Introduction

Fossil fuels such as coal are widely used for power generation. In the fossil fuels conversion process, CO$_2$ and other pollutants are generated and emitted into the atmosphere directly. CO$_2$ is a greenhouse gas and a major contributor to global warming.\(^1\)\(^,\)\(^2\) It is urgent to mitigate CO$_2$ emission from power plants.\(^3\)\(^,\)\(^4\) Oxy-fuel combustion is particularly attractive and proposed as a promising technology due to the following advantages: (a) CO$_2$ concentration up to 95% in the dry flue gas; (b) reduced flue gas volume flow rate and higher plant efficiency; and (c) reduced NO$_x$ and SO$_x$.\(^5\) In the process of oxy-fuel combustion, pure oxygen is mixed with recycled flue gas, and then the mixed O$_2$ and CO$_2$ gases are fed to the furnace for combustion. The remaining flue gases, mainly of CO$_2$, steam vapor, and trace NO$_x$ and SO$_x$, are then ready for flue gas treatment downstream. The production of pure oxygen is a major challenge in oxy-fuel combustion. The high cost and intensive energy of the current oxygen production technologies, commonly based on air separation using cryogenic distillation, restrict the application of oxy-fuel combustion in power plants. It is essential to reduce the energy penalty imposed by oxygen production to implement oxy-fuel combustion technology as a viable future option when carbon dioxide capture is a necessity.

Efforts have been made for developing new methods of air separation with a low energy penalty, such as ion transport membrane (ITM).\(^6\)\(^,\)\(^7\) Chemical looping air separation (CLAS) is a novel and promising technology for oxygen production. This paper presents the application of CLAS to the supercritical power plant for MILD oxy-combustion. Compared with the reference conventional supercritical power plant, the power generation efficiency of the CLAS integrated MILD oxy-combustion plant is only reduced by about ~1.37% points at the baseline case. CO$_2$ compression process imposes additional ~3.97% points efficiency penalty, which is inevitable to all of the CO$_2$ capture technologies. The net power efficiency of the CLAS integrated MILD oxy-combustion plant is ~37.37%. Even though a higher reduction reactor temperature could boost the power efficiency and a higher oxidization reactor temperature reversely decreases the power efficiency, the influence of reactor temperature is marginal. The performance of CLAS integrated MILD oxy-combustion plant is not sensitive to excess CO$_2$ and O$_2$ ratio. Different oxygen carriers have different suitable operating region, but possess similar power efficiency. The carbon capture rate of the CLAS integrated MILD oxy-combustion plant is up to ~100%, resulting in a virtually carbon-free fossil power plant.

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Funding information
National Key R&D Program of China, Grant/Award Number: 2016YFB0600802; National Natural Science Foundation of China, Grant/Award Number: 51606038; Natural Science Foundation of Jiangsu, Grant/Award Number: BK20160672

Abstract

Chemical looping air separation (CLAS) is a novel and promising technology for oxygen production. This paper presents the application of CLAS to the supercritical power plant for MILD oxy-combustion. Compared with the reference conventional supercritical power plant, the power generation efficiency of the CLAS integrated MILD oxy-combustion plant is only reduced by about ~1.37% points at the baseline case. CO$_2$ compression process imposes additional ~3.97% points efficiency penalty, which is inevitable to all of the CO$_2$ capture technologies. The net power efficiency of the CLAS integrated MILD oxy-combustion plant is ~37.37%. Even though a higher reduction reactor temperature could boost the power efficiency and a higher oxidization reactor temperature reversely decreases the power efficiency, the influence of reactor temperature is marginal. The performance of CLAS integrated MILD oxy-combustion plant is not sensitive to excess CO$_2$ and O$_2$ ratio. Different oxygen carriers have different suitable operating region, but possess similar power efficiency. The carbon capture rate of the CLAS integrated MILD oxy-combustion plant is up to ~100%, resulting in a virtually carbon-free fossil power plant.

Keywords

chemical looping air separation, CO$_2$ capture, MILD oxy-combustion, supercritical power plant
(CLAS) is an alternative oxygen production method. It is principally similar to chemical looping combustion (CLC). CLAS includes two reactors, one is reduction reactor and the other is the oxidation reactor. The solid particles circulating between the two reactors are oxygen carriers, based on transitional metal oxides, such as CuO-Cu2O, MnO2-Mn3O4, Mn3O2-MnO, and Co3O4-CoO.8,9

In the reduction reactor, the oxygen carrier in a higher oxidation state $Me_xO_y$ decouples and releases gaseous oxygen $O_2$ in the atmosphere of inertial purge gas, such as steam or $CO_2$, as shown in Equation (1). The decoupled oxygen carrier $Me_xO_{y-2}$ then enters the oxidation reactor, where the oxygen carrier is regenerated to its higher oxidation state $Me_xO_y$ with incoming air, as shown in Equation (2). Through the continuous circulation of oxygen carrier between the two reactors, oxygen is separated from air.

Reduction: $Me_xO_y(s) \rightarrow Me_xO_{y-2}(s) + O_2(g)$ \hspace{1cm} $\Delta H > 0$ \hspace{1cm} (1)

Oxidization: $Me_xO_{y-2}(s) + O_2(g) \rightarrow Me_xO_y(s)$ \hspace{1cm} $\Delta H < 0$ \hspace{1cm} (2)

In CLAS, the purge gas applied could be any gas agent that doesn’t react with the oxygen carrier. The most common gas is steam and $CO_2$. An oxy-fuel combustion power plant could exactly provide such CO2 stream needed by CLAS. The produced O2 and CO2 stream is then sent to furnace for fuel combustion. From the point of view of power efficiency, CLAS integrated oxy-combustion power plant could have higher efficiency because the conventional cryogenic air separation unit (ASU) is avoided and CLAS process separates oxygen in the air without severe energy penalty.

Mohgadheri et al.8 conducted thermodynamic analysis of metal oxides and identified Cu-, Mn-, Co-oxides were suitable oxygen carriers for CLAS. Li et al.10 prepared Co-based oxygen carrier and produced an O2- $CO_2$ stream in a fixed bed reactor. Song et al.11-13 prepared Al2O3- and SiO2-supported Cu-, Mn-, and Co- oxygen carriers and found the bimetallic oxygen carrier could have higher stability and reactivity. Wang et al.14-16 evaluated the Cu-based oxygen carrier for CLAS in a fixed bed reactor and TGA. Steam was used as a carrier gas. It showed that the reduction and oxidation complied with the nucleation and nuclei growth model. The oxygen carrier could remain stability after multicycles.

Moderate or intense, low-oxygen dilution (MILD) combustion is a novel combustion concept.17 The features of MILD combustion are the preheating and dilution of reactants. The preheated reactants are at a temperature higher than its autoignition temperature.18 The oxygen fraction of MILD combustion is supposed to be 2-9 vol.

% and distributes uniformly in the premixed combustion of fuels.19 The preheating and dilution of reactants is usually achieved by the in-furnace flue gas recirculation.20 MILD combustion is flameless, and it has the potential to offer ultralow pollutant emission, high thermal efficiency, enhanced combustion stability and fuel flexibility.21-23 MILD combustion has been successfully applied for gaseous fuels24-27 as well as pulverized fuels (with size 50-120 μm).28-31 Kiga et al.32 successfully implemented the MILD combustion of high volatile pulverized coal using a drop tube furnace. Suda et al.33 investigated the behavior of pulverized coal in high-temperature air combustion using a burner of 250 kW. It indicated that it was possible to form a stable flame even for low-volatile coals like anthracite. Mao et al.34 conducted experimental investigation of coal-fueled MILD oxy-combustion integrated with flue gas recirculation at a 0.3 MWth furnace. At a jet velocity of 100 m/s, MILD combustion was achieved. Meanwhile the experiment was operated under oxy-fuel atmosphere that was established by the flue gas recirculation. Swirl oxy-fuel combustion was also tested as a comparison. The CO2 concentration in flue gas could maintain at a high level in the combustion. Li et al.35 investigated the MILD oxy-combustion characteristics of light oil and pulverized coal in a pilot scale furnace. Different burner configurations were compared. The experimental tests proved that the coal-fueled MILD oxy-combustion was technologically feasible. MILD combustion requires a relatively low $O_2$ concentration feed gas but a high preheating temperature oxidizer. CLAS could exactly provide such a high temperature and low $O_2$ fraction stream. The general benefits of CLAS and MILD combustions have also stimulated the combination into MILD oxy-combustion.36

In this paper, CLAS is integrated with an on-site MILD oxy-combustion power plant. CLAS is operated under a region where heat balance is achieved and the CLAS integrated MILD oxy-combustion power plant is in full heat balance range without extra heat sources from outside. The comparison of a conventional supercritical power plant and the CLAS integrated oxy-combustion power plant is analyzed and discussed. A sensitivity analysis of the main process parameters is also performed and their effects on the power plant performance are discussed.

2 | SYSTEM DESCRIPTION

2.1 | Reference plant

The software Aspen Plus is applied in the simulation work. The reference power plant used in this work is a 1000 MWe supercritical power plant,37 in which approximately 2855
tonne/h steam generated in the boiler. The steam turbine conditions correspond to 26.0 MPa/600°C as main steam with 600°C at the reheater. Major subsections of the plant include coal milling, boiler, steam cycle with regenerative feed water heating train, and ash and dust removal units. The plant operates with a designed efficiency of 42.71% (LHV). In the boiler, heat exchangers are arranged in the order of high-temperature superheater, high-temperature reheater, low-temperature superheater, low-temperature reheater, economizer, and air preheater. For simplicity, the chemical processes of flue gas desulfurization and denitrification are not considered in the simulation. The regenerative feed water heating train includes three high-pressure and four low-pressure closed heat exchangers, and one open feed water heat exchanger, that is, deaerator. The diagram of the steam cycle is shown in Figure 1. Primary parameters of the reference plant are described in Table 1. A bituminous coal is adopted in the simulation and the coal analysis is shown in Table 2.

2.2 | CLAS integrated MILD oxy-combustion plant

The schematic diagram of the CLAS integrated MILD oxy-combustion plant, including CLAS, boiler, steam cycle, and \( \text{CO}_2 \) compressors, is presented in Figure 2.

2.2.1 | CLAS process

The CLAS process is modeled using two separate reactors. Air is preheated in a heat exchanger and then fed into the oxidation reactor. The reduced oxygen carrier from the reduction reactor is oxidized in the oxidation reactor. The exhaust gas from the oxidation reactor is oxygen-depleted air. The heat of the oxygen-depleted air is recovered by preheating the inlet fresh air. The exhausted oxygen-depleted air temperature is fixed constantly at 50°C. The oxygen carrier in a higher oxidation state leaves the oxidation reactor and enters the reduction reactor. \( \text{CO}_2 \)-rich

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**FIGURE 1** Diagram of the reference supercritical power plant

**TABLE 1** Primary parameters of the reference plant

| Description                                      | Value       |
|--------------------------------------------------|-------------|
| Steam cycle, MPa/°C/°C                           | 26.0/600/600|
| As received coal, kg/h                           | 348 274.1   |
| Coal lower heating value, kJ/kg                  | 24 200      |
| HP turbine isentropic efficiency, %              | 91          |
| IP turbine isentropic efficiency, %              | 93          |
| LP turbine isentropic efficiency, %              | 89.5        |
| Generator efficiency, %                          | 99          |
| Excess air, %                                    | 20          |
| Stack temperature, °C                            | 130         |
| Condenser pressure, kPa                          | 4.72        |
| Cooling water to condenser, °C                   | 15          |
| Cooling water from condenser, °C                 | 25          |
| Water recirculation pump discharge pressure, MPa | 0.245       |
| Feed water pump isentropic efficiency, %         | 82          |
| Regenerative heater terminal temperature difference, °C | 5        |
| Boiler inlet feed water temperature, °C          | 298         |
| Boiler inlet air temperature, °C                 | 345         |
gas is bled from the furnace flue gas channel. The required mass flow rate of CO₂-rich gas is determined by the reduction temperature. The flow rate of air and CO₂ stream is as close to stoichiometric as possible in order to minimize the flow rates. In the reduction reactor, gaseous oxygen is released from the oxygen carrier at the atmosphere of CO₂. The O₂ and CO₂ mixture stream is directly fed into the furnace for coal combustion. The reduced oxygen carrier then circulates back to the oxidization reactor for next cycle.

The heat from oxidization reactor is used to compensate heat required by reduction via inert solid circulation. The temperature of reduction is therefore lower than that of oxidization reactor. Only a small amount of heat is required by reduction reactor from outside, which comes from the inlet CO₂-rich gas. The CO₂-rich gas is bled from two ports of the boiler flue gas channel to mix into a stream with the target temperature demanded by reduction. The management of CLAS is as follows, and the detailed operating region of CLAS can be referred in our former work:\[38\]:

1. Select the oxidization reactor temperature;
2. Select the reduction reactor temperature (lower than oxidization temperature);
3. Temperature difference of the two reactors determines the inert solid flow rate (the inert solids take away all of the heat released by oxidization to reduction);
4. Reduction temperature determines the CO₂ flow rate (based on chemical equilibrium);

**TABLE 2** Analysis of Shuozhou bituminous coal

| Proximate analysis/% (mass, air dry) | Ultimate analysis/% (mass, air dry) |
|-----------------------------------|-----------------------------------|
| Moisture                          | C                                 |
| Volatile                          | H                                 |
| Fixed carbon                      | O                                 |
| Ash                               | N                                 |
| Ash                               | S                                 |

| Lower heating value (LHV)         | 24 200 kJ/kg                      |

**FIGURE 2** Schematic diagram of CLAS integrated MILD oxy-combustion plant
5. Heat deficiency of reduction reactor determines the inlet CO₂ temperature;
6. CO₂ flow rate and temperature determine the flue gas extraction flow ratio from two ports of the flue gas channel.

2.2.2 | Boiler

In the CLAS integrated MILD oxy-combustion plant, O₂ is produced from CLAS process and sent to the furnace. The oxygen concentration produced from CLAS process is at a relatively low level, <12 vol. %. This level is far less than what is available for conventional oxy-fuel combustion, which requires an oxygen concentration around 28-35 vol. %. Therefore, conventional oxy-fuel combustion cannot be directly adopted in existing boilers and novel combustion technology is needed. Here, MILD combustion is applicable and employed for such a low-oxygen concentration stream. The original boiler of the reference power plant is thereby not adopted due to the different characteristics of air firing and MILD combustion, but the general structures of the boilers are similar. For a fair comparison, critical parameters such as main steam temperature (600°C/600°C), stack temperature are not changed as possible in the MILD oxy-combustion boiler. In the MILD oxy-combustion boiler, the air preheater is removed, and a feed water preheater substitutes the air preheater at the end of the flue gas channel. After one regenerative feed water heater, a portion of the feed water to the boiler is bypassed to the feed water preheater in the flue gas channel instead of the feed water heating train. This arrangement diminishes steam bleeding from the steam turbine. CO₂-rich gas stream is bled from the flue gas channel of the boiler. The CO₂-rich gas stream is at high temperature, conventional compressors or blowers are not feasible for gas bleeding, and so an ejector is employed. The ejector operates as a compressor, but with no moving parts. The ejector utilizes a high-pressure fluid stream to drive a low-pressure stream. The primary fluid passes through a nozzle where the pressure energy is converted into kinetic energy. The high-velocity jet entrains the secondary fluid. The two streams mix in a confluence pipe. The ejector is widely used in SOFC system for fuel gas circulation. There are two bleeding ports in the flue gas channel to easily adjust the CO₂-rich gas temperature and flow rate. The first port is after the first superheater, that is, at the outlet of the furnace; the second port is after the economizer, that is, before the newly added feed water preheater. The bleeding ratio at the two ports is adjusted to meet the target CO₂ temperature and flow rate, which is determined by the CLAS process. At the second port, the flue gas at a lower temperature is bled and pressured as the primary flow of the ejector, and the flue gas at higher temperature at the first port is the secondary flow for the ejector. The two CO₂ streams are mixed together. The bled CO₂ stream is particulate-removed before entering CLAS reactors. For simplicity, the treatment of flue gas with a series of chemical process and scrubbers to remove sulfur dioxide and nitrogen oxide is not considered here.

2.2.3 | Steam cycle

The steam cycle arrangement is only marginally changed with the CLAS integration. The steam turbine is divided into three parts: a high-pressure part fed with main steam, an intermediate-pressure part fed with reheated steam and a low-pressure part. As part of efficiency improvement in the plant, regenerative feed water heating is still necessarily implemented, using steam bled at different ports of the turbine to heat the feed water as shown in Figure 2. The heating train includes three high-pressure, four low-pressure closed feed water heat exchangers and a deaerator. The boiler feed water pump is also driven by steam which is finally led to the condenser.

2.2.4 | CO₂ recovery and compression

CO₂-rich gas exhausted from the boiler is cooled to 30°C in a heat exchanger. The resulting CO₂ stream is compressed using a four stage intercooled compressor for pipeline transport and geological sequestration. Cooling water at environmental temperature is used to cool the compressed stream in each stage. The majority of water remaining in the CO₂ stream is removed in the flash drums of each compressor stage. The CO₂ is finally pressurized to 150 bar with a purity of 99.1%. In a practical facility, a flue gas desulfurization unit (FGD) needs to implement in order to control SO₂ in the CO₂-rich gas stream. A low temperature partial condensation process integrated with a distillation column may also be applied to remove other impurities from the CO₂, but this is not the scope of this work.

3 | ANALYSIS METHODOLOGY

The net power efficiency in the oxy-fuel combustion power plant is determined using the following equation:

$$\eta_e = \frac{W_e}{m_{coal} \text{LHV}_{coal}} \times 100\% \quad (3)$$

Here, $\eta_e$ is the plant net power efficiency, %; $m_{coal}$ is the input coal mass flow, kg/s; LHV$_{coal}$ is the coal lower heating value, kJ/kg.

The net power output of the oxy-fuel combustion power plant $W_e$ is calculated as follows:
Here, $W_{st}$ is the steam turbine power, kW; $W_{aux}$ is the auxiliary power, such as the condensate pump, water recirculation pump, blowers, etc., kW; $W_{CO_2 \cdot comp}$ is the CO$_2$ compression power, kW.

To evaluate the penalty imposed by CO$_2$ compression, the power generation efficiency excluding CO$_2$ compression is defined as following:

$$\eta_g = \frac{W_g}{m_{coal} LHV_{coal}} \times 100\%$$  \hspace{1cm} (5)

Here, $\eta_g$ is the power generation efficiency, %; $W_g$ is the power output excluding CO$_2$ compression, kW;

$$W_g = W_{st} - W_{aux}$$  \hspace{1cm} (6)

For reference power plant, the net power efficiency is also the power generation efficiency because there is no CO$_2$ compression.

CO$_2$ is bled from the flue gas channel. The CO$_2$ bled ratio is defined as:

$$\gamma_{i,CO_2} = \frac{M_{i,CO_2}}{M_{t,CO_2}} \times 100\%$$  \hspace{1cm} (7)

$\gamma_{i,CO_2}$ is the CO$_2$ bled ratio at Port $i$, %; $M_{i,CO_2}$ is the mass flow rate of the CO$_2$-rich gas bled at Port $i$, kg/h; $M_{t,CO_2}$ is the total mass flow rate of the CO$_2$-rich gas leaving the furnace, kg/h.

CO$_2$ capture efficiency is defined as:

$$\eta_{CO_2} = \frac{m_{CO_2}}{m_{CO_2, total}} \times 100\%$$  \hspace{1cm} (8)

### Table 3

| Primary parameters of the CLAS integrated MILD oxy-combustion plant in a typical operating condition | Value |
|---|---|
| CLAS oxygen carrier | Mn$_2$O$_3$-Mn$_3$O$_4$ |
| Reduction reactor temperature, °C | 830 |
| Oxidation reactor temperature, °C | 840 |
| CLAS reactor pressure drop, % | 8 |
| O$_2$ fraction, vol. % | 6 |
| Excess O$_2$ ratio in the furnace | 1.05 |
| Excess CO$_2$ ratio in the reduction reactor | 1.10 |
| Unconverted char ratio | 0.05 |
| CLAS inert solid support | Spinel |
| Steam cycle, MPa/°C/°C | 26.0/600/600 |
| Intermediate pressure steam reheat | |
| HP turbine isentropic efficiency, % | 91 |
| IP turbine isentropic efficiency, % | 93 |
| LP turbine isentropic efficiency, % | 89.5 |
| Generator efficiency, % | 99 |
| Condenser pressure, kPa | 4.72 |
| Cooling water to condenser, °C | 15 |
| Cooling water from condenser, °C | 25 |
| Water recirculation pump pressure, mmH$_2$O | 25,000 |
| Feed water pump isentropic efficiency, % | 82 |
| Regenerative heater terminal temperature difference, °C | 5 |
| Boiler inlet feed water temperature, °C | 293 |
| Stack temperature, °C | 130 |
| Single stage CO$_2$ compression ratio | 3.5 |
| CO$_2$ compressor isentropic efficiency, % | 75 |
| CO$_2$ compressor mechanical and electricity efficiency, % | 98 |
| CO$_2$ ready for delivery, bar/°C | 150/30 |
\( \eta_{\text{CO}_2} \) is the \( \text{CO}_2 \) capture efficiency, %; \( m_{\text{CO}_2} \) is the \( \text{CO}_2 \) flow after compression for storage, kg/s; and \( m_{\text{CO}_2,\text{total}} \) is the total \( \text{CO}_2 \) generated in the plant, kg/s.

4 | RESULTS AND DISCUSSION

4.1 | Performance analysis

A typical operating condition of the CLAS integrated MILD oxy-combustion plant is selected as a baseline case here, using the assumptions in Table 3. \( \text{Mn}_2\text{O}_3-\text{Mn}_3\text{O}_4 \) is used as the oxygen carrier as a result of its natural abundance, low cost, and non-toxic character.\(^{45} \) The essential simulation assumption of CLAS integrated MILD oxy-combustion plant is the same as the reference plant except for the CLAS process. The reduction reactor temperature is \( 830^\circ\text{C} \), and the oxidation reactor temperature is \( 840^\circ\text{C} \). \( \text{CO}_2 \)-rich gas stream bled from the boiler flue channel into the reduction reactor is at an excess ratio 1.1 to decouple all of the gaseous oxygen. The excess \( \text{O}_2 \) ratio here is less than that of air firing plant. The excess \( \text{O}_2 \) ratio in air firing plant is typically 1.2 to minimize carbon burning loss. In this work the excess \( \text{O}_2 \) ratio is 1.05 for a full coal conversion. This value is commonly adopted in oxy-fuel combustion to minimize the oxygen content in the flue gas.\(^{46,47} \)

Even though the \( \text{O}_2 \) content is relatively lower, the higher

| Power plant capacity, MW<sub>e</sub> | 875 | 1000 |
|---|---|---|
| Coal LHV input, MW | 2341.2 | 2341.2 |
| Coal input, t/h | 348.3 | 348.3 |
| Steam turbine, kW | 988 146.4 | 1 008 562.3 |
| Blowers, kW | 11 217.1 | 2947.6 |
| Water recirculation pump, kW | 4874.5 | 4870.1 |
| Condensate pump, kW | 730.0 | 744.7 |
| Bypass feed pump, kW | 3506.0 | N/A |
| \( \text{CO}_2 \) compressors, kW | 92 887.3 | N/A |
| \( \text{CO}_2 \) compression cooling pump, kW | 12.5 | N/A |
| Plant power generation efficiency (LHV), % | 41.34 | 42.71 |
| Plant net power efficiency (LHV), % | 37.37 | 42.71 |
| \( \text{CO}_2 \) capture efficiency \( \eta_{\text{CO}_2} \), % | \( \sim 100 \) | 0 |
| \( \text{CO}_2 \) temperature to reduction reactor, °C | 865.3 | N/A |
| Total flue gas mass flow, kg/h | 15 005 348 | 3 601 535 |
| Port I bleeding temperature, °C | 970 | N/A |
| Port I bleeding ratio \( \eta_{\text{I,CO}_2} \), % | 70.9 | N/A |
| Port II bleeding temperature, °C | 536 | N/A |
| Port II bleeding ratio \( \eta_{\text{II,CO}_2} \), % | 23.5 | N/A |
| \( \text{CO}_2 \)-rich gas recycle ratio, % | 94.5 | N/A |
| Stack \( \text{CO}_2/\text{O}_2 \) fraction, vol. % | 97.3/0.52 | N/A |
| \( \text{CO}_2/\text{O}_2 \) fraction before compression, vol. % | 97.3/0.52 | N/A |
| \( \text{CO}_2/\text{O}_2 \) fraction after compression, vol. % | 99.1/0.53 | N/A |

**Table 4** Performance summary of the CLAS integrated MILD oxy-combustion plant and the reference supercritical plant.
temperature (>800°C) of O₂ inlet gas may trade off this effect. CLAS is completely in a region of heat balance. It must be indicated that this case may not be the optimal one in power efficiency. The performance of the CLAS integrated MILD oxy-combustion plant and the reference plant is listed in Table 4, and the important selected flows within the CLAS integrated MILD oxy-combustion plant is shown in Table 5.

**Table 5** Detailed results for selected flows of the CLAS integrated MILD oxy-combustion plant in the baseline case

| Flow no. | Type                     | Temperature (°C) | Pressure (bar) | Mass flow (kg/s) |
|----------|--------------------------|------------------|----------------|------------------|
| 1        | Air                      | 15               | 1.013          | 1109             |
| 2        | Air                      | 26               | 1.113          | 1109             |
| 3        | Air                      | 702              | 1.113          | 1109             |
| 4        | Mn₂O₃/Spinel             | 840              | 1.013          | 92492            |
| 5        | Mn₃O₄/Spinel             | 830              | 1.013          | 92308            |
| 6        | CO₂-rich stream          | 961              | 1.013          | 3233             |
| 7        | CO₂-rich stream          | 553              | 1.013          | 1053             |
| 8        | CO₂-rich stream          | 863              | 1.113          | 4264             |
| 9        | Oxygen-depleted air      | 840              | 1.013          | 925              |
| 10       | Oxygen-depleted air      | 50               | 1.013          | 925              |
| 11       | O₂/CO₂                   | 830              | 1.013          | 4447             |
| 12       | Coal                     | 15               | 1.013          | 96.75            |
| 13       | Water                    | 293              | 260            | 725.6            |
| 14       | Water                    | 322              | 260            | 725.6            |
| 15       | Steam                    | 454              | 260            | 725.6            |
| 16       | Steam                    | 480              | 260            | 725.6            |
| 17       | Steam                    | 499              | 260            | 725.6            |
| 18       | Steam                    | 600              | 260            | 725.6            |
| 19       | Steam                    | 405              | 87.9           | 60.6             |
| 20       | Steam                    | 316              | 49.5           | 58.6             |
| 21       | Steam                    | 600              | 49.4           | 606.5            |
| 22       | Steam                    | 480              | 24.3           | 45.0             |
| 23       | Steam                    | 372              | 11.7           | 0.056            |
| 24       | Steam                    | 372              | 11.7           | 29.4             |
| 25       | Steam                    | 372              | 11.7           | 532              |
| 26       | Steam                    | 301              | 6.8            | 18.8             |
| 27       | Steam                    | 234              | 3.8            | 20.1             |
| 28       | Steam                    | 156              | 1.8            | 17.7             |
| 29       | Steam                    | 95               | 0.8            | 48.9             |
| 30       | Steam                    | 31.9             | 0.047          | 426.6            |
| 31       | Water                    | 31.9             | 0.047          | 561.4            |
| 32       | Water                    | 34.6             | 9.0            | 561.4            |
| 33       | Water                    | 90               | 9.0            | 110              |
| 34       | Water                    | 93.2             | 260            | 110              |
| 35       | Water                    | 160              | 7.0            | 451.5            |
| 36       | Water                    | 164              | 7.0            | 615.7            |
| 37       | Water                    | 293              | 7.0            | 615.7            |
| 38       | Water                    | 293              | 260            | 110              |
| 39       | CO₂-rich stream          | 130              | 1.013          | 239.2            |
| 40       | CO₂-rich stream          | 30               | 150            | 237.2            |
It is found that, the net power efficiency of the MILD oxy-combustion power plant decreases after adding CLAS process. The plant net power efficiency (LHV) for the reference plant is 42.71%, whereas the net power efficiency of the CLAS integrated MILD oxy-combustion plant is 37.37%. The energy penalty imposed by CCS generally comes from two aspects: CO2 capture and CO2 compression. The efficiency penalty typically associated with CO2 in this CLAS integrated MILD oxy-combustion power plant results from CO2 compression. If CO2 compression process is not considered, the power generation efficiency drop is only 1.37% points including CO2 capture. The CO2 compression imposes additional 3.97% points efficiency penalty. The total efficiency decrement including CO2 capture and CO2 compression is ~5.34% points. This efficiency decrement is low and less than other coal-fueled counterparts with post-combustion CO2 capture or cryogenic air separation oxy-fuel combustion, which commonly impose 8-12% penalty with final power efficiency about ~30-33%. Therefore, the efficiency drop in the proposed CLAS integrated MILD oxy-combustion plant is acceptable and satisfactory.

The bleeding of high-temperature CO2 is used for oxygen carrier decoupling to release gaseous O2. The produced O2 and CO2 mixture stream at a lower temperature level turns back to the furnace. It is a circle. The energy for the production of O2 comes from the thermal energy of flue gas, which means that less steam is produced for stream turbine and less power generation. This is the “capture penalty” of the entire CLAS integrated MILD oxy-combustion plant. For the bled flue gas, only a small portion of heat is consumed for oxygen carrier decoupling and a large portion of heat in the flue gas is recovered as the flue gas is recycled to the furnace. For cryogenic ASU, the cryogenic ASU requires electricity for compression and refrigeration. However, the electricity production requires more thermal energy. That is one reason of low efficiency penalty of CLAS. Moreover, the pure oxygen separated from air in the cryogenic ASU is then mixed with CO2. From the point of view of the second law of thermodynamics, the mixing process imposes enormous exergy loss. The exergy loss here means that the electricity for production of pure O2 is wasted. The CLAS process exactly provides a mixture stream of O2 and CO2 required by the furnace, which avoids pure oxygen production process and the later mixing loss. This is also an explanation why the CLAS integrated oxy-combustion power plant owns higher net power efficiency.

For CLC, there are commonly two ways to process solid fuels such as coal. The first is: coal is gasified in a gasifier, producing syngas. The resulting syngas reacts with the oxygen carrier in a fuel reactor. The disadvantage is the requirement of a gasifier and an ASU, which impose energy penalties. The second way for coal-fueled CLC is coal is in situ gasified in the fuel reactor with oxygen carrier. The coal pyrolysis, char gasification and oxygen carrier reduction occur in the same reactor. This eliminates the gasifier and ASU. However, the coal, char, ash, and oxygen carrier are mixed together, and the separation of unconverted char, ash, and oxygen carrier is a challenge. Li et al experimentally investigated the separation of char and oxygen carrier. The separation efficiency of char was around 80-90%, depending on operation condition, and the unconverted char will enter the air reactor and results in CO2 emission. For CLAS, it highlights gaseous O2 production in an individual reactor, that is, the reduction reactor, the produced O2 then reacts with the coal in the furnace of the boiler. The oxygen production and combustion processes are separated. Coal is burned in an O2/CO2 atmosphere and never mixed with the oxygen carrier. Char and volatile matter conversion are better in gaseous O2 than in CLC. The separation of unconverted char, ash from oxygen carrier is also avoided. This is the advantage of CLAS over CLC.

### 4.2 Sensitivity analysis

Sensitivity analysis could reveal the potential approaches to optimize the system. The steam cycle is technologically well-established and proven, it is thereby not necessary to conduct the sensitivity analysis in those sections. Several parameters in the newly added CLAS which may affect the performance of the entire system need to be considered, such as reduction reactor temperature, oxidization reactor temperature, CO2-rich gas excess ratio, and O2 excess ratio.

#### 4.2.1 Reduction reactor temperature and oxidization reactor temperature

Figure 3 presents the plant power efficiency as a function of the reduction reactor temperature and the oxidization reactor temperature.
reactor temperature. The reduction reactor temperature and the oxidization reactor temperature are varied, whereas other design parameters are kept constant. With the variation in temperature, the required CO$_2$-rich gas bleeding rate and temperature are also adjusted accordingly.

Figure 3 is the plant net power efficiency $\eta_e$ including CO$_2$ compression. The efficiency has already accounted CO$_2$ compression, which imposes approximate $\sim4\%$ points efficiency penalty. This is common and inevitable to all the CO$_2$ capture technologies that release CO$_2$ at near atmosphere pressure. It can be seen that with the rise of the oxidization reactor, the

**FIGURE 4** Selected indicators in the CLAS integrated MILD oxy-combustion plant with the variation in reduction reactor temperature
net power efficiency decreases. With the rise of the reduction reactor temperature, the net power efficiency increases. This tendency leads the region approaching the diagonal to own higher power efficiency, whereas the region near the bottom right corner is at a lower power efficiency. The highest net power efficiency of 37.51% is achieved at the reduction temperature of 810°C and oxidation temperature of 820°C. It also means that with the decrease in the temperature difference between the reduction reactor and the oxidation reactor, the CLAS integrated MILD oxy-combustion plant is of higher power efficiency. The power efficiency diminishes with the rise of the temperature difference between the two reactors. At the blank region in Figure 3, that is, the oxidation reactor temperature 880-890°C and reduction reactor temperature <790°C, the temperature of CO₂-rich gas bled from flue gas channel is always lower than the reduction reactor demand and therefore unsuitable for decoupling of the oxygen carrier.

Figure 4 illustrates some important indicators of the plant with the variation in reduction reactor temperature. The oxidation reactor temperature is kept constant at 820°C. As the reduction reactor temperature increases, the amount of CO₂ needed to decouple the oxygen carrier decreases due to an increased oxygen partial pressure in equilibrium. Accordingly, the oxygen fraction produced increases. As shown in Figure 4A, the combustion temperature and sequent furnace outlet temperature increases due to a lower amount of gas agent at higher reduction reactor temperature. Here, in the CLAS integrated MILD oxy-combustion plant, the air preheater is replaced by a feed water preheater after the economizer. The higher inlet temperature of the feed water preheater allows more water to bypass the regenerative heating train. It reduces the steam bleeding and augments the steam turbine power output. That’s why the power efficiency increases with the rise of the reduction reactor temperature. Meanwhile, the CO₂-rich flue gas is bled from two ports at different temperatures. One is at the furnace outlet, that is, the high-temperature port; the other is after the economizer, that is, the low-temperature port. The CO₂-rich gas bleeding portion from the two ports is flexibly adjusted according to the reduction reactor temperature.

As shown in Figure 4B, the rise of the reduction reactor temperature, the CO₂-rich gas bleeding ratio \( \gamma_{\text{ICO}_2} \) from Port I decreases, whereas the CO₂-rich gas bleeding ratio \( \gamma_{\text{ILCO}_2} \) from Port II increases. This is because with the rise of reduction reactor temperature, the required inlet CO₂ temperature for reduction reactor increases. As shown in Figure 4C, the required inlet CO₂ temperature increases from 756°C to 832°C, by 10.0%, Port I temperature also increases from 777.1°C to 907°C, by 16.8%, and Port II temperature increases from 394.6°C to 561.9°C, by 43.4%. The temperature increment of Port II is much higher than that of Port I, whereas the required CO₂ temperature is less increased than that of Port I and Port II, so the CO₂-rich gas bleeding ratio from Port I decreases. The drop of bleeding ratio in Port I means at a higher reduction reactor temperature more heat in high quality is used for heat transfer and power conversion rather than purging the oxygen carrier. It also reveals why the increase in reduction reactor temperature benefits the efficiency.

In Figure 3, it is also found that with the rise of the oxidation reactor temperature, the power efficiency decreases. This phenomenon is explained as follows: at a higher oxidation reactor temperature, more air is required for oxygen carrier oxidation due to equilibrium. Thus, the power needed by the air blower increases. Meanwhile, the oxidation reactor temperature has little influence on the reduction reactor performance, that is, the oxygen concentration and temperature do not change with the variation in the oxidation reactor temperature. So the oxidation is nearly independent and does not affect the performance of the boiler and steam cycle. Therefore, the increase in air blower power directly decreases the plant power output.

4.2.2 Excess CO₂ ratio

The minimal CO₂ flow rate into the reduction reactor is at the chemical stoichiometric of thermodynamic equilibrium to decouple all oxygen carriers to release gaseous oxygen. But in practical facility, CO₂ will be in excess for a better reduction performance or fluidization. The influence of excess CO₂ on the performance of the plant is shown in Figure 5.

The plant performance is not sensitive to the excess CO₂ ratio, even though a higher CO₂ blower power is required but its effect is marginal. The furnace outlet temperature decreases at a higher excess CO₂ ratio, but the amount of CO₂ increases in the furnace downstream channel. It does not affect the heat exchange for steam cycle, and there is little variation in the power output in the steam turbine.

\[ \text{Net power efficiency, } \eta_n \]

\[ \text{Power generation efficiency, } \eta_g \]

\[ \text{Excess CO}_2 \text{ ratio } [-] \]

\[ \text{Efficiency } [\%] \]

**FIGURE 5** Plant performance as a function of excess CO₂ ratio
4.2.3 | Excess O₂ ratio

In a conventional boiler, excess air is commonly adopted for full coal combustion. In the oxy-fuel combustion plant, oxygen could be also excessive to benefit the solid fuel combustion. Figure 6 illustrates the influence of excess O₂ ratio on the performance. It must be mentioned that the excess O₂ primarily provides a better combustion environment, benefiting the reaction kinetics and reducing the penalty from unburnt solid fuel. Some studies have shown that the burnout of coal was reduced under MILD combustion condition. The carbon burnout is significantly affected by the particle residence time, particle size, and reaction rate. Due to the lack of specific relationship of operation condition on carbon burnout, this effect is not directly reflected in the simulation. Here, it is still assumed that unconverted char ratio is constant, and the remaining oxygen goes into the furnace flue gas channel and CO₂ compressors.

Figure 6 shows that with the rise of oxygen excess ratio, the total power output is nearly not affected, that is, the boiler and the subsequent steam cycle are not influenced by the oxygen excess ratio. There is a slight decrease in the net power output. This is due to that CO₂ compression power is increased because O₂ is mixed into the CO₂-rich gas stream. The trace O₂ is removed in the flasher as non-condensate gas from the concentrated CO₂ stream after CO₂ is condensed. With the rise of oxygen excess ratio, the power of air blower increases as well, which reduces the net power output of the plant.

### Table 6 Performance of CLAS integrated MILD oxy-combustion plant using MnO₂-Mn₂O₃, Co₃O₄-CoO, CuO-Cu₂O as oxygen carrier

|                        | MnO₂-Mn₂O₃ | Co₃O₄-CoO | CuO-Cu₂O |
|------------------------|------------|-----------|-----------|
| Power plant capacity, MWₑ | 866        | 871       | 881       |
| Coal LHV input, MW      | 2341.2     | 2341.2    | 2341.2    |
| Coal input, t/h         | 348.3      | 348.3     | 348.3     |
| Steam turbine, kW       | 977 595.8  | 985 766.6 | 997 549.5 |
| Blowers, kW             | 16 346.4   | 12 943.9  | 13 269.5  |
| Water recirculation pump, kW | 4793.1   | 4855.9    | 4947.5    |
| Condensate pump, kW     | 721.6      | 728.1     | 737.4     |
| Bypass feed pump, kW    | 2698.0     | 3312.8    | 4245.8    |
| CO₂ compressors, kW     | 87 318.0   | 92 876.3  | 93 111.1  |
| CO₂ compression cooling pump, kW | 11.9    | 12.5      | 12.6      |
| Plant gross power efficiency (LHV), % | 40.70 | 41.17     | 41.62     |
| Plant net power efficiency (LHV), % | 36.98 | 37.21     | 37.64     |
| CO₂ capture efficiency, % | ~100      | ~100      | ~100      |
| Reduction reactor temperature, °C | 420   | 860       | 980       |
| Oxidation reactor temperature, °C | 430  | 870       | 990       |
| O₂ fraction, vol. %     | 8.1        | 6.3       | 7.7       |
| Total flue gas mass flow, kg/h | 10 645 118 | 13 746 976 | 11 332 152 |
| Port I bleeding ratio γ₂₂O₂, % | 0         | 72.5      | 70.9      |
| Port II bleeding ratio γ₂₂O₂, % | 92.8      | 21.5      | 21.8      |
| CO₂-rich gas recycle ratio, % | 92.8      | 94.0      | 92.6      |

**Figure 6** Plant performance with the variation in excess O₂ ratio

![Graph showing the influence of excess O₂ ratio on plant performance](https://example.com/graph.png)

- Total power output
- Net power output
- CO₂ compression power
4.2.4 | Different oxygen carriers

Besides \( \text{Mn}_2\text{O}_3-\text{Mn}_3\text{O}_4 \) oxides, \( \text{MnO}_2-\text{Mn}_2\text{O}_3 \), \( \text{CoO}-\text{Co}_3\text{O}_4 \), \( \text{Cu}-\text{Cu}_2\text{O} \) are also suitable candidates as oxygen carrier in CLAS. Because each oxygen carrier has its own suitable operating region determined by its intrinsic characteristics, it is not reasonable to compare the oxygen carrier at the same operating condition. Table 6 shows the typical performance of CLAS integrated MILD oxy-combustion plant using \( \text{MnO}_2-\text{Mn}_2\text{O}_3 \), \( \text{CoO}-\text{Co}_3\text{O}_4 \), \( \text{Cu}-\text{Cu}_2\text{O} \) oxygen carriers.

\( \text{MnO}_2-\text{Mn}_2\text{O}_3 \) oxides offer lower power plant efficiency. This is because the reduction is operated at a relatively low temperature, 420°C. The flue gas temperature at Port II is 465°C, which is still higher than the minimal \( \text{CO}_2 \) temperature 454°C required by the reduction reactor. Port I bleeding is also eliminated. The temperature of the bled \( \text{CO}_2 \)-rich gas is higher than that required, and the redundant sensible heat is not utilized in the integration. This results in an efficiency loss. In fact, any heat can be utilized if a more delicate heat network is implemented, but this will complicate the power plant system. For simplicity and comparison, it was not considered.

These CLAS integrated MILD oxy-combustion power plants possess similar power efficiency. CLAS process produces oxygen for oxy-combustion with small energy penalty. CLAS is in heat balance without tight connections to other components in the plant, and just needs a \( \text{CO}_2 \)-rich gas stream from the furnace flue channel. The bled \( \text{CO}_2 \)-rich gas is finally recycled back to the furnace. The oxygen production and heat integration of the entire system is not appreciably affected by the oxygen carrier variation. From the perspective of thermodynamics, CLAS is almost an independent block, and all of the oxygen carriers are suitable for this integration with small efficiency deficiency. So, other criteria should be imposed in oxygen carrier selection, for example, the \( \text{MnO}_2-\text{Mn}_2\text{O}_3 \) is operated at a temperature span of around 380-440°C. At this medium temperature range, the reaction kinetics needs to be considered. \( \text{CuO}-\text{Cu}_2\text{O} \) oxygen carrier particles tend to agglomerate at a temperature higher than 900°C due to the relatively low melting temperature of copper (1084°C). So kinetics, activity in multiple cycles, agglomeration, and other characteristics are points of attention in selection and preparation of oxygen carrier.

4.3 | Plant comparison

Due to the different characteristics of air firing and MILD oxy-combustion, the original boiler is not feasible for the proposed power plant. The MILD oxy-combustion boiler should be redesigned, for instance low \( \text{O}_2 \) concentration would result in a high flow rates and larger boilers. Compared with the reference supercritical power plant, the sequence of heat exchanger tubes involved in the MILD oxy-combustion boiler is not changed. The regenerative feed water heating train and steam turbine in steam cycle also remains. Heat transfer is definitely changed in the boiler because flue gas is mostly \( \text{CO}_2 \) rather than air. Table 7 presents the comparison of heat exchangers of the CLAS integrated MILD oxy-combustion plant in the typical operating condition and the reference plant.

Heat exchanger details are calculated by the HeatX block in the Aspen Plus software according to the stream properties, that is, temperature difference, gas components, etc. Radiation contributes a large portion of heat transfer in the first superheater and the water cooling wall. HeatX block cannot reveal the tube size in radiation. So heat duty is listed instead. It can be seen that for most of the heat exchangers, the size needs to be reduced in the CLAS integrated MILD oxy-combustion plant. The air preheater is replaced by a feed water preheater at the end of the flue gas channel. Because the heat transfer coefficient of water-air is higher than air-air, the feed water preheater has a much smaller tube size.

| Components                        | CLAS integrated MILD oxy-combustion plant | Reference plant |
|-----------------------------------|------------------------------------------|-----------------|
| High-temperature superheater I    | 239.0                                    | 274.8           |
| High-temperature superheater II   | 119.5                                    | 102.2           |
| Water cooling wall radiation, MW  | 1024.8                                   | 1120.4          |
| High-temperature reheater, m²     | 1081.6                                   | 1353.7          |
| Low-temperature superheater, m²   | 403.2                                    | 778.8           |
| Low-temperature reheater, m²      | 279.5                                    | 950.4           |
| Economizer, m²                    | 575.4                                    | 860.0           |
| Feed water preheater or air       | 1075.3                                   | 4361.3          |

**Table 7** Heat exchanger comparison between the CLAS integrated MILD oxy-combustion plant and the reference plant
Table 8 compares the flue gas flow rate at the outlet of each component within the CLAS integrated MILD oxy-combustion plant and the reference supercritical power plant. In the CLAS integrated MILD oxy-combustion plant, the flue gas into the furnace increases due to a recycled CO₂-rich gas. The flue gas flow rate along the channel is decreasing in the CLAS integrated MILD oxy-combustion plant due to gas bleeding. At the furnace, the flue gas flow rate of the CLAS integrated MILD oxy-combustion plant is about three times than the reference plant. After bleeding Port I, the flue gas flow rate of the CLAS integrated MILD oxy-combustion plant decreases to values lower than the reference plant, except the low-temperature reheater. In the CLAS integrated MILD oxy-combustion plant, the order of components in the flue gas channel are not changed. The size of heat exchangers is technologically reduced compared with the reference power plant. However, for the furnace, the flue gas volume will double the ignition and combustion stability may be affected, and a large size of the furnace is needed. This challenge requires further consideration.

5 | CONCLUSIONS

The CLAS process to produce a stream of O₂ and CO₂ mixture gas is coupled with the supercritical power plant for MILD oxy-combustion and CO₂ capture. The power generation efficiency of the CLAS integrated MILD oxy-combustion plant is reduced by ~1.37% points compared to the reference supercritical power plant. CO₂ compression imposes about ~3.97% efficiency penalty, which is common and inevitable to all of the CO₂ capture technologies.

Different oxygen carriers have different operating region. It is not reasonable to compare the oxygen carrier at the same operating condition, but different oxygen carriers present similar efficiency because CLAS is in heat balance without tight connections to other components in the plant except CO₂ stream. Using Mn₂O₃-Mn₃O₄ as oxygen carrier, a higher reduction reactor temperature increases the power plant efficiency, whereas a higher oxidation reactor temperature decreases the power plant efficiency. The influence of excess CO₂ and O₂ on the efficiency is marginal. The heat exchanger analysis finds that the size of heat exchanger tubes in the MILD oxy-combustion boiler flue gas channel will decrease, and it is therefore may be possible to retrofit the conventional supercritical power plant with CLAS process for oxy-combustion and CO₂ capture.

ACKNOWLEDGMENTS

The authors express appreciation to National Key R&D Program of China (2016YFB0600802), National Natural Science Foundation of China (51606038), and Natural Science Foundation of Jiangsu (BK20160672) for financial support of this project.

CONFLICT OF INTEREST

None declared.

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**How to cite this article:** Chen S, Hu J, Sun Z, Xiang W. Application of chemical looping air separation for MILD oxy-combustion in the supercritical power plant with CO$_2$ capture. *Energy Sci Eng*. 2018;6:490–505. [https://doi.org/10.1002/ese.224](https://doi.org/10.1002/ese.224)