



## Full Length Article

# The reactivity of CuO oxygen carrier and coal in Chemical-Looping with Oxygen Uncoupled (CLOU) and In-situ Gasification Chemical-Looping Combustion (iG-CLC)



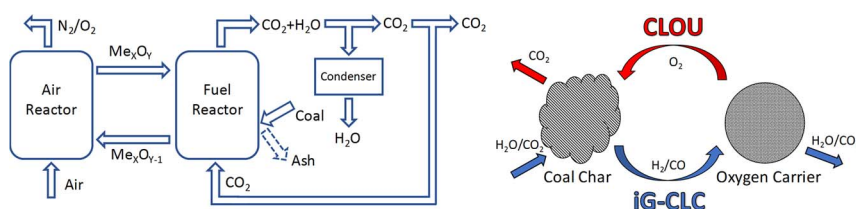
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Chemical-looping combustion (CLC) has the primary advantage of the generation of a CO<sub>2</sub> enriched flue gas, which greatly benefits CO<sub>2</sub> capture. Many researchers have been particularly interested in developing combined or mixed oxygen carriers (OC) to enhance and improve single metal OC properties. To advance the development of mixed OC, this study first focused on the conditions that impact the chemical reactions taking place in both In-situ Gasification Chemical-Looping Combustion (iG-CLC) and Chemical-Looping with Oxygen Uncoupled (CLOU) for single metal Cu based OC with coal and the gas product distributions. The Cu compounds present during CuO reduction (CuO → Cu<sub>2</sub>O → Cu) were also investigated using X-ray diffraction (XRD) as a function of carbon conversion during the reaction. In this study, the reactivity of char with CuO was tested at two different ratios of CuO to coal char ( $\phi = 26$  and 8) at 850 °C and 950 °C in Ar and Ar + H<sub>2</sub>O. Char conversion rates were greater at higher reaction temperatures (950 °C vs 850 °C) for all rests. At a high ratio of oxygen carrier to char ( $\phi = 26$ ), char was fully converted by reacting with O<sub>2</sub> released from CuO at both 950 °C and 850 °C in Ar. CuO was reduced to Cu<sub>2</sub>O resulting from the thermal release of gaseous oxygen. At a low ratio of oxygen carrier to char under Ar + H<sub>2</sub>O ( $\phi = 8$ ), char was fully converted at both 950 °C and 850 °C by char combustion with O<sub>2</sub> from the OC and syngas CLC from char-H<sub>2</sub>O gasification. Additionally, CuO was reduced to metallic Cu. iG-CLC had a lower CO<sub>2</sub> capture efficiency with CO in the product gas and a lower carbon conversion rate compared to CLOU. From a reactivity view point, CLOU is a promising process for coal chemical-looping combustion.

## 1. Introduction

Coal-fired electricity generation is a major energy resource and accounted for 32% of the total electricity produced in the United States

in 2016 [1]. Over the past decade, coal fired energy generation has declined due to carbon emission limits but is expected to remain a primary energy source for decades to come [1]. To meet the demand for clean energy, which cannot be met with renewable energy alone, clean

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coal technology development is very important [2]. Chemical-looping combustion (CLC) is one of the potential promising clean coal technologies to satisfy limits on carbon emissions. This process generates a CO<sub>2</sub> enriched flue gas which may easily be captured and has the potential to reduce the energy penalty of CO<sub>2</sub> capture from power plants [3].

CLC is a cycling process that uses an oxygen carrier (OC) to transfer oxygen from the air to the fuel via oxidation-reduction reactions [3]. This is different than coal firing using oxygen directly from air or pure O<sub>2</sub> from air separation in commercial coal power plants. In-situ Gasification Chemical-Looping Combustion (iG-CLC) [4–7] and Chemical-Looping with Oxygen Uncoupling (CLOU) [8,9] are two proposed coal CLC processes that involve a gas-solid reaction to increase the coal conversion rate and CO<sub>2</sub> capture efficiency. The gas-solid reaction is advantageous because fuel conversion through direct solid-solid contact between the coal and OC does not occur at an appreciable rate. Both processes have successfully been tested in 1.5–100 kW<sub>th</sub> (kilowatts from thermal energy by designed/perfect combustion of fuel) pilot scales [4,8,10]. In the iG-CLC process, coal is first gasified to produce syngas (CO and H<sub>2</sub>) in-situ by reaction with H<sub>2</sub>O and/or CO<sub>2</sub>. Then syngas reacts with the OC (syngas CLC) in the fuel reactor. Gasification is the limiting step in iG-CLC because the gasification reaction rate is significantly slower than the rate of syngas CLC. Fe-based OCs have been used in this process because they are relatively cheap and available from natural ores (ilmenite and iron ore) and industrial waste [7,11–13]. Some problems with Fe-based oxygen carriers are the slow reaction rate and low gas conversion (volatiles and syngas). The CLOU process burns coal with gaseous oxygen that is released by the oxygen carrier in the fuel-reactor, similar to conventional coal combustion. One advantage of the CLOU process is that it avoids the slow char gasification step resulting in higher conversion rates and complete fuel conversion compared to the iG-CLC process [9]. As a result, CLOU is considered a promising technology to combust solid fuels with CO<sub>2</sub> capture [8]. Cu-based OCs are often used in CLC but have a major issue of mechanical stability during continuous operation [14,15]. To date, attention has focused on combined or mixed OC (Cu and Fe) to enhance and improve the OC properties [16,17]. The study of single metal OC performance in both iG-CLC and CLOU may help the development of mixed OC and process design.

Cu-based oxygen carriers have been tested with coal in both iG-CLC [5,19] and CLOU systems. The primary advantages of this OC are the fast reaction rate, high oxygen transport capacity and favorable combustion thermodynamics that completely convert fuel to CO<sub>2</sub> and H<sub>2</sub>O [3,14,15]. However, agglomeration is a potential issue due to the low melting temperature of Cu (1085 °C). iG-CLC and CLOU use different approaches to prevent the Cu agglomeration. The CLOU process uses the CuO/Cu<sub>2</sub>O system to avoid generating metallic Cu. The iG-CLC process uses the CuO/Cu system but selects low CuO content OCs and low reaction temperatures to prevent agglomeration. The other main differences between these two processes in the fuel reactor are the reaction conditions summarized in Table 1. In CLOU, the operating temperature is high (900–950 °C) due to the Cu<sub>2</sub>O melting temperature

(1235 °C). The high temperature results in increased efficiency of CO<sub>2</sub> capture and power generation [10]. CLOU oxygen carriers typically contain high CuO content (e.g., 60 wt% CuO on a MgAl<sub>2</sub>O<sub>4</sub> support using a spray drying method) [8]. The ratio of OC/coal ( $\phi$ ) is typically high (~18–30) due to oxygen transport capability of CuO/Cu<sub>2</sub>O systems ( $R_o = 0.1$ ). The oxygen transport capability is defined as:  $R_o = (m_o - m_r)/m_o$ , the mass fraction of the theoretical maximum oxygen transport between the fully oxidized  $m_o$ , and reduced  $m_r$ , oxygen carrier [3]. Inert gas (N<sub>2</sub>) has been used as a reaction gas in lab scale studies because CuO autothermally decomposes and releases O<sub>2</sub>. The use of various fluidizing gases (CO<sub>2</sub> or H<sub>2</sub>O) may affect the CLOU process and needs to be studied. In iG-CLC, the operating temperature is low ( $\leq 850$  °C). iG-CLC oxygen carriers typically have low CuO content ( $\leq 21$  wt%) [18,20] (e.g., ~17 wt% CuO on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support using a wet impregnation method [18]). The ratio of OC/coal ( $\phi$ ) is low (~6–8) due to the high oxygen transport capability of the CuO/Cu system ( $R_o = 0.2$ ). Therefore, the CLC processes may be controlled in the desired direction by understanding the reactions that take place under various conditions.

To achieve high CO<sub>2</sub> capture efficiency, the key targets for the fuel reactor are: high solid fuel conversion (i.e., no unconverted char in the solid products) and high gas conversion (i.e., no unconverted fuel gases in the flue gas) [17]. It is important to measure the gas composition of the flue gas, which is often neglected in reported CLC research studies. This study focuses on the impact of reactor conditions on the chemical reactions taking place in the fuel reactor for iG-CLC and CLOU with the carbon conversion and the gas product distributions. The phase transformations of CuO reduction are CuO→Cu<sub>2</sub>O→Cu. Certain reactor conditions may cause Cu<sub>2</sub>O to further reduce to Cu in the CLOU process. Cu<sub>2</sub>O exists as an intermediate phase in the iG-CLC process. The determination of the copper oxide phase as a function of the degree of carbon conversion during reduction will help to understand the conversion routes and thermal behavior of coal at appropriate reaction conditions. The objective of this study is to investigate the reactivity of coal with CuO and the impacts of the ratio of CuO to coal char ( $\phi$ ), the reaction temperature and the reaction gas on the reactions that occur during iG-CLC and CLOU. This study will provide useful information for OC development, design and operation of chemical-looping processes.

## 2. Materials and methods

### 2.1. Materials and coal char sample preparation

Coal char, a Cu-based oxygen carrier and mixtures of the coal char and oxygen carrier were the experimental feedstocks used in this study. The coal sample was a Powder River Basin (PRB) sub-bituminous coal obtained from the U.S. Department of Energy's National Carbon Capture Center (NCCC) managed by Southern Company. The coal was sieved and a particle size of 106–180  $\mu$ m was selected to avoid mass and heat transfer limitations during the char reaction. The char sample was prepared by pyrolyzing the PRB coal. Pyrolysis was conducted at 1000 °C in a fixed bed reactor under flowing nitrogen. The coal was pyrolyzed by placing the quartz reactor tube containing the coal, into a furnace preheated to 1000 °C for 1 h. The prepared char was stored in a desiccator to prevent the absorption of water from the room air. A pyrolysis temperature was selected that was higher than the iG-CLC and CLOU temperatures to remove all available volatile content from the char sample. Table 2 lists the proximate and ultimate analysis results of the coal and the coal char on a dry basis. The moisture contents of the char and coal were 1.20 wt% and 12.29 wt%, respectively. The oxygen carrier was cupric oxide (CuO) powder with 99.99% trace metals basis obtained from Sigma-Aldrich. The mixtures of char and CuO were weighed separately and physically mixed together before each test.

**Table 1**  
Summary of main differences between iG-CLC and CLOU in the fuel reactor.

CLOU	iG-CLC
CuO reduced to Cu <sub>2</sub> O	CuO reduced to Cu
High temperature (900–950 °C) due to Cu <sub>2</sub> O melting temperature 1235 °C	Low temperature ( $\leq 850$ °C) due to Cu melting temperature 1083 °C
OC with high CuO content and prepared using spray drying method 60 wt% CuO on a MgAl <sub>2</sub> O <sub>4</sub> support (Cu60MgAl) [8]	OC with low CuO content and prepared using wet impregnation method ~17 wt% CuO on a $\gamma$ -Al <sub>2</sub> O <sub>3</sub> support [18]
High OC/coal ratio (~18–30)	Low OC/coal ratio (~6–8)
Reaction gas: NA (decomposition)	Reaction gas: H <sub>2</sub> O and/or CO <sub>2</sub>

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