

# Thermodynamic investigation on the performance difference between heat supply method of calcium looping for CO<sub>2</sub> capture

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## ABSTRACT

Calcium looping process (CaL) is a promising alternative for realizing low-energy-penalty of post-combustion technologies. This study investigates the CO<sub>2</sub> enrichment difference of three types of calcium looping heating supply methods: calcium looping combustion (CaLC), oxy-fuel combustion (CaL-Oxy), and Cu-based chemical looping combustion (CaL-CLC). and the three calcium looping processes are integrated with power plant to evaluate the energy efficiency and energy penalty of the power plants with CO<sub>2</sub> capture based on these calcium processes. The results show that the CaL-CLC has the highest energy efficiency (39.4%) and the lowest energy penalty (3.46%), which indicates that reducing the gas separation cost plays important role caused by CO<sub>2</sub> enrichment in the heat supplying method of calcium looping process.

**Keywords:** post-combustion CO<sub>2</sub> capture, calcium looping, energy penalty, carbon enrichment

## NONMENCLATURE

### Abbreviations

CCS	CO <sub>2</sub> capture and storage
CaL	Calcium looping process
CaLC	Calcium looping combustion
CaL-Oxy	Calcium looping oxy-fuel combustion
CaL-CLC	Calcium looping Cu-based chemical looping combustion
HRS	Heat recovery steam generator
ASU	Air separation unit
PC	power plant

## 1. INTRODUCTION

The tremendous scale of CO<sub>2</sub> emissions caused by fossil fuel combustion in sectors of power and industry present an urgent environmental challenge. CO<sub>2</sub> capture and storage (CCS) are expected to be essential for mitigating the CO<sub>2</sub> emission and reducing the environmental impact. Among the different CO<sub>2</sub> capture technologies, post-combustion CO<sub>2</sub> capture technologies are the only “end-of-pipe” solutions that would allow the mitigation of carbon emissions from stationary sources

without modifications to the power plant itself. However, the post-combustion CO<sub>2</sub> capture technologies struggle to be cost-effective at commercial scale due to the relatively high capital cost and energy penalty, which makes post-combustion CO<sub>2</sub> capture technology less economically attractive at this moment[1]. Therefore, post-combustion CO<sub>2</sub> capture technologies with low energy penalty need to be developed.

Calcium looping (CaL) process is a promising option for low-energy-penalty of post-combustion CO<sub>2</sub> capture, which has been currently validated with success in the pilot-scale coal fired plants of 1-2 MWth [2]. And related studies have been conducted to show the potential of the process and its feasibility from the aspects of understanding of reaction mechanism, process simulation, reactor modeling and economic analysis. The CaL process is based on the use of CaO as a regenerable sorbent through carbonation/calcination cycles at high temperature. In the CaL process, CO<sub>2</sub> in the flue gas stream (3-20%) is captured by partial carbonation of the CaO particles in the carbonator reactor operating under atmospheric pressure. Then the partially carbonated particles are subsequently circulated into the calciner reactor where calcination of CaCO<sub>3</sub> to regenerate the sorbent and a highly concentrated CO<sub>2</sub> gas exiting the calciner is ready for condensation and purification. However, the calcination reaction is endothermic and high-temperature heat is required by combustion of fossil fuel. To supply heat for the calcination of CaCO<sub>3</sub>, three heat supply methods are employed including calcium looping combustion (CaLC), oxy-fuel combustion (CaL-oxy), and Cu-based chemical looping combustion (CaL-CLC), and the energy penalty of the CaL processes integrating with power plants has been studied. However, the former studies were based on different sets of assumptions regarding the CO<sub>2</sub> capture plant. Furthermore, the CO<sub>2</sub> enrichment difference during three heat supply methods and its influences on the performance has not been investigated deeply.

To solve the problem, this paper investigates the theoretical separation work requirement during fuel combustion in the three heat supply methods. And then

the energy efficiency is evaluated to reveal the performance difference of three heat supply methods.

## 2. SYSTEM DESCRIPTION

### 2.1 Reference power plant

To investigate the influence of calcium looping process, a typical 600 MW supercritical coal-fired power plant (PC) is selected as the reference power plant, its steam cycle flow diagram is shown in Fig. 1. The steam turbine consists of a reheat, single axis, dual exhaust and extraction condensing system with eight extractions. The extractions supply steam for three high-pressure heaters (1#, 2#, 3#), deaerator (DEA), four low-pressure heaters (5#, 6#, 7#, 8#), two pump turbines and auxiliary steam system.

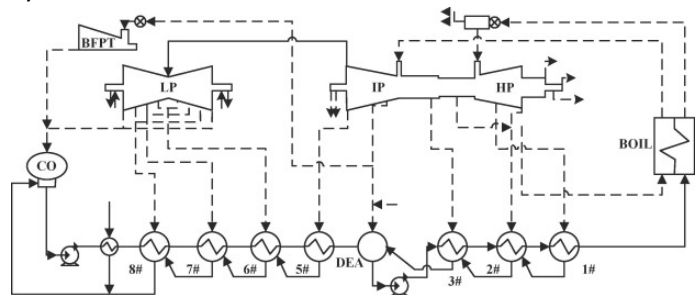


Fig. 1. The schematic of the reference power plant

### 2.2 The CaLC power plant

As shown in Fig. 2, the coal-fired flue gas is sent to the carbonator, where CO<sub>2</sub> is absorbed by the CaO and converted to CaCO<sub>3</sub>. Then the carbonated solids are separated with decarbonized flue gas and sent to the calciner. In the calciner, the CaCO<sub>3</sub> is decomposed into CO<sub>2</sub> and CaO. And the heat required of the calcination process is provided by the external air combustor. Besides, the reaction heat and the sensible heat of high-temperature gas is recovered by heat recovery steam generator (HRSG) and the high-pressure steam generated is produced for power generation in the steam cycle unit.

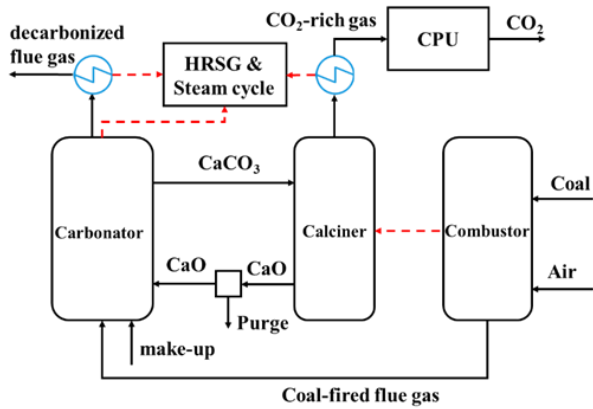


Fig. 2. The schematic of the CaL process

### 2.3 PC with the CaL-oxy process

The schematic of PC with the CaL-oxy process is shown in Fig. 3. In the CaL-Oxy process, the reaction process that takes place in the carbonator and calciner has been mentioned before. However, the heat required for calcination is supplied through coal oxy-combustion, where an air separation unit is necessary for high-purity O<sub>2</sub> production. Same as CaL-PCC, HRSG and steam cycle is also employed to recover the reaction heat and the sensible heat of high-temperature gas for power generation.

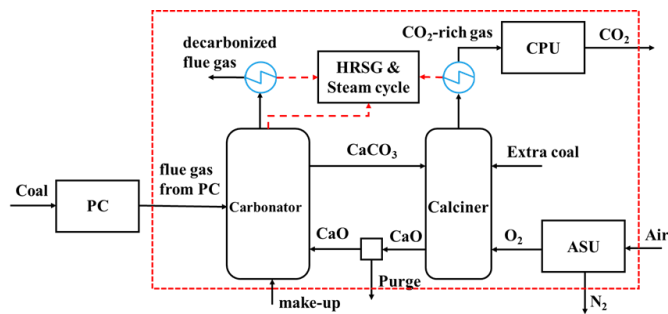


Fig. 3. The schematic of PC with the CaL-oxy process

### 2.4 PC with the CaL-CLC process

The schematic of PC with the CaL-CLC process is presented in Fig. 4. The coal-fired flue gas from PC enters the carbonator. In the carbonator, the CaO absorbs CO<sub>2</sub> from the flue gas. The high temperature solid stream is then transported into the calciner. In the calciner, calcination of CaCO<sub>3</sub> and reduction of CuO occur simultaneously. Then, the solid products are circulated into the air reactor. In the air reactor, Cu is oxidized by air. The outlet stream of the air reactor is also separated into a solid stream, and O<sub>2</sub>-depleted air. The solid stream then

circulates back to the carbonator for the next cycle, while the O<sub>2</sub>-depleted air is used to preheat the air. In the CaL-CLC process, the heat requirement for calcination is provided by coal chemical looping combustion, including the reduction of CuO and the oxidation of Cu. Similarly, the reaction heat of carbonator and sensible heat are recovered through HRSG and steam cycle for power generation.

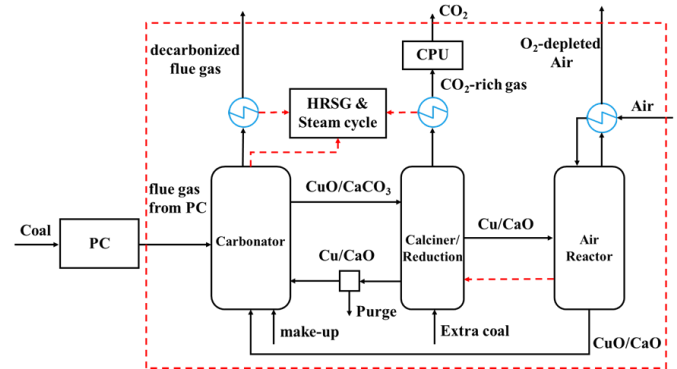


Fig. 4. The schematic of the CaL-CLC process

## 3. KEY PARAMETERS DESIGN AND EVALUATION CRITERIA

### 3.1 Key parameters design

The specific processes of the proposed system and the reference systems are simulated by Aspen Plus V 11.0. And the PR-BM is selected as the global method during the simulation. The bituminous coal is selected as the input fuels for the systems, its proximate analysis and ultimate analysis are presented in Table. 1. Besides, other key parameters in these processes are shown in Table. 2.

Table. 1. Proximate analysis of the bituminous coal[3]

Fuel	Proximate analysis (wt%)					Ultimate analysis (wt%)					LHV(MJ/kg)
	V	FC	A	M	C	H	O	N	S		
Coal	30.80	56.81	8.79	3.60	71.63	4.53	10.28	0.84	0.33	29.5	

Table. 2. Key design Parameters of other process[4-8]

	Parameter	value
Reference power plant	Coal input (kg/s)	48.4
	Inlet temperature of main steam (°C)	566
	Inlet pressure of main steam (MPa)	24.2
Common units in CaL process	Carbonator operating temperature (°C)	650
	Calciner operating temperature (°C)	900
	Carbonator capture efficiency	90%
	Carbonator sorbent conversion	20%
	Steam temperature in HRSG (°C)	566
	Triple-pressure reheat steam cycle(bar)	126/26/5.5
	Isentropic efficiency of ST	0.88/0.89/0.87
CaLC	Outlet of gas temperature in HRSG (°C)	104
	Air combustor temperature (°C)	950
CaL-Oxy	Air excess ratio in air combustor	1.3
	oxygen purity, mol%	95%
	Excess oxygen (%vol,dry) in CO <sub>2</sub> -enriched gas	2.13%
CaL-CLC	Energy consumption of ASU (kg/t O <sub>2</sub> )	180
	Air reactor operating temperature (°C)	950
	Air excess ratio	1.05
	O <sub>2</sub> -depleted air outlet temperature (°C)	90

### 3.2 Evaluation criteria

In this study, energy efficiency and energy penalty are selected to evaluate the thermodynamic performance of the CO<sub>2</sub> capture systems and reference system. The energy efficiency and energy penalty are calculated as follows:

$$\eta = \frac{\sum P_{out}}{\sum E_{in}} \quad (1)$$

$$\eta_{ep} = \eta_{CCS} - \eta_{ref} \quad (2)$$

Where  $\eta$  and  $\eta_{ep}$  refer to the energy efficiency of selected systems and energy penalty of systems with CO<sub>2</sub> capture.  $P_{out}$  refers to the power output of the power plant,  $E_{in}$  refers to the energy input of the power plant including coal input in power plant and extra input in the calcium looping process.  $\eta_{CCS}$  and  $\eta_{ref}$  refer to the energy efficiency of the power plant with CO<sub>2</sub> capture and the reference system, respectively.

## 4. RESULTS

### 4.1 Energy analysis

The simulation results of the three CO<sub>2</sub> capture systems are shown in Table. 3. Under the same carbonator capture efficiency (90%), the PC with CaL-CLC has the highest energy efficiency (39.4%), while the energy efficiency of CaLC and the PC with CaL-Oxy are 31.3% and 36.9%, respectively. Besides, the energy efficiency of the reference system is calculated, which is 42.9% with 1428.8 MW coal energy input. Therefore, among the energy penalties caused by the CO<sub>2</sub> capture system, PC with CaL-CLC has the least energy loss (3.5%), and the energy penalty of the CaLC and PC with CaL-Oxy are 11.5% and 5.92%, respectively. Among them, power consumption for ASU in the CaL-Oxy process and the flue-gas separation in the CaLC power plant brings about the efficiency reduction, while the CaL-CLC process offsets the separation work loss by introducing chemical looping combustion. The separation work requirement contributes to the difference in energy efficiency and energy penalty between the three systems based on calcium looping process for CO<sub>2</sub> capture.

Table. 3. Energy analysis of three systems

Parameter	CaLC	CaL-Oxy	CaL-CLC
<b>Coal input</b>			
Coal in power plant (MW)		1428.8	1428.8
Coal in calcium looping (MW)	1428.8	1025.2	687.4
Total coal inout (MW)	1428.8	2454.0	2116.2
<b>Power output</b>			
Recovered from carbonation reaction heat (MW)	285.8	55.9	28.5
Recovered from Carbonator flue gas (MW)	122.5	125.3	125.3
Recovered from Calciner flue gas (MW)	39.7	167.0	67.6
Pure oxygen production (MW)	0	54.4	0
Power output in PC	0	612.2	612.2
Total electricity output (MW)	447.9	906.1	833.6
Energy efficiency	31.3%	36.9%	39.4%
energy penalty	11.5%	5.93%	3.46%

#### 4.2 CO<sub>2</sub> ENRICHMENT DIFFERENCE IN THE THREE HEAT SUPPLY HEAT METHODS

To further reveal the separation work requirement in the three CO<sub>2</sub> capture systems, the CO<sub>2</sub> enrichment difference is discussed in this section. In the three heat supply methods for calcium looping process, CO<sub>2</sub> enrichment during fuel conversion plays important role on the thermodynamic performance of the calcium looping process. To reveal the influence of the CO<sub>2</sub> enrichment during fuel conversion on the thermodynamic performance, the ideal separation work (calculated by Eq. (3)) and energy consumption (calculated by Eq. (4)) required for gas (O<sub>2</sub> or CO<sub>2</sub>) separation is analyzed in the three heat supply methods. As shown in Fig. 5, the CaL-CLC process avoids gas separation work during fuel conversion and little work is required for CO<sub>2</sub> purification. In the CaL-PCC process, the air external combustion brings about the CO<sub>2</sub> dilute in the flue gas from air combustor, where CO<sub>2</sub> concentration is 13.5%. To avoid the CO<sub>2</sub> emission from the air external combustor, energy consumption for CO<sub>2</sub> separation will cause more fuel consumption to supply heat for the calciner. In the CaL-oxy process, high-purity O<sub>2</sub> is required to avoid the CO<sub>2</sub> dilution during the oxy-combustion, but the energy consumption for air separation unit also causes the work output reduction. Therefore, CO<sub>2</sub> in the dilute flue gas from external air combustion process and high-purity O<sub>2</sub> required for oxy-combustion contribute to the separation work and energy consumption for fuel conversion. The energy consumption for CO<sub>2</sub> enrichment during fuel conversion causes the reduction of work net output.

$$W_{ideal} = RT_0 \cdot \frac{X(1-K)\ln[X(1-K)] - (1-XK)\ln(1-XK) - X\ln(X)}{XK} \quad (3)$$

$$W_{eq} = W_{ideal} / \eta_{sep} \quad (4)$$

Where X refers to the CO<sub>2</sub> concentration of the mixed gas to be separated, and K is the CO<sub>2</sub> recovery ratio. And  $W_{ideal}$  and  $W_{eq}$  are the ideal work and energy consumption equivalent required to separate a gaseous component from its mixture, respectively.  $\eta_{sep}$  is the energy efficiency of the gas separation process.

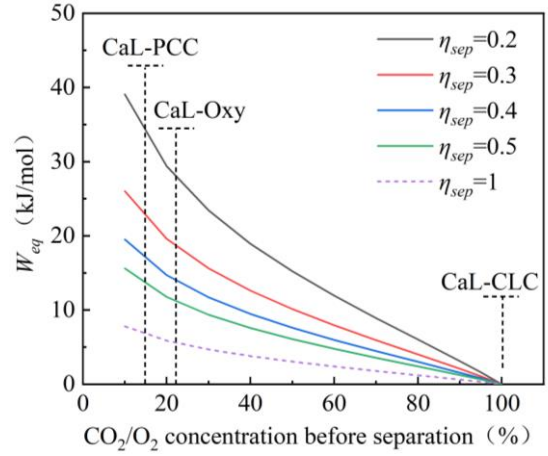


Fig. 5. Ideal separation work and energy consumption for gas separation in the three heat supply methods

#### 5. CONCLUSIONS

Calcium looping process (CaL) is a promising alternative for realizing low-energy-penalty of post-combustion technologies. In this paper, three different methods of providing heat for CaCO<sub>3</sub> calcination are compared, including calcium looping combustion (CaLC), oxy-fuel combustion (CaL-oxy), and Cu-based chemical looping combustion (CaL-CLC). Then three CaL systems are modeled, and a 600 MW coal-fired reference power plant is selected to evaluate the energy efficiency and energy penalty values at the same coal-fired flue gas CO<sub>2</sub> capture rate of 90%. The results show that CaL-CLC has the highest energy efficiency of 39.4%, and the lowest energy penalty with 3.5%. Through the energy analysis and CO<sub>2</sub> enrichment difference comparison, the introduction of chemical looping combustion avoids the consumption of separation work. The results indicate that reducing the gas separation cost plays important role caused by CO<sub>2</sub> enrichment in the heat supplying method of calcium looping process.

#### DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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