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Research Paper

# Application of chemical looping air separation for MILD oxy-combustion: Identifying a suitable operational region

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## HIGHLIGHTS

- Chemical looping air separation (CLAS) produces $O_2$ and $CO_2$ mixture for oxy-fuel combustion.
- Heat balance is achieved just by internal solid flow and inlet $CO_2$ feeding.
- Suitable operational regions of different oxygen carriers in CLAS are identified.
- Sensitivity analysis of CLAS parameters is conducted.

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## ABSTRACT

In this study, chemical looping air separation (CLAS) is integrated with moderate or intense low-oxygen dilution (MILD) oxy-combustion. $CO_2$-rich flue gas is used as a purging agent for oxygen decoupling in a reduction reactor. This work identifies the suitable operational region of different oxygen carriers for CLAS based on heat balance. The oxygen fraction in air determines the maximum temperature in the oxidization reactor. The maximum oxygen fraction produced for CuO-$Cu_2O$, $Co_3O_4$-CoO, $Mn_2O_3$-$Mn_3O_4$, and $MnO_2$-$Mn_2O_3$ are 16.8%, 13.2%, 14.4%, and 12.0%, respectively, with a reduction temperature 10 °C less than that of the maximum oxidization temperature. The inert solid flow is determined by the temperature difference between the two reactors and the reaction enthalpy change. The inert solid flow increases with decreasing temperature difference between the two reactors. With a drop in temperature difference between the two reactors, the inert solid flow increases. A higher change in reaction enthalpy of oxides also increases the inert solid flow. A higher reduction temperature generates a higher oxygen fraction level of the product mixture stream.



## 1. Introduction

Global warming caused by anthropologic $CO_2$ emission from fossil fuel conversion is a critical concern worldwide [1]. In addition to improving energy efficiency and using alternative sustainable energy, another approach to reducing $CO_2$ emission is carbon capture and storage (CCS) [2–4]. However, one barrier to implementing CCS is the large capital cost and decreased power efficiency compared with those of conventional plant without CCS. Of all the CCS steps involved, $CO_2$ capture is the most challenging from an economic point of view [5]. The high-purity separation of $CO_2$ accounts for a considerable share of the energy penalty in CCS technologies. Three general options exist for $CO_2$ capture in power plants [6]: pre-combustion [7], oxy-fuel combustion [8] and post-combustion [9,10].

Oxy-fuel combustion is one of the alternative pathways in the portfolio of low-emission technologies, primarily because of its ability to retrofit a current serving plant at a low cost [11]. However, the oxy-fuel combustion process, which is similar to that of other CCS technologies, also incurs high energy penalties associated with an air separation unit (ASU) for oxygen production [12]. Many available technologies, such as the well-established cryogenic distillation, as well as emerging adsorption and membrane technologies, produce oxygen [13–16]. In industry, cryogenic distillation is currently the most mature and proven technology for large-scale high-purity oxygen production. It is suitable for oxy-fuel combustion power plants. Cryogenic distillation compresses and liquefies the air at low temperatures, and then several components, like $N_2$, $O_2$ are distilled. The specific energy requirement of the advanced cryogenic distillation can be as low

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**Nomenclature**

$c_{co_2}$ $CO_2$ heat capacity (kJ/kg·°C)
$c_{inert}$ inert support heat capacity (kJ/kg·°C)
$c_{oc}$ oxygen carrier heat capacity (kJ/kg·°C)
$\Delta H$ reaction enthalpy (kJ/kg)
$m_{co_2}$ $CO_2$ flow rate (kg/s)
$m_{inert}$ inert solid flow rate (kg)
$m_{oc}$ oxygen carrier flow rate (kg/s)
$\Delta t$ temperature drop from oxidization to reduction (°C)
$\Delta t_{co_2}$ temperature difference between inlet $CO_2$ stream and reduction reactor (°C)

*Acronyms*
ASU Air separation unit
CCS Carbon capture and storage
CLAS Chemical looping air separation
CLC Chemical looping combustion
LHV Lower heating value
MILD Moderate or intense low-oxygen dilution
TGA Thermogravimetric analyzer

as 200–350 kWh/tonne of $O_2$ [17,18]. However, even with such low energy demand, the final energy penalty for oxy-fuel combustion remains as high as 4–6%, which diminishes the competitiveness of the oxy-fuel combustion plant in terms of power efficiency. In this scenario, efficient options for oxygen production that incur low energy penalties are urgently required.

Moderate or intense low-oxygen dilution (MILD) combustion is a new combustion technology. The oxygen concentration of MILD combustion is supposed to be 2–9 vol% [19], and the oxygen distributes uniformly in the premixed combustion of fuel. MILD combustion is characterized by high stability, uniform thermal field [20], and reduced temperature peak [21], with the advantages of high heat efficiency and extremely low $NO_x$ emission during fossil fuel combustion [22]. Most studies on MILD combustion have primarily been focused on gaseous fuel [23–26], however, recently an increasing number of studies have examined coal MILD combustion [27–29].

Although oxy-fuel and MILD combustions are usually studied separately, the general benefits of the two technologies have stimulated their being combined into a more efficient and cleaner combustion process [30]. Thus, MILD oxy-combustion offer more advantages over classic oxy-fuel combustion. Combining the two technologies allows for pollutants reduction and $CO_2$ separation. Tu et al. [31] conducted a numerical study of combustion characteristics for pulverized coal under MILD oxy-combustion, and found that adding $H_2O$ improved the ignition of coal [32]. Liu et al. [33] proposed MILD oxy-combustion in order to utilize biogas more efficiently. Mardani et al. [34] investigated the MILD oxy-combustion of $CH_4$-$H_2$, and determined that formation of NO and CO was reduced during the process. Li et al. [35] investigated MILD oxy-combustion of gaseous fuels in a laboratory-scale furnace, and the results indicated that a high $CO_2$ concentration could lower furnace temperature and $NO_x$ emission. They suggested that the $CO_2$ concentration should be increased to 95 mass% to achieve carbon capture. In conventional oxy-fuel combustion using coal as fuel, the oxygen concentration required for oxy-fuel combustion is in a range of 28–35 vol% to achieve gas-temperature and heat-transfer performance similar to that in air-coal combustion [36]. By contrast, MILD combustion can utilize a relatively low $O_2$ concentration feeding gas and an oxidizer inlet preheated at higher temperature. Chemical looping air separation (CLAS) could provide exactly such a high-temperature $O_2/CO_2$ stream.

CLAS is derived from chemical looping combustion (CLC), which is a promising technology to convert carbonaceous fuels and separate $CO_2$ with low energy penalty [37,38]. CLC is composed of two interconnected reactors, viz. fuel and air reactors. These are usually fluidized beds. An oxygen carrier circulates between the two reactors to achieve fuel combustion. The oxygen carrier, which is usually a metal oxide, is reduced from its higher oxidization state by means of fuels in the fuel reactor:

$$(2n+m)Me_xO_y(s) + C_nH_{2m}(g) \rightarrow (2n+m)Me_xO_{y-1}(s) + nCO_2(g) + mH_2O(g) \quad (1)$$

The outlet stream from the fuel reactor is composed of $CO_2$ and steam that are easily separated by condensation. The reduced oxygen carrier enters the air reactor. Air reacts with the reduced oxygen carrier at a lower reduction state in the air reactor. The outlet stream from the air reactor is mostly nitrogen and unreacted oxygen:

$$2Me_xO_{y-1}(s) + O_2(g) \rightarrow 2Me_xO_y(s) \quad (2)$$

The oxygen carrier commonly used in CLC is NiO [39,40], $Fe_2O_3$ [41,42] and CuO [43,44]. The overall reaction of CLC is merely fuel combustion in air with the following advantages: air is never mixed with the fuel (thus reducing $NO_x$ emission), and energy penalties for $CO_2$ capture are much lower than those with other technologies. The schematic flowsheet of CLAS is similar to that of CLC. CLAS also consists of two reactors: reduction and oxidization. The solid particles circulating between the two reactors are oxygen carriers, which are transitional metal oxides, such as CuO, $MnO_2$, $Mn_2O_3$ and $Co_3O_4$ [45]. In the reduction reactor, the oxygen carrier decomposes and releases gaseous oxygen in the presence of an inertial purge gas, such as steam or $CO_2$, as shown in Eq. (3). If steam is used as a purge gas, the mixture of steam and oxygen exiting the reduction reactor could pass through a condenser, allowing the gas to be cooled and the steam to be separated from $O_2$. If $CO_2$ is used as the purge gas, the mixture of $CO_2$ and oxygen can be directly fed to an on-site utilization facility, such as MILD oxy-combustion. The reduced oxygen carrier is then transported to the oxidization reactor, where air is fed into the oxidization reactor. The incoming oxygen carrier in a lower state is then regenerated to its higher state, as shown in Eq. (4). Through the continuous circulation of metal oxide oxygen carrier between the two reactors, oxygen is inherently separated from air.

$$\text{Reduction}: \ Me_xO_y(s) \rightarrow Me_xO_{y-2}(s) + O_2(g) \ \Delta H > 0 \quad (3)$$

$$\text{Oxidization}: \ Me_xO_{y-2}(s) + O_2(g) \rightarrow Me_xO_y(s) \ \Delta H < 0 \quad (4)$$

This chemical looping concept for oxygen production from air may date back to the Brin process introduced in 1811. This process is based on the thermal reversibility of reaction between BaO and $Ba_2O$ [46]. Moghtaderi et al. [47] conducted thermodynamic calculations and preliminary experiments on oxides of Cu, Mn and Co to ascertain the feasibility of the air separation method. Results confirmed its feasibility and showed that the oxides were quite suitable for air separation application. Zhou et al. [48,49] performed a techno-economic assessment of integrated CLAS for oxy-fuel combustion. The results showed that by replacing a cryogenic-based ASU with CLAS, the average reduction in the ASU power demand increased by as much as 47–76%, depending on the CLAS