



# A clean coal utilization technology based on coal pyrolysis and chemical looping with oxygen uncoupling: Principle and experimental validation



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## ABSTRACT

The coal poly-generation system offers the possibility to produce value-added chemicals, synthetic gas fuels and electricity simultaneously, which can improve the coal utilization efficiency. To realize the multi-generation of gas, tar and heat/electricity with CO<sub>2</sub> capture, a new clean coal utilization technology integrating coal pyrolysis and CLOU (chemical looping with oxygen uncoupling) process was proposed. Both thermodynamic process simulation and batch-scale fluidized bed CLOU experiments were conducted to verify its feasibility and obtain some fundamental features. From simulation results, the total exergy efficiency had been improved by 0.82 percent points compared to the typical coal poly-generation system. Based on CLOU experiments of two pyrolytic semicokes of SL lignite (SL-20 and SL-60), it was found that the reactor temperature and the semicoke characteristic were two key factors in determining the CLOU process, in which higher fuel reactor temperature and semicoke with shorter pyrolysis time were favorable to the conversion process. In addition, both the semicokes showed very high CO<sub>2</sub> gas yield (higher than 99%) and relatively low unburned gas yields, whilst the combustion efficiencies reached to higher than 93%. The results suggested that SL-20 with CLOU temperature of 900 °C was more favorable for the operation of the new system.

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## 1. Introduction

Coal is the most abundant fossil fuel resource in the world and has been widely used for electricity generation, which provides about 30% of the global energy consumption in 2013, and remains the main fossil fuel [1]. However, the direct combustion of coal for electricity generation leads to a host of environmental problems. Large amount of SO<sub>2</sub> and NO<sub>x</sub> emissions result in severe air pollution, and huge CO<sub>2</sub> emission gives rise to the global warming. Meanwhile, some valuable hydrocarbons in the coal are directly burnt out, which is not economically favorable and reduces the coal utilization efficiency. Due to growing energy demands of the world and climate concerns caused by anthropogenic greenhouse gas emissions, the technologies focusing on efficient and clean coal utilization have attracted great attentions these years [2].

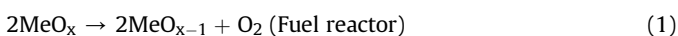
Among the available approaches proposed, the coal poly-generation technology based on coal pyrolysis/partial gasification

and combustion, which realizes the poly-generation of high value-added chemicals, synthetic gases and heat/electricity [3,4], gives the possibility to improve the coal utilization efficiency. The technology is especially suitable for the low-rank coal, which can be more easily converted to syngas, methanol, coke, oil and other value-added products [5], though it has been regarded as a poor quality fuel because of its high moisture and ash contents, low caloric value and low ash melting point. Li et al. [6] have investigated this type of technology and found that the gross electric efficiency and thermal efficiency of the system is 1.9% higher and 5.1% higher than the conventional steam cycle system. Guo et al. [7] also have reported a lignite-based poly-generation system coupling an atmospheric pressure fluidized bed pyrolyzer with a CFB (circulating fluidized bed). Results showed that poly-generation system with higher energy and exergy efficiency is more efficient than CFB power plant. Moreover, the coal poly-generation technology has the advantage of removing some of the sulfur compounds during the coal pyrolysis and reducing the desulfurization burden of CFB boiler, as reported in Refs. [8] and [9]. Despite of many favorable properties, the coal poly-generation technology still suffers from the CO<sub>2</sub> emission problem as the result of direct combustion of

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semicoke after pyrolysis. Therefore, it is necessary to develop new technologies to reduce the CO<sub>2</sub> emission significantly.

Regarding CO<sub>2</sub> capture technologies, there are three main categories: pre-combustion [10,11], post-combustion [12] and oxy-fuel combustion [13,14]. Most of these technologies suffer from the disadvantage of a significant thermal efficiency penalty to obtain the CO<sub>2</sub> in pure form, ready for sequestration [15,16]. Recently, a low-cost CO<sub>2</sub> capture technology called CLC (chemical looping combustion) has been proposed and becomes a very promising fossil fuel combustion technology [17,18]. CLC divides fuel combustion into two steps, including the reduction of a solid OC (oxygen carrier) by the fuels and the re-oxidation of the OC by the air. This two-step reaction process avoids the direct contact between the fuel and air, realizing the inherent CO<sub>2</sub> separation while maintaining the heat release by fuel conversion to CO<sub>2</sub> and H<sub>2</sub>O. However, using directly solid fuels in the conventional CLC process is challenged by the rate-limiting gasification step of the solid fuels (e.g., coal) in a fuel reactor [17]. Recently, a novel CLC process called CLOU (chemical looping with oxygen uncoupling) has been proposed to overcome this issue [19,20]. CLOU takes advantage of the properties of some OCs (such as CuO/Cu<sub>2</sub>O [21], Mn<sub>2</sub>O<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub> [22], perovskite-type oxides [23] and raw ores [24]) that release gaseous O<sub>2</sub> at high temperatures (800–1000 °C) and oxygen-deficient atmosphere. Unlike typical CLC process, CLOU process divides fuel combustion into three steps: (i) the OC particles release gaseous O<sub>2</sub> in a fuel reactor at oxygen-deficient atmosphere; (ii) the fuel combusts with the released gaseous O<sub>2</sub>, whilst CO<sub>2</sub> and H<sub>2</sub>O without N<sub>2</sub> are produced; (iii) the reduced OC particles are then sent to another reactor (air reactor) and reoxidized by the air. In CLOU, fuel reacts with the gas-phase oxygen released by the OC, efficiently increasing the reaction rate between fuels and OCs. For instance, Leion et al. [23] carried out a CLOU experiment for six different solid fuels and found that CLOU gave a factor 3–15 faster fuel conversion than CLC. Therefore, CLOU shows better performance compared to CLC, especially for the solid fuels difficult to gasification, such as petroleum coke and anthracitic coal. The reacting equations involved in CLOU processes are shown below:



To improve the coal utilization efficiency and realize low-cost CO<sub>2</sub> capture, a novel coal utilization process integrated coal pyrolysis and CLOU is proposed, where the coal particles are first pyrolyzed to obtain high value-added chemicals and synthetic gases and the remaining semicoke is used as the fuel for CLOU. With the purpose of clarifying the feasibility and fundamental features of the new technology, CLOU experiments and process simulation are performed in this work. Process simulation based on Aspen Plus has been used because it has been successfully used to simulate the complex energy systems and chemical process plants, such as various coal-fired power plants [25,26] and coal-based poly-generation system [4]. From process simulation results, exergy analysis is further conducted to evaluate thermodynamic performance of the proposed system, and then compared with those of the conventional coal poly-generation system for identifying its superiority. Cu-based OC is used in the experiments because of its high reactivity and oxygen transport capacity. The oxygen uptake and release performance of this kind of OC has been fully investigated in Refs. [27] and [28].

It should be noted that semicoke is a low-reactivity fuel. Whether the semicoke demonstrates a good performance in the

CLOU is one of the most critical issues for the coupled system. The CLOU concept of solid fuels has been conducted in a batch-operated fluidized bed reactor and interconnected fluidized-bed reactor recently. Mattisson et al. [20] investigated the reactivity of Cu-based OCs towards petroleum coke. They found that the OC could decompose rapidly to promote the combustion of the fuels. Adánez-Rubio et al. [29] investigated the performance of CLOU for coals of different rank in an interconnected fluidized-bed reactor. With all the coals used, unburnt compounds were not present in the fuel reactor outlet. The carbon capture efficiency increased with fuel reactor temperature and this increase was more relevant for low reactivity fuels. These studies demonstrate that the CLOU process is a favorable technology to combust some low-reactivity solid fuels with high combustion efficiency and CO<sub>2</sub> capture efficiency. However, few existing literatures have paid attention to the CLOU performance of semicoke, though it is the main product of the coal pyrolysis and partial gasification. Therefore, CLOU experiments are conducted using a batch fluidized bed reactor in the current study, and the effects of temperature in the fuel reactor on the gas yields of the semicokes and the carbon conversion rate are investigated.

## 2. Establishment of the new poly-generation system

### 2.1. Process description

Pyrolysis and combustion are two common coal utilization types. The utilization efficiency of coal will be improved greatly when the two types are integrated reasonably. Fig. 1(a) shows a simplified schematic of a typical coal poly-generation system coupling pyrolysis and combustion. First, the coal particles are introduced into a pyrolysis unit for extracting high value-added products, including gaseous and liquid fuels or chemicals. Next, the remaining semicoke particles are transported to the combustion unit to generate heat for power generation. The atmospheric pressure fluidized bed can be used as pyrolysis unit and CFB can be used as combustion unit [6,7]. The process realizes the co-production of coal gas, tar and electricity. However, the direct combustion of semicoke in CFB would lead to large CO<sub>2</sub> emission. Thus, a new poly-generation scheme based on pyrolysis and CLOU is proposed to address the issue, as shown in Fig. 1(b).

The whole process mainly consists of four sections: pyrolysis unit, cooling and separation unit, fuel reactor and air reactor. Different from that in typical coal poly-generation system, the remaining semicoke from the pyrolysis unit is sent to fuel reactor, in which it reacts with gaseous oxygen released by OC to produce CO<sub>2</sub> and H<sub>2</sub>O. After removing H<sub>2</sub>O by cooling and separation unit, a high purity of CO<sub>2</sub> can be obtained, which can be further utilized in industry or directly deposited by geological storage. Finally, the reduced OC in fuel reactor is transported into and reoxidized in the air reactor, and then sent back to the fuel reactor for realizing OC reutilization.

The pyrolysis temperature ranges from 500 °C to 900 °C, and the fuel and air reactor temperatures are among 850–1000 °C. It is noted that OC particles in new system can be used as solid heat carriers to provide energy for coal pyrolysis. The reduced OC and some unconverted OC, such as Cu<sub>2</sub>O and CuO, can provide ionic or gaseous oxygen to promote the coal pyrolysis or coal partial gasification. Therefore, the new system has a potential to obtain high quality pyrolysis gas containing much CO and H<sub>2</sub>.

### 2.2. Simulation and assumptions

To identify the thermodynamic performance of new system, process model is established in Aspen Plus, and the typical system

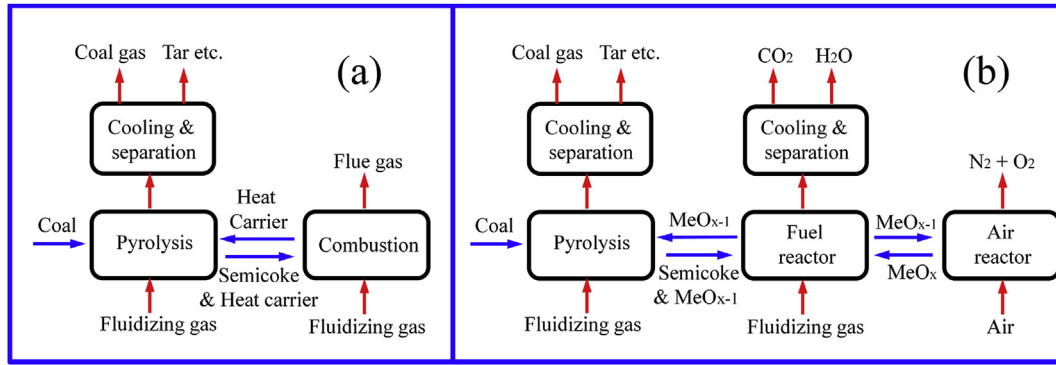


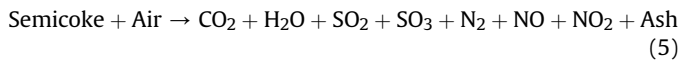
Fig. 1. Schematic of (a) typical coal poly-generation system and (b) coal pyrolysis coupled with CLOU system.

is also simulated as base case for comparison. Identical capacity for pyrolysis unit in these two systems is used to lay a reasonable comparative basis. The pyrolysis unit was simulated by the RYIELD model, in which the decomposition reaction was expressed as follows:



RYIELD model has been widely used in coal pyrolysis or gasification [30,31]. A challenge is that the coal pyrolysis phenomenon is complex and the mass fractions of gaseous products in coal pyrolysis are still difficult to be estimated or obtained. Until now, published studies on the modeling of the pyrolysis process using Aspen Plus or other commercial software have not attempted to model the volatile product composition. Thus, in order to more practically predict the actual products of coal pyrolysis, the amount of each pyrolysis product is based on the literature data by Wen et al. [32]. The proximate and ultimate analyses of coal are presented in Table 1 and the product yield data of coal pyrolysis at 900 °C are listed in Table 2.

The combustion unit consists of RYIELD model, RGIBBS model and Fortran modules. Semicoke is decomposed into its constituent reactants, including O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>, S, C, ash, etc. through Fortran modules according to the semicoke proximate and element analysis, mainly resulting from that semicoke is an unconventional component and cannot be handled by Aspen Plus directly, in either chemical or phase equilibrium. Next, the combustion of these conventional components proceeding in the combustion unit is modeled by RGIBBS model based on the principle of the minimum of Gibbs free energy. The semicoke combustion at 900 °C can be described as below:



In the process of semicoke and OC reaction in the new proposed system, RYIELD model and RGIBBS model is also used to model the reaction of OC in fuel reactor and air reactor. The reaction of oxygen carrier and semicoke at 900 °C can be described as follows:

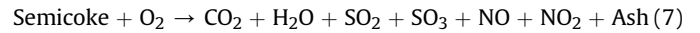


Table 1  
Proximate and element analysis for raw coal [32].

Proximate analysis (wt%)				Ultimate analysis (wt%, dr)						
Moisture	Fix char	Volatiles	Ash	C	H	N	Cl	S	O	Ash
0.2	58.01	26.46	15.53	74.05	6.25	0.71	0.37	1.77	1.32	15.53

Table 2  
The products yield of coal pyrolysis [32].

Components	CO	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> S	N <sub>2</sub>	CH <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	Semicoke
Yield (wt%)	0.59	0.84	0.3	0.79	0.94	0.35	16.37	7.1	72.72



The OC reoxidation in the air reactor at 900 °C can be described as follows:



The following assumptions are considered in modeling the two systems:

- 1) Reactors are isothermal and adiabatic.
- 2) Based on the principle of Gibbs free energy minimization, the coal pyrolysis and semicoke combustion are assumed to be combusted completely.
- 3) The C, H, S, O and N in the semicoke are converted to gas phase and the ash does not participate in chemical reactions.
- 4) Since tar mainly consists of aromatic hydrocarbons and its composition is very complicated, C<sub>6</sub>H<sub>6</sub> has been chosen as the tar model because it is the simplest and one of the most common aromatic hydrocarbon in tar [33,34].
- 5) Raw coal flow rate is 10 kg/s and OC particles flow rate is assumed as 152 kg/s to ensure enough gaseous oxygen being released by the OC in fuel reactor to supply the semicoke combustion.

### 2.3. Materials used in experiments

The OC used in this investigation is CuO/CuAl<sub>2</sub>O<sub>4</sub> prepared by sol–gel method [35] with sizes of 125–180 μm and the CuO content is 60 wt. %. Table 3 shows the main physical characteristics of the prepared OC.

A typical kind of Chinese lignite, Shengli coal (SL-coal), which has high volatile content, is used in the experiment. The coal particles with sizes of 0.2–0.3 mm are firstly dried in an air dry oven at 150 °C, followed by pyrolysis for 20 min and 60 min in a tube furnace at 900 °C using N<sub>2</sub> with a flow rate of 1000 ml/min as the carrier gas. In order to examine the effect of semicoke properties on the CLOU performance, we prepare two kinds of pyrolysis semicoke of SL-coal (undergoing pyrolysis of 20 min and 60 min). Table 4 presents the proximate analysis and the ultimate analysis of raw coals and semicokes. Note that the raw coal contains a large amount of volatiles of above 41%, which is not conducive to the

**Table 3**  
Physical characterization of fresh oxygen carrier.

Phases of oxidized OC	CuO and CuAl <sub>2</sub> O <sub>4</sub>
Phases of reduced OC	Cu <sub>2</sub> O, CuAlO <sub>2</sub> , Cu <sup>m</sup> and CuAl <sub>2</sub> O <sub>4</sub> <sup>m</sup>
Crushing strength (N)	1.89
Particle diameter (mm)	0.125–0.180

<sup>m</sup> = Minor phase.

comprehensive utilization of the fuels when directly combusting them in CLOU. The SL-20 and SL-60 have a volatile content of 11.49% and 10.33%, respectively, suggesting that most of the volatiles can be extracted.

#### 2.4. Experimental setup and procedure

Due to the limitations of experimental conditions, only batch experiments were conducted. Batch experiments can partly simulate the real continuous system, yet it has been widely used and gave many beneficial results about the features of fuels and OC in CLOU [20,21]. The fluidized bed system used in this experiment consists of atmosphere control unit, reaction unit and outlet gas detection unit, as shown in Fig. 2. The atmosphere control unit provides air or N<sub>2</sub> as the fluidized gas to simulate the air reactor or fuel reactor atmosphere in CLOU. An electrical furnace is used to heat the stainless reaction tube with a length of 892 mm. A porous plate with a diameter of 26 mm is located at 400 mm from the bottom of the reaction tube. Besides, temperature in the reaction unit is measured using a K-type thermocouple, along with the pressure kept in constant. Exhaust of the reactor is led to the electric condenser, where water is condensed and removed; and then to a gas analyzer, where compositions of the dry gas could be determined. The flow rate of the fluidization gas is set at 800 mL/min, so that the inlet gas velocities were 4–9 times  $u_{mf}$ , where  $u_{mf}$  is the minimum fluidized velocity. The concentrations of CO<sub>2</sub>, CO, CH<sub>4</sub>, and O<sub>2</sub> from gas analyzer (Wuhan Cubic Optoelectronics, Gasboard-3000) are real-time recorded by the computer with a time interval of 1 s. The effects of sulfur on the experiments are not measured in the experiment for the following reasons: 1) the Shengli lignite used in the work is a low-sulfur coal (0.48 wt.% S), as can be seen in Table 4, which will have much less influence on the OC performance; 2) during the pyrolysis of a lignite, a lot of sulfur will convert to gaseous H<sub>2</sub>S and COS, and the residual sulfur in the semicokes are mainly organic sulfur and mineral sulfur, which are much stable and could hardly convert to H<sub>2</sub>S in combustion process, as described in many references such as [8] and [36]; 3) most of the S in fuels is released as SO<sub>2</sub> in the fuel reactor, slightly affecting to the quality of the CO<sub>2</sub> produced, but having little detrimental effect on the OC sintering resistance and reactivity [37,38]. However, a more detail study is needed on the sulfur behavior under different reaction conditions, such as the reaction temperature, the sulfur content in the semicoke and the OC used.

At the beginning of the experiment, 40 g of CuO/CuAl<sub>2</sub>O<sub>4</sub> particles is fed onto the porous plate through the funnel placed on the top of the furnace, and is exposed to the air for 30 min at a preset temperature to ensure complete oxidation. Following this, the

**Table 4**  
Proximate and ultimate analyses of the fuels.

	Proximate analysis (wt%, ar)				Ultimate analysis (wt%, dr)			
	Moisture	Fix char	Volatiles	Ash	C	H	N	S
SL-coal	8.31	35.47	41.59	14.32	48.33	4.11	0.85	0.48
SL-20	6.15	57.21	11.49	25.15	70.34	1.00	0.84	0.15
SL-60	6.36	44.93	10.33	38.39	53.53	0.97	0.74	0.46

fluidization gas is switched rapidly to N<sub>2</sub> to simulate the inert atmosphere in fuel reactor. In all cases, following with the N<sub>2</sub> introduced, O<sub>2</sub> partial pressure in the reactor tube sharply decreases as a function of time and then tended to reach to a constant value. When oxygen concentration in the reactor is stable, 0.3 g of semicoke particles is fed into the reactor tube, where fuel combusts with the released oxygen. When the combustion is finished (no CO<sub>2</sub> was detected in the exhaust), gaseous environment is converted to air to oxidize the reduced OC. When O<sub>2</sub> concentration at the reactor exit reaches to 20.95%, the oxidation process is complete. Thus, it realizes simulating the cyclic conditions of a CLOU system with consecutive alternating oxidizing and reducing processes.

#### 2.5. Data evaluation

Carbon conversion has been used to assess the fuel reactivity and is of significance in designing and operating the reactor. The concentrations of different gases are obtained in the experiment from the flue gas composition analysis during the reduction and oxidation cycles as a function of time. The carbon conversion of the fuel is established by integration of these concentrations as a function of time and calculated from Eq. (9):

$$X_C = \frac{\int_{t_0}^t Q_{out}(t) [p_{CO}(t) + p_{CO_2}(t) + p_{CH_4}(t)] dt}{\int_{t_0}^{t_{total}} Q_{out}(t) [p_{CO}(t) + p_{CO_2}(t) + p_{CH_4}(t)] dt} \quad (9)$$

where  $t_0$  and  $t_{total}$  are the initial time and the end time of the combustion process;  $t$  is the time elapsed since the start of the combustion;  $Q_{out}(t)$  (mol/s) denotes the molar flow of gas from the outlet of the reactor; and  $p_{CO_2}(t)$ ,  $p_{CO}(t)$ ,  $p_{CH_4}(t)$  are the partial pressure of the CO<sub>2</sub>, CO, CH<sub>4</sub> (dry basis).

The average carbon conversion rate  $X_{Cavg}$  (%/s) of different fuels is calculated by Eq. (10) to measure the reaction rate in the fuel reactor.

$$X_{Cavg} = \frac{X_C}{t - t_0} \times 100\% \quad (10)$$

The time  $t_{0.95}$  when 95% of combustible carbon is converted and the average carbon conversion rate  $X_{Cavg,0.95}$  are calculated to investigate the effects of the temperature and the volatile content on the conversion rate of the fuels.

Besides, the ratio of hydrogen and carbon in the flue gas is calculated to evaluate the temperature effect on the volatiles combustion. Gas yields of H<sub>2</sub>, CO and CO<sub>2</sub> are also calculated to evaluate the CO<sub>2</sub> capture efficiency. They are calculated by Eqs. (11)–(13), considering the total carbon detected in the reduction.

$$\gamma_{H_2} = \frac{\int_{t_0}^{t_{total}} Q_{out} p_{H_2} dt}{\int_{t_0}^{t_{total}} Q_{out} (p_{CH_4} + p_{CO_2} + p_{CO}) dt} \quad (11)$$

$$\gamma_{CO} = \frac{\int_{t_0}^{t_{total}} Q_{out} p_{CO} dt}{\int_{t_0}^{t_{total}} Q_{out} (p_{CH_4} + p_{CO_2} + p_{CO}) dt} \quad (12)$$



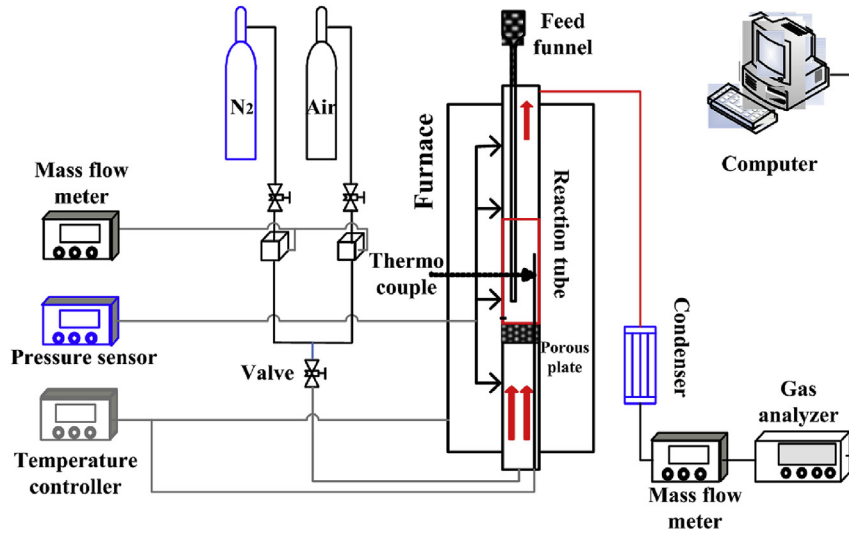


Fig. 2. The fluidized bed reactor system.

$$\gamma_{\text{CO}_2} = \frac{\int_{t_0}^{t_{\text{total}}} Q_{\text{out}} p_{\text{CO}_2} dt}{\int_{t_0}^{t_{\text{total}}} Q_{\text{out}} (p_{\text{CH}_4} + p_{\text{CO}_2} + p_{\text{CO}}) dt} \quad (13)$$

In addition, the combustion efficiency  $\eta_{\text{comb,F}}$ , defined as the degree of fuel conversion in the fuel reactor, is also calculated. The combustion efficiency can be obtained through calculating the heat loss and the heat released by fully combusting the fuels added to the fuel reactor, as shown in Eq. (14):

$$\eta_{\text{comb,F}} = \frac{\int_0^{t_f} Q_{\text{out,red}} (H_{\text{CO}} M_{\text{CO}} p_{\text{CO}} + H_{\text{CH}_4} M_{\text{CH}_4} p_{\text{CH}_4} + H_{\text{H}_2} M_{\text{H}_2} p_{\text{H}_2}) dt}{m_{f,\text{added}} H_{f,\text{added}}} \quad (14)$$

$H_i$  (MJ/kg) denoting the lower heating value of the respective fuel, and  $M_i$  (kg/mol) the molar mass of species  $i$  in the exhaust. And  $m_{f,\text{added}}$  is the mass of the added fuel.

### 3. Results and discussion

#### 3.1. Mass and energy balances

Detailed material flows for the two systems are shown in Fig. 3. The products of coal pyrolysis are identical since same capacity of the pyrolysis units are used in the two models. However, for different semicoke utilization processes, simulation results for flue gas composition summarized in Table 5 are distinctive. For typical system, its flue gas mainly contains  $\text{N}_2$  and  $\text{CO}_2$ , while for new system the flue gas mainly contains  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The higher  $\text{SO}_2$  and  $\text{CO}_2$  contents in new system mainly result from little  $\text{N}_2$  in fuel reactor. It is a big problem to separate  $\text{CO}_2$  from the  $\text{N}_2$  in the typical system, because the  $\text{CO}_2$  content is low in flue gas (about 17.65 vol. %). But for the new system, there are 92.87 vol. %  $\text{CO}_2$  and 6.08 vol. %  $\text{H}_2\text{O}$  in the flue gas of fuel reactor. Thus, the new system can sharply reduce the energy penalty for  $\text{CO}_2$  capture.

Fig. 3 also shows the distribution of the energy consumption. In both of the systems, the energy consumption for coal pyrolysis is

29.9 MW. In a realistic process, the needed energy can be supplied by solid heat carrier or flue gas from combustion unit and fuel reactor. For typical system, the semicoke produced by pyrolysis is sent to combustion unit and burned to produce energy of 119.6 MW. The value is almost equal to the total energy produced by fuel reactor (73.1 MW) and air reactor (46.4 MW) in the coupled system. The enthalpy of the flue gas of the coupled system is also comparable to that of the typical system. That means the new system realizes  $\text{CO}_2$  concentration without energy penalty and obtains coal gas and tar yields simultaneously, which is beneficial to the coal utilization improvement.

#### 3.2. Exergy analysis

Exergy represents the maximum obtainable work to bring a system to thermodynamic equilibrium with its surroundings. Exergy analysis is useful in designing new thermal system or improving old system by reducing sources of inefficiency. The total exergy ( $E$ ) can be expressed by the sum of physical exergy ( $E^{\text{PH}}$ ), kinetic exergy ( $E^{\text{KN}}$ ), potential exergy ( $E^{\text{PT}}$ ) and chemical exergy ( $E^{\text{CH}}$ ) [39], which can be described as:

$$E = E^{\text{PH}} + E^{\text{KN}} + E^{\text{PT}} + E^{\text{CH}} \quad (15)$$

Only physical and chemical exergies are considered because velocity and elevation have negligible when applied to coal combustion process [40].  $E^{\text{PH}}$  is the maximum work that can be obtained as a system passes from its initial state ( $T$  and  $P$ ) to the environment state ( $T_0$  and  $P_0$ ). While  $E^{\text{CH}}$  is the maximum work that can be obtained as a substance turns to chemical equilibrium with the environment at the environment state ( $T_0$  and  $P_0$ ).

Exergy efficiency is known as the second-law efficiency, which is used to assess the system efficiency. It can be written as: [41]

$$\eta_{\text{exergy}} = \frac{E_{\text{out}}}{E_{\text{in}}} = 1 - \frac{E_{\text{in}} - E_{\text{out}}}{E_{\text{in}}} \quad (16)$$

where  $E_{\text{out}}$  and  $E_{\text{in}}$  are the output exergy and input exergy of a system, respectively.

Based on the simulation results, exergy streams of the two systems were acquired and shown in Table 6. It can be seen that, for the typical system, the exergy loss mainly came from the semicoke combustion process, where exergy efficiency is 78.57%. For the

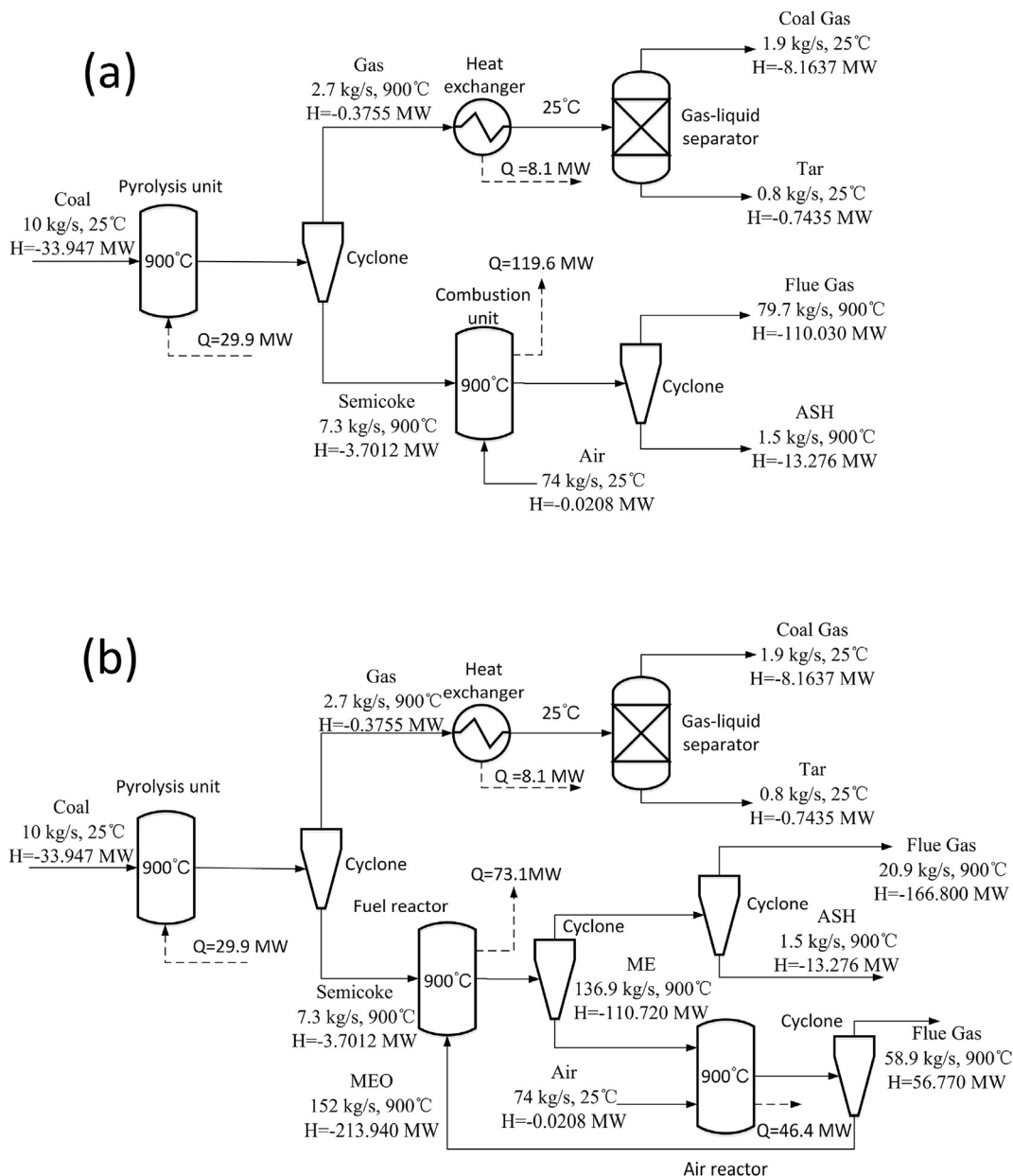


Fig. 3. Material and energy flows of (a) the typical system and (b) the new system.

Table 5  
The outputs of the different reaction steps for the two models.

Output	Pyrolysis (wt. %)	Typical system		
		Combustion boiler (vol. %)	Fuel reactor (vol. %)	Air reactor (vol. %)
CO	0.59	Trace	Trace	0
H <sub>2</sub>	0.84	Trace	Trace	0
CO <sub>2</sub>	0.30	17.65	92.87	0
H <sub>2</sub> O	0.79	1.16	6.08	0
H <sub>2</sub> S	0.94	Trace	Trace	0
N <sub>2</sub>	0.35	79.83	0.26	98.50
CH <sub>4</sub>	16.37	–	–	–
TAR	7.10	–	–	–
NO	–	Trace	Trace	Trace
NO <sub>2</sub>	–	Trace	Trace	Trace
SO <sub>2</sub>	–	0.10	0.56	0
SO <sub>3</sub>	–	Trace	Trace	0
O <sub>2</sub>	–	1.25	0.22	1.49
Semicoke	72.72	–	–	–

coupled system, the exergy loss mainly came from the semicoke combustion in fuel reactor, where exergy efficiency is 89.80%. According to the results, total exergy efficiency for new system is 83.22%, about 0.82% higher than that for the typical system, implying that the new system has reduced the exergy loss and improved the exergy efficiency.

Table 6  
The exergy analysis of the two models.

	Input (MW)	Output (MW)	Exergy efficiency (%)
<b>Typical system</b>			
Pyrolysis	320.843	308.321	96.10
Combustion	190.683	149.812	78.57
Total	329.040	271.132	82.40
<b>New system</b>			
Pyrolysis	320.843	308.321	96.10
Fuel reactor	247.105	221.899	89.80
Air reactor	152.192	139.219	91.48
Total	329.040	273.818	83.22

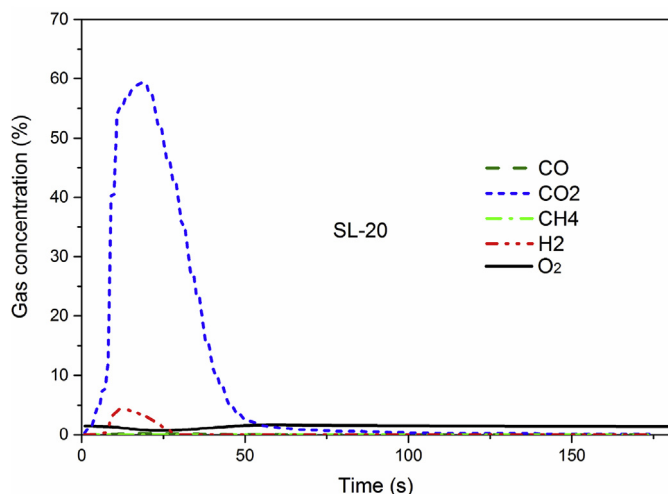


Fig. 4. Concentration profile for the reduction of 0.3 g of SL-20 at 900 °C with 40 g of CuO/CuAl<sub>2</sub>O<sub>4</sub>. The fluidizing gas is pure nitrogen.

### 3.3. CLOU process of SL-20 and SL-60

To evaluate the performance of the CLOU for combustion of semicoke, 0.3 g of SL-20 or SL-60 is fed into the fuel reactor at five temperatures: 850 °C, 885 °C, 900 °C, 925 °C and 950 °C. Pure nitrogen is used as the fluidizing gas during the reduction. Gas measurements of CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub> and O<sub>2</sub> versus time provide the basis for the analysis. Fig. 4 shows the dry flue gas concentrations during reducing period for SL-20 at 900 °C. It can be seen that, as the fuel combusts, only a small peak of H<sub>2</sub> is detected. These H<sub>2</sub> are released from SL-20 particles at a high temperature and do not participate in the combustion because they do not sufficiently contact with the gaseous oxygen in the reactor. Meanwhile the CO<sub>2</sub> concentration increases to about 60% immediately accompanied with the oxygen concentration sharply decreasing, indicating the rapid reaction rate of SL-20. As O<sub>2</sub> concentration decreases, the OC continues to release oxygen to supply the following combustion. After about 50 s, the O<sub>2</sub> concentration rises up again while no carbon containing species is found, indicating the semicoke converts completely and the combustion is fast. Fig. 5 shows the

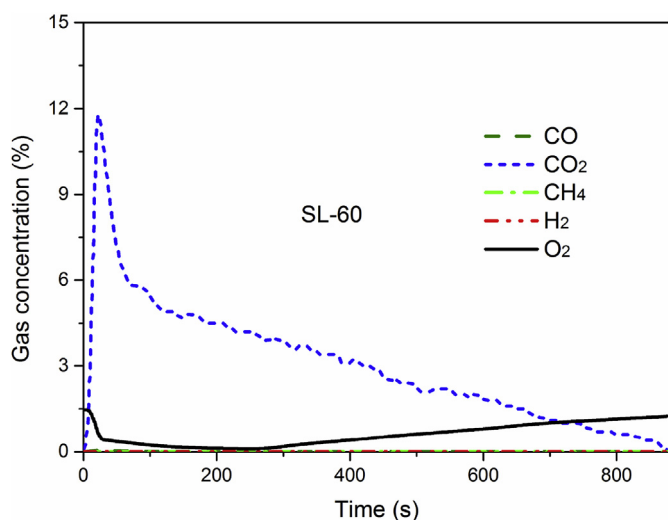


Fig. 5. Concentration profile for the reduction of 0.3 g of SL-60 at 900 °C with 40 g of CuO/CuAl<sub>2</sub>O<sub>4</sub>. The fluidizing gas is pure nitrogen.

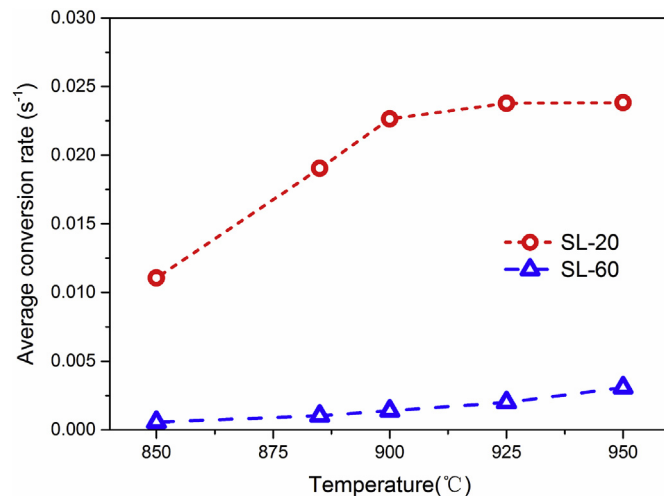


Fig. 6. Average carbon conversion rate for 95% conversion of the carbon' as a function of temperature.

corresponding results for SL-60, and nearly no CO or CH<sub>4</sub> or H<sub>2</sub> is found. However, the reaction time of SL-60 is about 8–10 times higher than that of the SL-20.

Higher conversion rate of semicoke is conducive to the operation of the realistic system, since it reduces the solids inventory needed as well as the reactor size. As the results shown above, SL-20 has more desirable reactivity in CLOU at 900 °C compared to SL-60. It is also noted that the OC can provide sufficient gaseous oxygen for the semicoke conversion, considering that the O<sub>2</sub> concentration keeps higher than zero and the SL-20 can be fully converted in 100 s. We have also calculated the average conversion rates of the two fuels at different temperatures (see Fig. 6). The average conversion rates of SL-20 are always much higher than SL-60.

### 3.4. Effect of the reaction temperature on the CLOU process

Next, we also analyzed the effect of the reactor temperature on the CLOU process of the semicokes, including the average conversion rate and the gas yield of the semicokes. Fig. 6 shows the effects of temperature on the average rate to convert 95% of the semicokes. It is found that a high temperature is beneficial to increasing the average conversion rate. The average conversion rate at 950 °C is apparently faster than that at 850 °C. This mainly results from that a high temperature increases the equilibrium oxygen partial pressure of the OC, and gaseous oxygen will be released more rapidly by the OC. Thus, the fuel particles have more chances to contact with the oxygen, which increases carbon conversion rate and promotes the combustion. It can be also seen that SL-20 shows high average conversion rates at different temperatures. The average carbon conversion rates of SL-20 have little difference at 900–950 °C, suggesting this temperature range is favorable for the CLOU of SL-20.

In addition, at different reaction temperatures, some unburned gases exist in the flue gas, as seen in Figs. 7 and 8, but no CH<sub>4</sub> is found in any case. The ratio of hydrogen and carbon in the flue gas for SL-20 rises up with temperature increasing and no H<sub>2</sub> is found for SL-60, as seen in Fig. 7. We speculate that the unburned H<sub>2</sub> mainly comes from the released H<sub>2</sub> that has insufficient time to react with O<sub>2</sub> and escape from the reactor. Fig. 8 shows the gas yield of CO for SL-20 and SL-60. The CO yield is high for SL-20 and tends to decrease with temperature rises up. on the contrary, the CO yield relatively low and tends to increases for SL-60. The existence of the

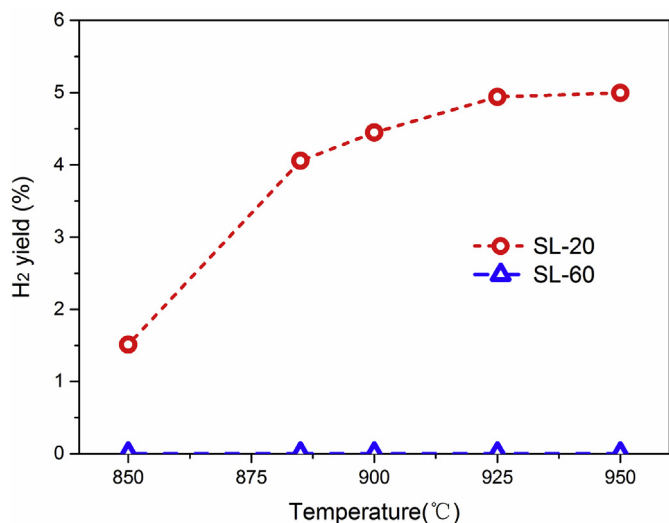


Fig. 7. The ratio of hydrogen and carbon in the flue gas as a function of temperature at 850 °C, 885 °C, 900 °C, 925 °C and 950 °C.

unburned gases will reduce the combustion efficiency. The combustion efficiency for SL-20 is about 93% at 900 °C, and for SL-60, it is higher than 96%. A realistic interconnected fluidized-bed reactor [29] will allow a longer residence time of some volatiles from the semicoke in the fuel reactor, which can reduce the unburned gases in the flue gas and increase the combustion efficiency.

Fig. 9 shows that the CO<sub>2</sub> yields for SL-20 and SL-60. The CO<sub>2</sub> yields are very high, reaching to 99.5% or more in all cases, that is, high CO<sub>2</sub> capture efficiencies can be obtained. Because more unburned gases, such as CO in the flue gas for SL-20, the CO<sub>2</sub> yield is lower than that for SL-60. It is clear from the experimental results that, the output of different products from the fuel reactor unit is dominated by the operation condition in the fuel reactor unit, where the ambient temperature is a key factor. SL-20 has much higher conversion rate than SL-60, though more unburned gases exist in the flue gas. And the suitable reactor temperature range for CLOU of SL-20 is 900–950 °C.

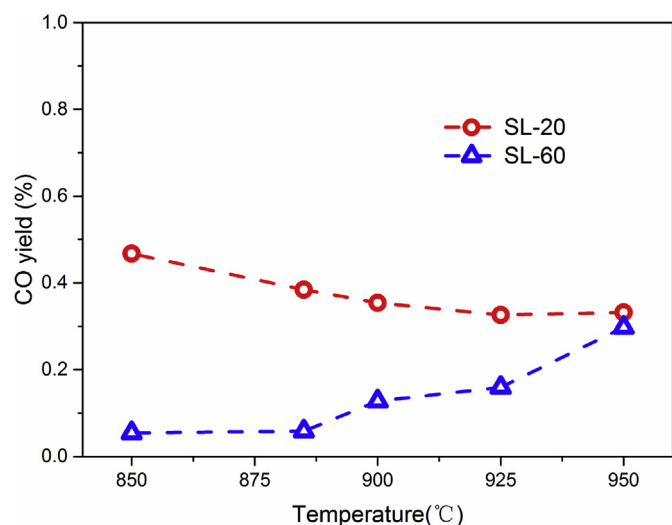


Fig. 8. Gas yield of CO as a function of temperature at 850 °C, 885 °C, 900 °C, 925 °C and 950 °C.

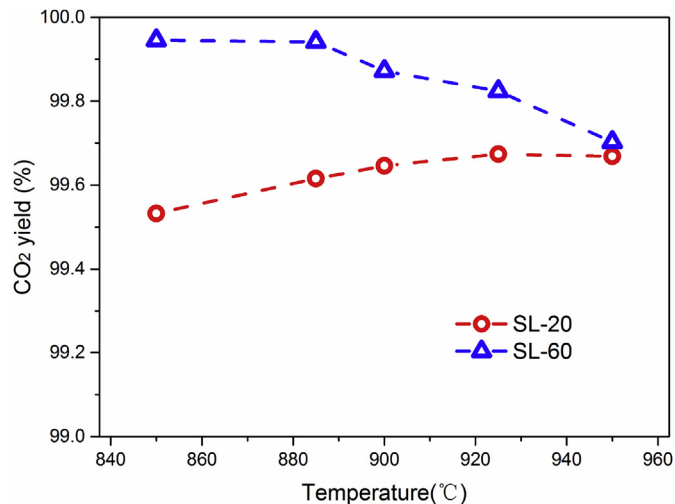


Fig. 9. Gas yield of CO<sub>2</sub> as a function of temperature at 850 °C, 885 °C, 900 °C, 925 °C and 950 °C.

Besides the CLOU performance of semicokes, the matching performance between pyrolysis unit and fuel reactor should also be taken into consideration to scale up this technology. Results of this work showed that SL-20 semicoke can be fully converted in 100 s in CLOU at 900 °C, and longer pyrolysis time will increase the combustion time. For SL-20 semicoke, the residence time of coal in the pyrolysis unit (20 min) is much higher than the needed residence time of semicoke in the fuel reactor (100 s). In this case, the solids inventory of pyrolysis unit will be relatively high. The problem can be addressed by increasing the pyrolysis temperature, adding catalyst or regulating the solid circulation rate among reactors.

#### 4. Conclusions

In this work, a coal pyrolysis process coupled with CLOU technology is proposed. It has a potential to make full use of the volatiles in the coal and co-produce coal gas, tar and heat/electricity accompany with substantially reducing costs for CO<sub>2</sub> capture. The mass flow and exergy efficiency of the new system are evaluated and compared to the typical system. As the simulation results shown, the coupled system has high concentration of CO<sub>2</sub> (92.87%) in the flue gas, which can significantly reduce the energy penalty for CO<sub>2</sub> capture. Furthermore, exergy analysis shows that the exergy efficiency for new system increases 0.82%. Therefore, the coupled system can realize the coal utilization efficiency improvement and near-zero emissions of CO<sub>2</sub>.

CLOU performance of the semicoke is studied in a fluidized-bed reactor. Result shows that semicoke can be fully converted, the reactor temperature and the semicoke characteristic are two key factors in determining the CLOU process, in which higher fuel reactor temperature and semicoke with shorter pyrolysis time are favorable to the conversion process. The average carbon conversion rate of the SL-20 is much higher than the SL-60, suggesting too longer pyrolysis time can be not conducive to the following CLOU of the semicoke. In addition, the CO<sub>2</sub> yield of the CLOU of SL-20 reaches to higher than 99.5% with no CH<sub>4</sub> and little CO observed in the flue gas during the reduction stage. The study suggests that the semicoke fits the CLOU process very well and the new system shows higher exergy efficiency and coal utilization efficiency with low cost CO<sub>2</sub> capture. It deserves a further investigation on the heat transfer between the coal particles and the solid heat resource (such as the reduced OC particles) in the pyrolysis unit, which may



be favorable for improving the coal pyrolysis or partial gasification efficiency.

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## Nomenclature

$Q_{out}(t)$	outlet gas molar flow in the oxidation period (mol/s)
$t_0$	initial time of the combustion process
$t_{total}$	end time of the combustion process
$p_{CO_2}(t)$	partial pressure of CO <sub>2</sub>
$p_{CO}(t)$	partial pressure of CO
$p_{CH_4}(t)$	partial pressure of CH <sub>4</sub>
$X_C$	carbon conversion
$X_{Cavg}$	average carbon conversion rate (%/s)
$H_i$	lower heating value of species $i$ (kJ/kg)
$M_i$	molar mass of species $i$ (kg/mol)
$m_{f,added}$	mass of the added fuel (kg)

## Greek letters

$\gamma_i$	mass fraction of the component $i$ in flue gas (%)
$\eta_{comb,F}$	combustion efficiency of coal

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