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Fate of sulfur in coal-direct chemical looping systems

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HIGHLIGHTS

- The fate of sulfur in a coal-direct chemical looping system is determined.
- 69% of sulfur exits as H_2S and SO_2 in the CO_2-rich stream from the reducer.
- Less than 5% of sulfur exits as SO_2 in the combustor spent air.
- Emission of sulfur in combustor spent air is dominated by char carry-over.
- Projected SO_2 emission for a CDCL 550 MW_e plant is in compliance of EPA regulation.

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ABSTRACT

The fate of sulfur in the coal-direct chemical looping system was investigated in the sub-pilot reactor system. The sulfur balance was successfully closed during the injection of high sulfur coal. More than 69% of the total amount of atomic sulfur in coal was released as SO_2 and H_2S from the reducer flue gas stream while less than 5% was emitted as SO_2 from the combustor spent air. The remaining atomic sulfur was retained in coal ash as inorganic sulfur compounds. The finding suggests an acid gas removal system targeting both H_2S and SO_2 is required to meet the recommended quality of CO_2 stream for sequestration and transportation. Using the determined ratio of SO_2 and H_2S, a properly designed Claus plant can enable the recovery of elemental sulfur as a value-added byproduct. The combustor spent air was found to comply with the US EPA sulfur emission regulation and can be released to the atmosphere without a costly acid removal system. The relationship between the sulfur and carbon capture efficiencies was established experimentally and was found to be proportional to each other throughout the experiment at a slope of 0.8 below 93% of carbon capture efficiency and near 1 above 93%. This was attributed to the delayed release of organic sulfur during incomplete char gasification in the reducer. The finding affirms the effectiveness of the counter-current moving bed design for minimizing the amount of carbon and sulfur emission in the combustor spent air with an average carbon and sulfur capture efficiency of 96.5 and 95%, respectively. Sulfur deposition on the iron based oxygen carriers did not affect the system performance, and complete removal of deposited sulfur was observed during oxidation in a thermogravimetric analyzer. Compared with chemical looping systems using circulating fluidized bed configuration, the use of a moving bed reducer has the additional benefit of minimizing slippage of char into the combustor due to the use of large oxygen carrier; resulting in lower sulfur emission in the combustor spent air. The findings demonstrate the robustness of the coal-direct chemical looping system to handle high sulfur coal without a complicated acid gas cleaning scheme or severe performance penalties.

1. Introduction

Chemical looping combustion (CLC) refers to the use of a metal oxide or metal sulfate as an oxygen carrier chemical intermediate to perform a set of reduction and oxidation sub-reactions for the combustion of carbonaceous feedstocks (e.g. coal, natural gas, and biomass). The redox reaction cycle decreases the irreversibility of the fuel combustion process which then results in an increase in the recoverable work for steam/power generation [1,2]. Additionally, the CLC reaction pathway inherently separates the carbonaceous fuel feedstocks from the inert species present in the reactant air, and thus, is capable of producing a nearly pure CO_2 product stream for further

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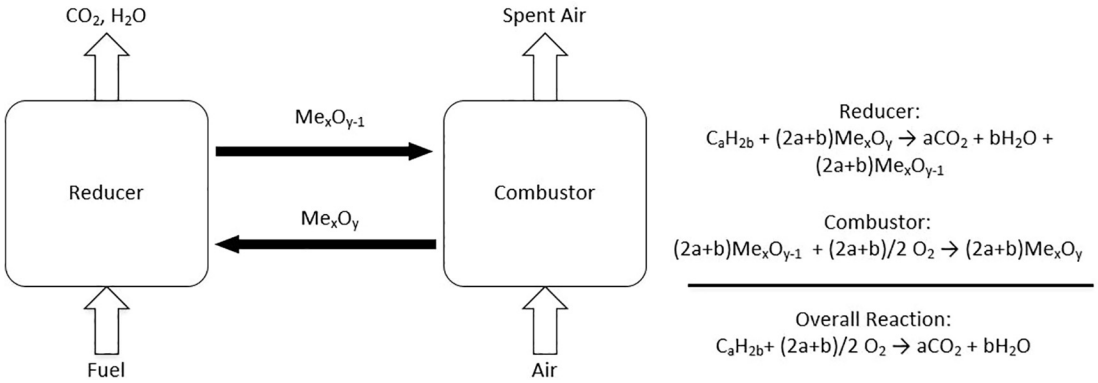

Fig. 1. Simplified block flow diagram of CLC.

utilization and/or capture and sequestration. As such, the United States Department of Energy (USDOE) considers CLC one of the most advanced oxy-combustion carbon capture technologies for fossil fuel power generation [3].

Fig. 1 below illustrates the general block flow diagram of a CLC process. Here, a metal oxide (Me_xO_y) serves as the chemical intermediate to transfer oxygen from air to the fossil fuel. The primary metal oxide(s) (Me_xO_y) in the oxygen carrier reacts with the fossil fuel in one reactor, i.e. the reducer, to form a reduced metal oxide (Me_xO_{y-1}) while producing CO_2 and H_2O as the product gas. The reduced metal oxides are then transported to a second reactor, i.e. the combustor, where oxygen from air regenerates the oxygen carrier, and in turn produces heat to drive the endothermic reactions in the reducer and to generate steam for power production. The fully oxidized Me_xO_y subsequently returns to the reducer reactor to complete the loop. The CLC reaction scheme produces high purity CO_2 for sequestration without N_2 dilution of the flue gas from air present in the traditional coal power plants. Since the oxygen carriers' purpose is to transport oxygen and heat from one reactor to the next, the overall net reaction is identical to the conventional combustion process.

The concept of chemical looping has been in practice since the early 1900 s with the Lane process for producing H_2 from syngas and the Dupont process for producing $C_4H_2O_3$ from C4's, to select a few [4,5]. Ishida et al. in 1987 were the first researchers to coin the term "Chemical Looping" and analyze its specific application for increasing the exergy efficiency of a fossil fuel combustion power generation plant [6]. With the growing demand for electricity with cost-effective CO_2 emissions control, research in CLC has grown exponentially from the start of the 21st century. Major research efforts in both the reactor design and oxygen carrier development has been focused on CLC systems with scales ranging from 300W_{th} to 3 MW_{th} with over 6000 h of operational results obtained [7]. Oxygen carriers based on Fe, Ni, Cu, Mn, Co, and CaS have all been tested extensively. Table 1 below summarizes solid-fuel CLC units in demonstration above 10 kW [8]. Given the current developmental status of CLC systems, emission of criteria pollutants from CLC systems of various configurations should be carefully examined to begin evaluating the environmental impact of a CLC system beyond the carbon capture and oxygen carrier development.

1.1. Characterizing pollutants in chemical looping combustion

To date, limited data has been reported for the emission of criteria pollutants from CLC processes. For power generation systems utilizing CLC processes, existing and future regulations of criteria pollutants must be met during the plants' life time. Contrary to traditional boilers where only one flue gas stream is treated before emission, the CLC process shown in Fig. 1 produces two flue gas streams with two separate destinations: atmospheric emission for the combustor spent air and sequestration for the CO_2-rich reducer flue gas. Therefore, the number of units for flue gas treatment in a CLC-based plant could potentially double and incur additional capital and operating cost if criteria pollutants in both streams exceed the limits imposed by regulation. The distribution and concentration of criteria pollutants in each stream is of interest as it provides cost-saving opportunities if the measured concentration is under the regulated limits without additional treatments. For CLC processes with coal as fuel feedstock, the challenge is even greater due to the significant amount of pollutants present in coal and the accompanying environmental regulations. Table 2 below summarizes the major efforts to date in measuring the emission of pollutants in CLC systems, including both solid and gaseous fuels.

For solid fuel based CLC systems, the concentrations of pollutants in the combustor spent air were found to be inversely proportional to the percent conversion of coal, hence the carbon capture efficiency, in the reducer reactor. For circulating fluidized bed, CFB, the carbon capture efficiency ranged between 70% to 98% and was dependent on the temperature of the reducer, the type of oxygen carriers and the amount of char slippage from the reducer to the combustor during oxygen carrier transportation. Most fuel nitrogen from coal formed N_2 instead of thermal-NO_x due to the flameless nature of chemical looping scheme compared to a traditional boiler. For sulfur emissions in both flue gas streams, the observations were less transparent. The estimated SO_2 emission from the combustor spent air ranged between 2 and 10% relative to the inlet sulfur from coal. In some cases, the amount of sulfur was not measured directly, but calculated by assuming a constant S/C ratio during the entirety of char conversion. The assumption has shown to be inaccurate for estimating the sulfur emission in the combustor spent air [11]. For CLC systems using gaseous fuels, sulfur emission

Table 1
Solid-fuel CLC demonstrations units above 10 kW_{th} [8]

Location	Capacity	Reactor type	Fuel
Chalmers University of Technology, Chalmers, Sweden	10 kW_{th}	Interconnected CFB-BFB	Coal, pet coke
Southeast University, China	10 kW_{th}	CFB-spouted bed	Coal, biomass
Ohio State University, Ohio, USA	25 kW_{th}	Interconnected Moving bed-Entrained bed	Coal
ALSTOM Windsor, Connecticut, USA	65 kW_{th}	Interconnected CFB-CFB	Coal
Darmstadt University of Technology, TUD, Germany	1 MW_{th}	Interconnected CFB-CFB	Coal
ALSTOM Windsor, Connecticut, USA	3 MW_{th}	Interconnected CFB-CFB	Coal