was studied, and the gasification characteristics were obtained. A computation fluid dynamics (CFD) model based on Eulerian–Lagrangian multiphase framework was established, and a numerical simulation of the coal chemical looping gasification processes in fuel reactor (FR) was investigated. In addition, the heterogeneous reactions, homogeneous reactions and Fe₂O₃ oxygen carriers' reduction reactions were considered in the gasification process. The characteristics of gas flow and gasification in the FR were analyzed and it was found that the experiment results were consistent with the simulation values. The results show that when the O/C mole rate was 0.5:1, the gasification temperature was 900 °C and the water vapor volume flow rate was 2.2 ml·min^{−1}, the mole fraction of syngas reached a maximum value of the experimental result and simulation value were 71.5% and 70.2%, respectively. When the O/C mole rate was 0.5:1, the gasification temperature was 900 °C, and the water vapor volume flow was 1.8 ml·min^{−1}; the gasification efficiency reached the maximum value was 62.2%, and the maximum carbon conversion rate was 84.0%.

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1. Introduction

Coal is a significant part of the world's fossil fuels, which is mainly used for combustion power generation. The carbon dioxide (CO₂) emission from coal combustion is intensifying the process of global warming [1]. Nowadays, CO₂ capture and separation technology has been widely concerned, but it will increase the energy consumption and reduce the total efficiency of the system [2]. It is essential to develop the clean coal combustion and gasification technology to reduce the emission of CO₂ [3,4]. Coal gasification technology is widely concerned for conversion to syngas (CO + H₂). Chemical looping gasification (CLG) is also a novel technology for the production of syngas as coal conversion [5–7]. The schematic of CLG process is showed in Fig. 1; there are two fluidized bed reactors in the CLG system, they are air reactor (AR) and fuel reactor (FR), respectively [8,9]. The CLG process employs the lattice oxygen [O] from oxygen carriers (OCs) to instead of molecular oxygen from air, and then coal is partially oxidized into syngas [10]. Coal and oxidants feed into the FR, where the OCs supply [O] to generate syngas, the OCs transport the AR to recovered [O] by oxygen. In addition, the OCs play an important role in CLG process, the highly quality oxides not only can provide [O], but also can reduce the production of SO_x and NO_x [11–13]. Several metal oxides have been considered as oxygen carriers

for CLG, mainly including CuO, NiO, CdO, Mn₂O₃, Fe₂O₃ and CoO and so on [14,15]. The iron-based OCs perform well in CLG process, owing to its stronger chemical properties, high oxygen carrying capacity and mechanical strength than other metal oxides [16,17]. Although great processes have been made in the study of the CLG process, the research on the coal as fuel is relatively limited. Guo *et al.* [18] reported the gasification performance of CLG using the coal as the fuel. The results show that the carbon conversion rate, gasification efficiency and syngas content reach maximum of 96.8%, 84.3% and 66.9% at the temperature of 900 °C, and the Ca-based oxides were used as the OCs in this process. Abad *et al.* [19] developed a theoretical model for CLC process in FR using the nature iron ore. They described the dynamics characteristic of gas flow and the reaction of OCs with gases which are released from coal. Huang *et al.* [20] analyzed that the reaction characteristics of nature iron ore in CLG with the biomass char, the results indicated that the iron ore as the OCs still had reaction activity after undergoing 20-cycles of redox experiments. Moreover, Zhang *et al.* [21] studied the reactivity, recyclability and consumption performance of OCs using natural pyrite as the OCs of coal CLC. The results showed that pyrite slag was an ideal candidate for iron-based OCs.

In addition, with the improvement of numerical methods and more advanced hardware technology, the computational fluid dynamics (CFD) is widely used to simulate the complex gas–solid flow, heat transfer and chemical reaction characteristics in CLG process. Jung *et al.* [22] and Deng *et al.* [23] simulated the CLC process in fluidized bed FR with

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NiO and CaSO₄ oxygen carriers, respectively. The results showed the 3D fluidized bed was simplified to 2D, which had an impact on the simulation results. Besides, Shuai *et al.* [24] and Kruggel *et al.* [25] performed the CFD simulation of FR using gaseous fuels. Wang *et al.* [26] and García *et al.* [27] carried out the numerical model of FR using the solid fuels.

Fe₂O₃ was used as the OCs in coal CLG process in the study, and the synthesis gas contents, carbon conversion and gasification efficiency were investigated. Meanwhile, the ANSYS FLUENT was applied to establish the coal CLG progress in FR. The characteristics of gas flow, temperature and each component distribution in the FR were examined with the changing of the parameters of O/C molar ratio, gasification temperature and water vapor flow.

2. Experimental Methods

2.1. Samples

The Fe₂O₃ was used as OCs in this study. The raw Fe₂O₃ (purchased chemicals, purity of 99.8%, density of 5240 kg·m⁻³) was made into particles with a diameter of 75 μm. In addition, the coal sample came from the coalfield of Ningdong, Ningxia, China. The coal was ground and sieved to a particle size of 150 μm. The proximate analysis and ultimate analysis of coal sample were shown in Table 1. The proximate analysis was determined by the Chinese National Standard GB/T 212-2008, and the ultimate analysis was determined by the Chinese National Standard GB/T 476-2008.

2.2. Experimental apparatus

The experimental apparatus is shown Fig. 2. It composes of FR, gas distribution system, electric heating system, temperature control and gas sampling and analysis system. The coal particle gasification experiment was performed on the FR experimental device. The total height of the FR is 1000 mm, and the inner diameter is 60 mm. A porous gas distribution plate is located at the bottom of reactor to distribute gas and carry the OCs particles. The feed tube is arranged at 300 mm at bottom of the reactor with an aperture of 12 mm. The FR is equipped with an electric heating system and controlled the bed temperature for k-type thermocouples. The gas supply system is controlled by the mass flow controller (MFC, S4933), which is mainly controlled the flow of nitrogen and air. Water vapor is provided as a gasification agent by a constant flow pump (2PB, Beijing Xingkeda Tech. Inc.). The online flue gas analyzer (MRU Vario Plus) is used to analyze and measure the gasification products.

2.3. Experimental conditions

In order to study the coal gasification characteristics in the CLG process, the experimental scheme is shown in Table 2. The entire bed of FR was heated to 850 °C in air atmosphere before starting the experiment. The OCs of Fe₂O₃ was placed on a gas distributor equipped with an asbestos screen, and the Ningdong coal was placed in a storage bin. Afterwards, the air was replaced by N₂ into the FR, and the gas flow rate was always 2 L·min⁻¹, the purpose of which was to exclude the air in the bed and as a fluidizing gas. Then, the coal from storage bin fed into the FR when the temperature reached experimental setting value, and contents of gasification products measured by an online gas analyzer.

2.4. Experimental date evaluation

The O/C mole ratio in Table 2 is defined as:

$$\frac{O}{C} = \frac{R_{oc} \times m_{oc}}{\phi_{coal} \times m_{coal}} \quad (1)$$

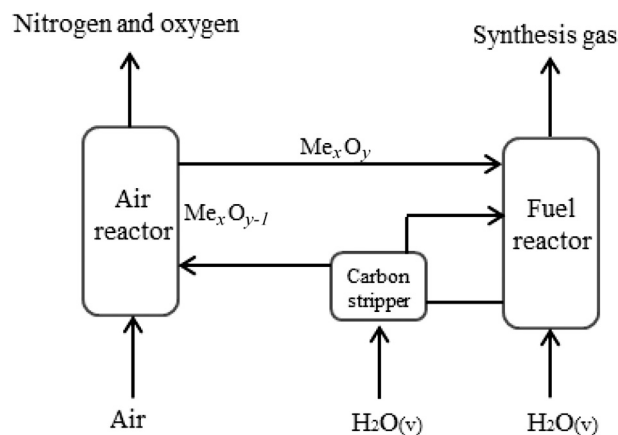


Fig. 1. Schematic of chemical looping gasification process.

where m_{oc} and m_{coal} are the molar mass of the OCs and coal respectively, g·mol⁻¹. R_{oc} is the oxygen donating capacity of OCs, g. ϕ_{coal} is the oxygen needed to completely combust per unit molar mass of coal, g·mol⁻¹.

As for the repeatability experimental tests of coal in fluidized bed, the gas relative composition ($\varphi_i/\%$) in reaction process is calculated as:

$$\varphi_i = \frac{\int_0^t v \chi_i dt}{\int_0^t v \chi_{co} dt + \int_0^t v \chi_{co_2} dt + \int_0^t v \chi_{CH_4} dt + \int_0^t v \chi_{H_2} dt + \int_0^t v \chi_{N_2} dt} \quad (2)$$

where χ_i , v are expressed as the volume fraction of species i , vol%, and synthesis gas flow rate, L·min⁻¹ respectively. χ_{co} , χ_{co_2} , χ_{CH_4} and χ_{H_2} are represented the volume fractions of CO, CO₂, CH₄ and H₂ in the flue gas, vol% respectively.

The gas yield ($F_{out}/L \cdot \min^{-1}$) in CLG process was evaluated following N₂ balance, which is calculated as:

$$F_{out} = \frac{F_{N_2}}{1 - \chi_{co} - \chi_{co_2} - \chi_{CH_4} - \chi_{H_2} - \chi_{O_2}} \quad (3)$$

where F_{N_2} is the inlet flow rate of N₂, L·min⁻¹. χ_i are the volume fraction of CO, CO₂, CH₄, H₂ and O₂ at the outlet, vol%.

Besides, synthesis gas content ($\varphi_{syn}/\%$), carbon conversion ($X_C/\%$) and gasification efficiency ($\eta/\%$) in CLG process are calculated as following:

$$\varphi_{syn} = \frac{\int_0^t F_{out} \chi_{co} dt + \int_0^t F_{out} \chi_{H_2} dt}{\int_0^t F_{out} \chi_{co} dt + \int_0^t F_{out} \chi_{co_2} dt + \int_0^t F_{out} \chi_{CH_4} dt + \int_0^t F_{out} \chi_{H_2} dt} \quad (4)$$

$$X_C = \frac{\int_0^t F_{out} (\chi_{co} + \chi_{co_2} + \chi_{CH_4}) dt}{22.4 n_c} \quad (5)$$

$$\eta = \frac{\sum (Q_i \int_0^t F_i dt)}{Q_{W_0}} \quad (6)$$

where n_c represents the total number of moles containing carbon gas during the CLG process, mol. Q_i is low thermal value for gas products, kJ·m⁻³. Q_{W_0} is low thermal value of coal, MJ·kg⁻¹. F_i is the volume flow rate of gas component, L·min⁻¹. i is present the gas compositions (CO, H₂ and CH₄).

3. Numerical Model

3.1. Geometry and meshing

In this work, a three-dimensional model of the FR based on Cartesian coordinates was established. The structure diagram and grids were

Table 1
Proximate analysis and ultimate analysis of Ningdong coal

Sample	Proximate analysis /wt%				Ultimate analysis /wt%					Low calorific value/MJ·kg ⁻¹
	M _{ad}	V _{ad}	A _{ad}	FC _{ad}	C _{daf}	H _{daf}	N _{daf}	O _{daf}	S _{daf}	
YCW	6.60	29.06	4.84	59.50	75.99	3.60	1.02	18.32	0.56	27.04

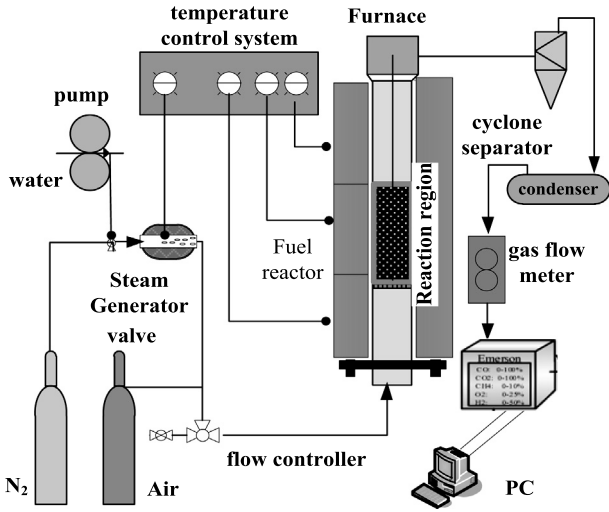


Fig. 2. Schematic illustration of experimental apparatus.

shown in Fig. 3. The schemes in the simulation were listed in Table 3. In addition, grid independence verification was performed on computational domains containing 360 k, 720 k and 1190 k cells, respectively.

3.2. CFD model

3.2.1. Continuity equations

The continuity equations for gas and particle phases are given by [28]:

$$\nabla(\alpha_g \rho_g \vec{v}_g) = \dot{m}_{gp} \quad (7)$$

$$\nabla(\alpha_p \rho_p \vec{v}_p) = \dot{m}_{pg} \quad (8)$$

where α , ρ and $\vec{v}$ are the volume fraction, density and instantaneous velocity, respectively. $\dot{m}$ is the source term, and characterizes the mass transfer between the gas phase and solid phase.

3.2.2. Momentum equations

For the gas phase:

$$\nabla(\alpha_g \rho_g \vec{v}_g \vec{v}_g) = -\alpha_g \nabla p_g + \nabla \cdot \bar{\tau}_g + \alpha_g \rho_g \vec{g} + \dot{m}_{gp} \vec{v}_p + \beta(\vec{v}_p - \vec{v}_g) \quad (9)$$

Table 2
Experimental conditions in Ningdong coal CLG process.

Description	#1	#2	#3	#4	#5	#6	#7
Ningdong coal /g	12.0	12.0	12.0	12.0	12.0	12.0	12.0
OCs of Fe ₂ O ₃ /g	57.0	142.0	228.0	142.0	142.0	142.0	142.0
Gasification temperature /°C	900	900	900	850	950	900	900
Water vapor /ml·min ⁻¹	1.8	1.8	1.8	1.8	1.8	2.0	2.2
O/C mole ratio	0.2:1	0.5:1	0.8:1	0.5:1	0.5:1	0.5:1	0.5:1

where $\vec{g}$ is gravity, $\bar{\tau}_g$ is the gas-phase stress strain tensor and β is the interphase momentum exchange coefficient between the gas phase and the solid phase, which can be followed as [29]:

$$\beta = \begin{cases} 0.75 C_D \frac{\alpha_p \alpha_g \rho_g |\vec{v}_p - \vec{v}_g|}{d_p} \alpha_g^{-2.65}, & (\alpha_g > 0.8) \\ 150 \frac{\alpha_p^2 \mu_g}{\alpha_g d_p^2} + 1.75 \frac{\alpha_p \rho_g |\vec{v}_p - \vec{v}_g|}{d_p}, & (\alpha_g \leq 0.8) \end{cases} \quad (10)$$

where

$$C_D = \frac{24}{\alpha_g Re_p} [1 + 0.15(\alpha_g Re_p)^{0.687}] \quad (11)$$

$$Re_p = \frac{\alpha_p \rho_g |\vec{v}_p - \vec{v}_g| d_p}{\mu_g} \quad (12)$$

and

$$\bar{\tau}_g = \mu_g \alpha_g [\nabla \vec{v}_g + (\nabla \vec{v}_g)^T] - \frac{2}{3} \mu_g \alpha_g \nabla \cdot \vec{v}_g \bar{I} \quad (13)$$

where

$$\mu_g = \mu_{gl} + \mu_{gt} \quad (14)$$

In Eq. (14), μ_g is the gas-phase shear viscosity; μ_{gl} is the gas-phase laminar viscosity, and μ_{gt} is the gas phase turbulent viscosity, and computed as a function of κ and ε :

$$\mu_{gt} = \rho_g C_\mu \frac{\kappa^2}{\varepsilon} \quad (15)$$

where C_μ is the constant, which is the 0.09.

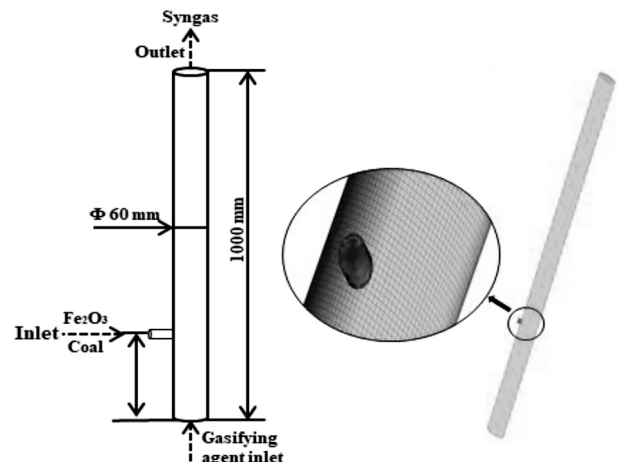


Fig. 3. Structure diagram and grids of the FR.

Table 3
Schemes of the simulations

Scheme	Gasification temperature /°C	O/C mole ratio	Water vapor /ml·min ⁻¹
1	900	0.2:1, 0.5:1, 0.8:1	1.8
2	900	0.5:1	1.8, 2.0, 2.2
3	850, 900, 950	0.5:1	1.8

The turbulence models equations for κ and ε can be expressed as:

$$\nabla(\alpha_p \rho_p \vec{v}_p \kappa) = \nabla \left(\alpha_g \frac{\mu_{gt}}{\sigma_k} \nabla \kappa \right) + \alpha_g G_k - \alpha_g \rho_g \varepsilon + \alpha_g \rho_g \Pi_k \quad (16)$$

$$\nabla(\alpha_p \rho_p \vec{v}_p \varepsilon) = \nabla \left(\alpha_g \frac{\mu_{gt}}{\sigma_\varepsilon} \nabla \varepsilon \right) + \alpha_g \frac{\varepsilon}{\sigma_k} (C_1 G_k - C_2 \rho_g \varepsilon) + \alpha_g \rho_g \Pi_\varepsilon \quad (17)$$

where Π_k and Π_ε represents the influence of the solid phase on the gas phase. G_k is the production of turbulent kinetic energy. The constants of $C_1 = 1.44$ and $C_2 = 1.92$. The turbulent Prandtl numbers for κ and ε of $\sigma_k = 1.0$ and $\sigma_\varepsilon = 1.3$.

For the solid phase:

$$\nabla(\alpha_p \rho_p \vec{v}_p \vec{v}_p) = -\alpha_p \nabla p_p + \nabla \bar{\tau}_p + \alpha_p \rho_p \vec{g} + \dot{m}_{pg} \vec{v}_p + \beta(\vec{v}_g - \vec{v}_p) \quad (18)$$

where p_p is the solid phase pressure from the particle collisions, $\bar{\tau}_p$ the solid particle-phase stress strain tensor. They are expressed as [30].

$$\bar{\tau}_p = \alpha_p \mu_p (\nabla \vec{v}_p + \vec{v}_p \nabla) + \alpha_p \left(\xi_p - \frac{2}{3} \mu_p \right) \nabla \nabla \vec{v}_p \bar{I} \quad (19)$$

$$p_p = \alpha_p \rho_p \theta + 2g_o \alpha_p^2 \rho_p \theta (1 + e) \quad (20)$$

where, in Eq. (19), ξ_p is the solid particle-phase bulk viscosity. μ_p is the solid particle-phase shear viscosity. In Eq. (20), g_o is the radial distribution function. They have the following form:

$$\xi_p = \frac{4}{3} \alpha_p \rho_p d_p g_o (1 + e) \sqrt{\frac{\theta}{\pi}} \quad (21)$$

$$\mu_p = \frac{4}{5} \alpha_p \rho_p d_p g_o (1 + e) \sqrt{\frac{\theta}{\pi} + \frac{10 \rho_p d_p \sqrt{\theta \pi}}{96 \alpha_p g_o (1 + e)}} \left[1 + \frac{4}{5} \alpha_p g_o (1 + e) \right] \quad (22)$$

$$g_o = \left[1 - \left(\frac{\alpha_p}{\alpha_{p, \max}} \right)^{1/3} \right]^{-1} \quad (23)$$

where θ is the granular temperature, which is proportional to the kinetic energy of the random motion of solid particles. The transport equation derived from kinetic theory takes the form:

$$\nabla(\alpha_p \rho_p \vec{v}_p \theta) = \frac{2}{3} \left[\left(-p_p \bar{I} + \bar{\tau}_p \right) : \nabla \vec{v}_p + \nabla(\Gamma_\theta \nabla \theta) - \gamma_p + \phi_p \right] \quad (24)$$

where γ_p , Γ_θ and ϕ_p represents the collisional dissipation of energy, the diffusion coefficient and the energy exchange between the gas phase and the particle phase, respectively. They are given by:

$$\gamma_p = \frac{12(1-e^2)g_o}{d_p \sqrt{\pi}} \rho_p \alpha_p^2 \theta^{3/2} \quad (25)$$

$$\phi_p = -3\beta\theta \quad (26)$$

$$\Gamma_\theta = \frac{150 \rho_p d_p \sqrt{\theta \pi}}{384(1+e)g_o} \left[1 + \frac{6}{5}(1+e)g_o \alpha_p \right]^2 + 2 \rho_p \alpha_p^2 d_p \alpha_p (1+e) \sqrt{\frac{\theta}{\pi}} \quad (27)$$

3.2.3. Energy equations

$$\nabla(\alpha_g \rho_g \vec{v}_g H_g) = \nabla(\lambda_g \nabla T_g) + h_{gp}(T_g - T_p) + \dot{m}_{gp} H_p \quad (28)$$

$$\nabla(\alpha_p \rho_p \vec{v}_p H_p) = \nabla(\lambda_p \nabla T_p) + h_{pg}(T_p - T_g) + \dot{m}_{pg} H_p \quad (29)$$

where H , λ and h ($h_{gp} = h_{pg}$) are the specific enthalpy, the mixture thermal conductivity and the transfer coefficient between phases, respectively. The third term on the right-hand is the heat transfer from the particle phase to the gas phase.

The heat transfer coefficient is related to the solid particle phase Nusselt number, Nu_p given by:

$$h_{pg} = \frac{6 \lambda_g \alpha_g \alpha_p Nu_p}{d_p^2} \quad (30)$$

and

$$Nu_p = \left(7 - 10 \alpha_g + 5 \alpha_g^2 \right) \left(1 + 0.7 Re_p^{0.2} Pr^{1/3} \right) + \left(1.33 - 2.4 \alpha_g + 1.2 \alpha_g^2 \right) Re_p^{0.7} Pr^{1/3} \quad (31)$$

3.2.4. Species transport equations

$$\nabla \cdot (\alpha_g \rho_g Y_{g,i} \vec{v}_g) = -\nabla \cdot \alpha_g J_{g,i} + S_i \quad (32)$$

where $J_{g,i}$ is the diffusion flux of species i in the gas phase. S_i is the net rate of production of species i .

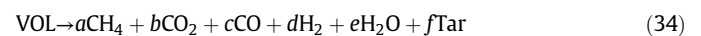
Diffusion flux $J_{g,i}$ is calculated by:

$$J_{g,i} = - \left(\rho_g D_{i,m} + \frac{\mu_{gt}}{Sc_t} \right) \nabla Y_{g,i} \quad (33)$$

where Sc_t is the turbulent Schmidt number, and is set as 0.7, $D_{i,m}$ is the diffusion coefficient for species i in the mixtures.

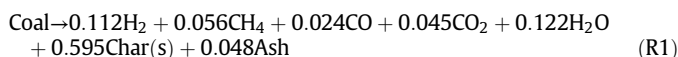
3.3. Chemical reactions mechanism

In this work, a preliminary chemical reaction of coal was studied at the FR in CLG process. For the coal, the global reaction modeling was adapted with the de-volatilization reaction, and assumed to take place in a single reaction. The volatile released in the de-volatilization process and rapidly decomposes, and then the final mixture species were formed in a rapid volume reaction. Considering the complexity of model building, the main products of the volatilization were regarded as CO, H₂, CH₄, CO₂, H₂O and Tar. It was described as flowing:



From the Eq. (34), it can be seen that the volatiles in coal particles were mainly considered four gases of CO, CO₂, CH₄ and H₂. In addition, considered the tar was the liquid phase mixture, it would be ignored in this simulation. The coefficient of a - f in Eq. (34) was calculated from the conservation of mass and elemental conservation based on the chemical analysis of Ningdong coal. The de-volatilization reaction

of the entire coal can be expressed as:



The reaction mechanisms of Ningdong coal CLG are given in Table 4. The gasification reactions are R2 to R5, and the Fe_2O_3 oxygen carrier's reduction reactions were R6 to R8.

3.4. Model setups

ANSYS FLUENT software was employed to simulate the CLG of Ningdong coal in the study. The SIMPLE was used the steady-state simulation, which was applied for the pressure–velocity coupling equations. The equations mentioned above were solved by a finite volume method, and a first-order upwind discretization was chosen for all solution. The radiation model was set to P1. The standard residual of the convergence of the solution was the default value, the residual of the continuity equation installed to 10^{-5} , and the remaining equations were set to 10^{-4} . The important boundary and simulation conditions could be referred from Table 5.

4. Results and Discussion

4.1. Experiment pathway analysis

The reaction pathway for the conversion of Fe_2O_3 and Ningdong coal in CLG progress is described, as shown in Fig. 4. As the coal CLG is an extremely complex process, the main reactions are considered in the FR and divided into three stages: coal pyrolysis and volatilization release, gasification reactions and oxygen carrier's reduction reactions. The coal pyrolyzed rapidly and volatiles released under high temperature after coal was fed into FR. The volatiles consist of H_2O , CO_2 , CO , H_2 and CH_4 . Afterwards, a series of subsequent reactions (R2–R5) between volatiles and water vapor to generate the syngas were considered, then the chemical components and contents of syngas were improved and promoted by redox reactions between Fe_2O_3 and volatiles reaction (R6–R8). The characterization analysis of samples was shown in Fig. 5. Among which, Fig. 5(a) and Fig. 5(b) display the SEM photographs of the OCs of Fe_2O_3 before the CLG experiments. It can be seen that the samples of Fe_2O_3 show a polyhedral shape and the surface are smooth and flat, and there are large pores. Fig. 5(c) and Fig. 5(d) display the SEM photographs of the OCs particles after the CLG experiments. It can be seen that the crystal structure of OCs has changed, showing an irregular hexagonal structure and a rough surface. The granulation degree of OCs is enhanced, and the surface area is increased, thereby improving the reactivity of the OCs. Meanwhile, the OCs particles do not appear agglomeration or sintering. Fig. 5(e) and Fig. 5(f) display the XRD transform of the OCs particles in coal CLG process. It can be seen that OCs of Fe_2O_3 are converted into Fe_3O_4 after CLG, which is used as a basis for numerical simulation to establish the Fe_2O_3 reduction reaction mechanism. Moreover, it has been reported that the iron-based oxygen carrier evolution process and pathway used in CLG and CLC, and verified by Parker *et al.* [34] and Chen *et al.* [35].

4.2. Simulation analysis

4.2.1. Grid independency

In this section, the grid independence study was performed to choose an adequate grids number, and the simulation computation was conducted by using the number of grids with 360 K (Case 1), 720 K (Case 2) and 1190 K (Case 3). The simulation results at FR outlet were listed Table 6. The results indicated that the content of each component of in Case 1 was quite different compared with Case 2 and Case 3, so the Case1 to be ignored. The content of each component at outlet was less than 1% between Case 2 and Case 3, but the calculation time

Table 4

Kinetic parameters for important reactions in coal CLG

Reactions	A	b	E_a /a	Ref.
R2 $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{(g)}$	2.2×10^2	1	212.0	[31]
R3 $\text{C(s)} + \text{CO}_2\text{(g)} \rightarrow 2\text{CO(g)}$	3.9×10^{-4}	1	109.2	[31]
R4 $\text{CO(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$	2.1×10^7	0.5	192.5	[31]
R5 $\text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + 3\text{H}_2\text{(g)}$	1.4×10^2	0.5	56.6	[31]
R6 $\text{CO(g)} + 3\text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{CO}_2\text{(g)} + 2\text{Fe}_3\text{O}_4\text{(s)}$	6.2×10^{-4}	3	20.2	[32]
R7 $\text{CH}_4\text{(g)} + 12\text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{CO}_2\text{(g)} + 8\text{Fe}_3\text{O}_4\text{(s)} + 2\text{H}_2\text{O(g)}$	8.1×10^{-4}	12	49.0	[33]
R8 $\text{H}_2\text{(g)} + 3\text{Fe}_2\text{O}_3\text{(s)} \rightarrow 2\text{Fe}_3\text{O}_4\text{(s)} + \text{H}_2\text{O(g)}$	2.4×10^{-3}	3	24.1	[32]

Note: $k = A T^b e^{-(E_a/RT)}$, A is pre-exponential factor, E_a is activation energy, $\text{kJ} \cdot \text{mol}^{-1}$, b is temperature index.

of Case 3 was 1.75 times that of Case 2. Hence, the Case 2 was used for the computational model.

4.2.2. Model validation

In order to validate the numerical model, the simulation results of the temperature and the mole fraction of each component at reactor outlet were compared with the experimental results, as listed in Table 7. It shows a relatively good agreement for each component at outlet of FR. The difference of all components was less than 5%. The results show that the accuracy of the numerical simulation was acceptable. Therefore, the calculation model could be used to describe the coal CLG process.

4.2.3. Computation analysis

Fig. 6 shows the contours of temperature and mole fraction of each species on a vertical mid-plane in the FR under the condition #2. Fig. 6(a) shows the distribution of temperature in the FR. Coal, H_2O and OCs are mixed vigorously when coal particles entered into the reactor. Volatile gas (CO , CO_2 , CH_4 , H_2) is released by rapid pyrolysis of coal and a small amount of $[\text{O}]$ react with volatile gas and coke. Meanwhile, the water–gas shift reaction (R4) takes place, too. These are exothermic reactions. The exothermic reactions result in higher temperature in the area near inlet. Subsequently, synthesis gas is formed by chemical reaction of char and oxidizing gas ($[\text{O}]$ comes from the OCs and H_2O) at high temperature. The temperature decreases gradually with the gasification reaction (R2) and reduction reaction (R6, R8) going on, which are endothermic reactions. The temperature has a tendency to stabilize at the upper part of the FR. Fig. 6(b) shows the distribution of the H_2 in the FR. The highest mole fraction of H_2 is at the top of the reactor. This is mainly due to the hydrogen produced by the gasification reaction (R2), water gas shift reaction (R4) and methane steam reforming reaction (R5). In addition, the mole fraction of H_2 fluctuates slightly in the middle of the FR, which is mainly due to the consumption of the reduction reaction (R8). Fig. 6(c) shows the distribution of CO in the FR. It should be noted that the mole fraction of CO gradually increases and reaches a maximum value at the outlet of the FR. The content of CO

Table 5

Boundary conditions and others simulation details

Parameter	Details
Number of cells used	720,000
Type of cells used	Regular hexahedron
Multiphase model	Eulerian–Lagrangian
Mass flow of coal	$0.0120 \text{ kg} \cdot \text{s}^{-1}$
Mass flow of OCs	$0.057 \text{ kg} \cdot \text{s}^{-1}$, $0.142 \text{ kg} \cdot \text{s}^{-1}$ and $0.228 \text{ kg} \cdot \text{s}^{-1}$
Volume flow of water vapor	$1.8 \text{ ml} \cdot \text{min}^{-1}$, $2.0 \text{ ml} \cdot \text{min}^{-1}$ and $2.2 \text{ ml} \cdot \text{min}^{-1}$
O/C mole ratio	0.2:1, 0.5:1 and 0.8:1
Pressure	Atmospheric
Gasification temperature	850 °C, 900 °C and 950 °C
Couple	SIMPLE
Particles	Ningdong coal (particles size of 0.15 mm) OCs of Fe_2O_3 (particles size of 0.075 mm)
Under factors relaxation	pressure: 0.1, Density: 1 and Body force: 1 Momentum: 0.3 and Energy: 0.7

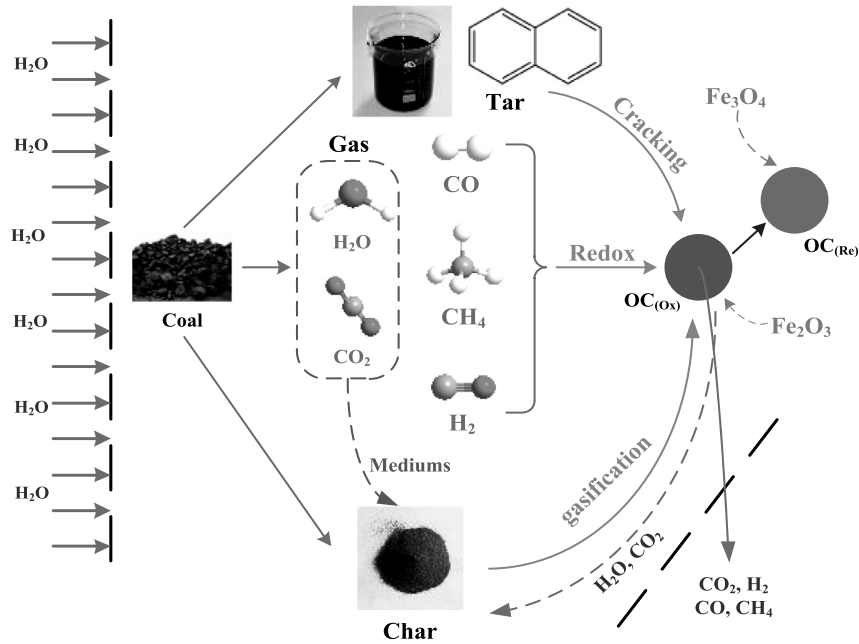


Fig. 4. Reaction pathway of OCs of Fe_2O_3 in bituminous coal CLG process

mainly comes from gasification reaction (R2) and methane steam reforming reaction (R5). Meanwhile, the reduction reaction (R6) and water–gas shift reaction (R4) consumes a small amount of CO to reduce its content. Fig. 6(d) shows the distribution of CO_2 in FR. It can be described that the change of CO_2 content is relatively obvious. In the middle part, the content of CO_2 increases due to the water–gas shift reaction (R4) and the reduction reaction (R6, R7), then the content decreases due to the boudouard reaction (R3) consumption of CO_2 . Fig. 6 (e) shows the distribution of CH_4 , which is derived from coal pyrolysis (R1). The content of CH_4 is the highest at the inlet, and then gradually decreases due to the methane steam reforming (R5) and reduction reaction (R7) consumption of CH_4 . Fig. 6(f) shows the distribution of H_2O . With the reaction proceeding, the water vapor consumption increased,

the content gradually decreases and reaches the minimum at the outlet of the FR.

Fig. 7 shows the variation of components at different heights in FR. At 300 mm, the content of each component at the feed pipe shows a small fluctuation, mainly due to the release of volatile gases from the R1 reaction. With increase of the FR height, the reaction reaches equilibrium and the content of each component tends to be stable at 900 mm.

4.3. Effects of process parameters

4.3.1. O/C mole ratio

Fig. 8 shows the effects of different O/C mole ratios on gasification characteristics of Ningdong coal CLG. With the increase of the O/C

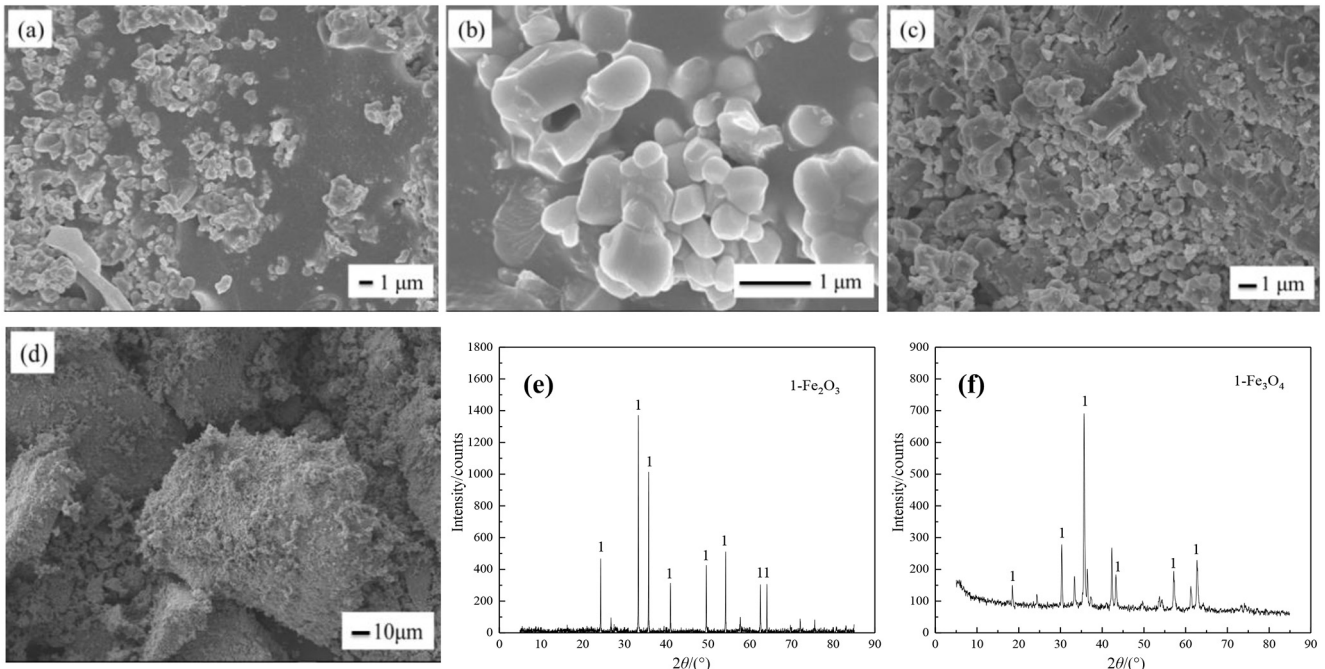


Fig. 5. SEM photographs of OCs of Fe_2O_3 and XRD patterns of OCs before and after CLG (The JCPDS numbers of (e) and (f) are PDF#33-0664 and PDF#26-1136.)

Table 6
Species contents, temperature and calculation time in CLG process

	$\varphi_{H_2}/\%$	$\varphi_{CO}/\%$	$\varphi_{CO_2}/\%$	$\varphi_{CH_4}/\%$	Temperature/K	Calculation time/h
Case1	41.28	20.68	11.25	5.12	1330	48
Case2	45.50	23.22	13.05	5.50	1347	96
Case3	45.52	23.21	13.00	5.48	1348	168

mole ratio, the mole fraction of the syngas, carbon conversion rate and gasification efficiency increases first and then decreases at the outlet of the FR. With the O/C mole ratio raise from 0.2:1 to 0.5:1, the content of OCs of Fe_2O_3 increases, which leads to an acceleration of thermal cycle and promotes the gasification reaction (R2). In addition, the Fe_2O_3 oxygen carrier's reduction reactions (R6, R8) are enhanced, consuming the

Table 7
Compared with experimental results and simulation values.

Term	Mole fraction of components at outlet $\varphi/\%$					Temperature of outlet /K
	H_2	CO	CO_2	CH_4	H_2O	
Experimental results	48.67	21.33	15.79	1.22	12.99	—
Simulation values	45.50	23.22	13.05	5.50	12.73	1347

H_2 and CO generated by the gasification reaction (R2) and accelerating the forward reaction rate. The results show that the mole fraction of syngas, the carbon conversion rate and gasification efficiency increase. When the O/C mole ratio is raised from 0.5:1 to 0.8:1, the mass of the reaction bed augments to affect the gas–solid flow, resulting in a decrease in the rate of gasification reaction (R2). In addition, the [O] provided in the OCs of Fe_2O_3 increases, and the syngas generated by the gasification reaction (R2) is oxidized to H_2O and CO_2 . As a result, the mole fraction of the syngas, carbon conversion rate and gasification efficiency are decreased. At the O/C mole ratio of 0.5:1, the experimental result and simulation value of the syngas mole fraction reaches a maximum value of 70.1% and 68.3%, respectively. Meanwhile, the carbon conversion is 84.0%, and the gasification efficiency is 56.2%.

4.3.2. Water vapor volume flow

Fig. 9 shows the effects of different water vapor volume flow on gasification characteristics of Ningdong coal CLG. With the increase of

water vapor volume flow, the mole fraction of syngas increases first and then decreases, the carbon conversion rate decreases and the gasification efficiency increases at the outlet of the FR. When the water vapor volume flow is increased from 1.8 to 2.0 $ml \cdot min^{-1}$, the gas–solid contact is intensified in the FR, which is beneficial to the gasification reaction (R2) to generate syngas. However, the water–gas shift reaction (R4) is able to consume CO, thereby promoting the reduction reaction (R8), resulting in the mole fraction of syngas decreases slightly and the gasification efficiency increases. When the water vapor volume flow is increased from 2.0 to 2.2 $ml \cdot min^{-1}$, the fluidization velocity is accelerated, and the residence time of the gas is reduced in the FR, which is beneficial to the forward progress of each reaction, resulting in the molar fraction of syngas and gasification efficiency are increased. At the water vapor volume flow of 2.2 $ml \cdot min^{-1}$, the experimental results and simulation values of the syngas mole fraction reaches a maximum value of 71.5% and 70.2%, respectively. Meanwhile, the carbon conversion is 78.1% and the gasification efficiency is 62.2%.

4.3.3. Gasification temperature

Fig. 10 shows the effects of different gasification temperature on gasification characteristics of Ningdong coal CLG. With the increase of gasification temperature, the syngas mole fraction, carbon conversion rate and gasification efficiency increases first and then decreases at the outlet of FR. When the gasification temperature is increased from 850 to 900 °C, the gasification reaction rate (R2) elevates because it is an endothermic reaction, which promoted more char consumption and produces more H_2 and CO, resulting in the molar fraction of syngas, the carbon conversion rate and gasification efficiency are increased. When the gasification temperature is increased from 900 °C to 950 °C, the mole fraction of syngas, the carbon conversion rate and gasification efficiency are decreased, because the temperature increase is not conducive to the water–gas shift reaction (R4). In addition, the high temperature inhibits the reduction reactions (R6, R8), because of this reactions are exothermic. At the gasification temperature of 900 °C, the experimental results and simulation values of the mole fraction of syngas reaches a maximum value of 70.1% and 68.3%, respectively. Meanwhile, the carbon conversion is 84.0%, and the gasification efficiency is 56.2%.

5. Conclusions

In this study, a three-dimensional numerical model was investigated about the Ningdong coal CLG progress. The gas flow and gasification characteristics were obtained. The main conclusions as follow:

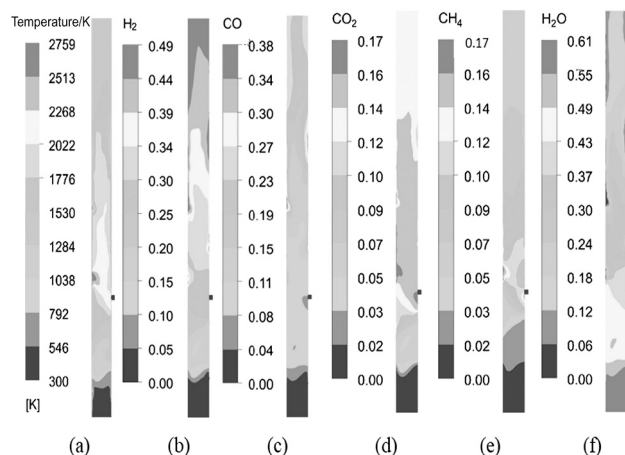


Fig. 6. Contours of temperature and species mole fraction on a vertical mid-plane in the FR.

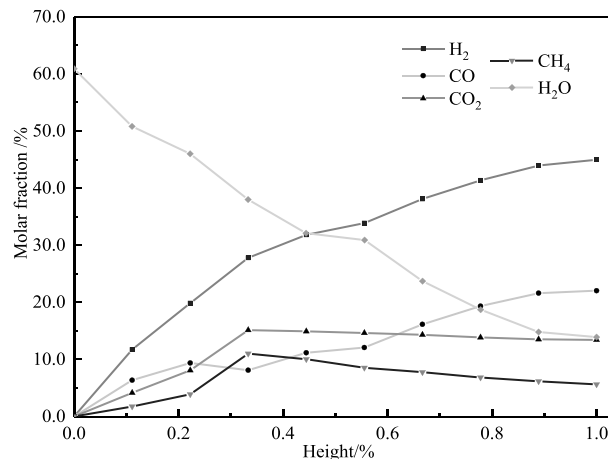


Fig. 7. Variations the contents of each component with different heights in the FR.

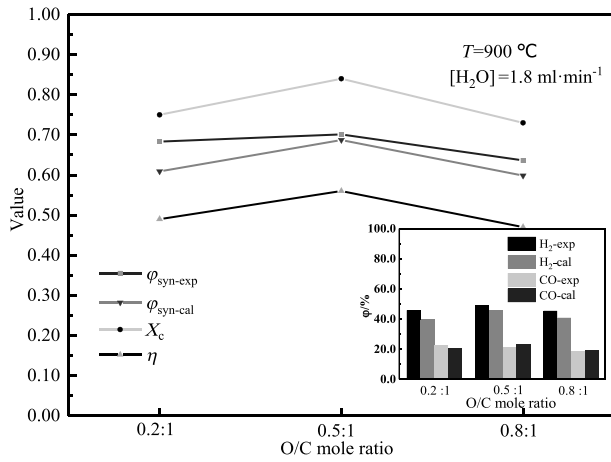


Fig. 8. Effect of O/C mole ratio on gasification characteristics.

- (1) The optimum O/C mole ratio is 0.5:1. The high O/C mole ratio is beneficial for the gasification reaction (R2) to produce more syngas, but excessively high O/C mole ratio will improve the bed quality to affect the gas flow efficiency.
- (2) The optimal water vapor volume flow rate is 2.2 ml·min⁻¹. With the increase of water vapor volume flow rate, the gas flow characteristic enhances, resulting in the rate of gasification reaction (R2) improves. However, in order to ensure the normal fluidization and heat transfer of the particles, the volume flow of water vapor must be controlled within a certain range.
- (3) The optimum gasification temperature is 900 °C. With the increase of the gasification temperature, the conversion rate of coal increases, thereby the rate of the gasification reaction (R2) increases, but excessively high temperature is not conducive to the water–gas shift reaction (R4) and Fe₂O₃ oxygen carrier's reduction reactions (R6–R8).

Nomenclature

C_D	Drag coefficient
$D_{i,m}$	Diffusion coefficient for species i in the mixture, m ² ·s ⁻¹
d_p	Granular diameter, m
G_K	Production of turbulent kinetic energy
g	Gravity, m·s ⁻²
g_o	Radial distribution function

H	Specific enthalpy, J·kg ⁻¹
h	Heat-transfer coefficient, W·m ⁻² ·K ⁻¹
J_i	Diffusion flux of species i , kg·m ⁻² ·s ⁻¹
m	Mass source term, kg·m ⁻³ ·s ⁻¹
Nu	Nusselt number
P	Solid phase pressure, Pa
Pr	Prandtl number
Sc_t	Turbulent Schmidt number
S_i	Net rate of production of species i , kg·m ⁻³ ·s ⁻¹
T	Temperature, K
$\vec{v}$	Instantaneous velocity, m·s ⁻¹
Y	Mass fraction of species
α	Volume fraction
β	Interphase momentum exchange coefficient, kg·m ⁻³ ·s ⁻¹
Γ_θ	Diffusion coefficient between the gas phase and the particle phase
γ	Collisional dissipation of energy, W·m ⁻³
ε	Dissipation rate of turbulent kinetic energy, m ⁻² ·s ⁻³
θ	Particle-phase pseudo-temperature, m ² ·s ⁻²
κ	Turbulent kinetic energy, m ² ·s ⁻²
λ	Thermal conductivity, W·m ⁻² ·K ⁻¹
μ	Viscosity, kg·m ⁻¹ ·s ⁻¹
ξ_P	Particle-phase bulk viscosity, kg·m ⁻¹ ·s ⁻¹
ρ	Density, kg·m ⁻³
Π_k	Influence of the particle phase on the solid phase, m ² ·s ⁻³
Π_ε	Influence of the particle phase on the gas phase, m ⁻² ·s ⁻⁴
σ_ε	Turbulent Prandtl number for ε
σ_k	Turbulent Prandtl number for k
$\bar{\tau}_g$	Stress strain tensor, Pa
ϕ_P	Energy exchange between the gas phase and particle phase, W·m ⁻³

Subscripts

g	Gas phase
i	i th species
j	j th reaction
p	Particle phase
t	Turbulent flow

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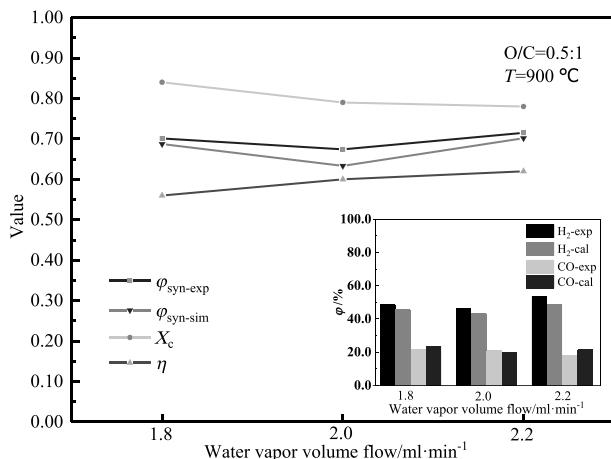


Fig. 9. Effect of water vapor volume flow on gasification characteristics.

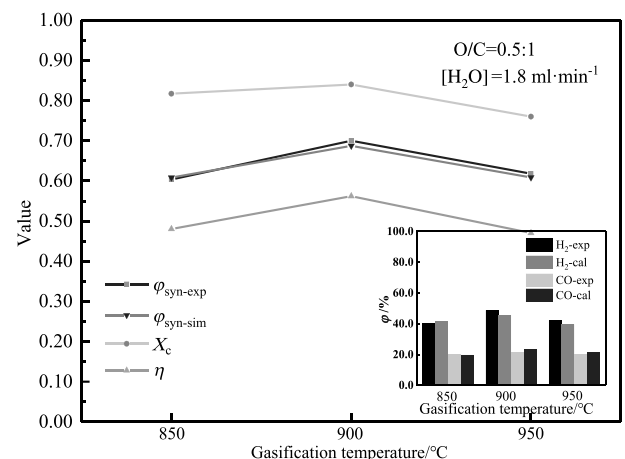


Fig. 10. Effect of gasification temperature on gasification characteristics.

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