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Experimental evaluations of solid-fueled pressurized chemical looping combustion – The effects of pressure, solid fuel and iron-based oxygen carriers

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HIGHLIGHTS

- Initial understanding of complex fuel reactor reactions in solid-fueled PCLC unit.
- Use of OC and elevated steam partial pressure to improve in-situ gasification.
- Combustion efficiency of PCLC is unaffected by the type of coal char.
- Combustion efficiency of PCLC is unaffected by the steam partial pressure.
- Combustion efficiency is heavily dependent on OC performance.
- The best iron-based OCs almost eliminate the gasification inhibition from CO or H_2.
- Ilmenite OC is less favorable for intermediate syngas conversion at higher pressure.

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ABSTRACT

Coal-based Pressurized Chemical Looping Combustion Combined Cycle (PCLC-CC) is the second generation of coal-fueled CLC plant, which possesses much higher plant efficiency and lower-CO_2 capture cost compared to the first generation - Coal-based CLC combined solely with steam cycle. PCLC-CC has a similar plant configuration to the Pressurized Fluidized Bed Combined Cycle (PFBC), and is composed of a PCLC Island, gas turbine, Heat Recovery Steam Generator (HRSG) and steam cycle. In the fuel reactor of PCLC Island, the metal-based oxygen carrier (OC) supplies oxygen for coal combustion and in-situ CO_2 capture. The air reactor of PCLC Island, where the OC is re-oxidized by air, serves as a combustion reactor to produce oxygen-depleted air of high temperature and high pressure to drive the gas turbine and the following steam cycle for large-scale power generation. This research provides an initial understanding of the complex reactions in the fuel reactor of the solid-fueled PCLC Island in the pressures range of 1–6 bars. Experiments conducted in the TGA apparatus and the fixed- and fluidized-bed reactors demonstrated the effects of operational pressure, coal char reactivity and different iron-based OCs behavior on the performance of PCLC.

1. Introduction

Chemical Looping Combustion (CLC) is an advanced technology under development to achieve efficient energy conversion of carbon fuels with in-situ CO_2 capture. The CLC process is composed of two-step combustion in which oxygen carrier (OC) materials, generally metal oxides supported by inert material, provide lattice oxygen for fuel combustion in one reactor (fuel reactor, FR), and in another reactor (air reactor, AR) the oxygen-depleted OC is separately re-oxidized by air back to the full oxidized form for the next cycle. Due to the separation between air and fuel, a high purity CO_2 stream can be recovered from the FR for sequestration. By avoiding an energy intensive gas separation processes, a CLC plant could potentially provide much higher efficiency than the conventional combustion technologies with CO_2 capture [1].

Gaseous-fueled CLC units have been successfully demonstrated in the last ten years, with capacity ranging from 10 kW_{th} to the 140 kW_{th} [1–4]. These CLC units are usually configured with two

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interconnected fluidized-bed reactors operated at atmospheric pressure. Recently, coal-fueled CLC has become attractive due to the extensive availability and low cost of coal [5–8]. Research also demonstrated the feasibility of using pet-coke, solid wastes and biomass for CLC [9–11]. Solid fuel can be utilized via in-situ gasification chemical looping combustion (iG-CLC), where solid fuel is introduced directly to the FR. This allows solid fuel gasification and syngas combustion with metal oxide to occur simultaneously. The major advantages of iG-CLC are the elimination of an air separation unit and extra gasifier. Another advantage is that coal gasification can be improved at an extremely low concentration of gasification inhibitors (CO/H_2) in the FR [12,13]. Currently, a number of iG-CLC facilities (ambient pressure) with thermal inputs ranging from 1 kW_{th} to 3 MW_{th} have been constructed worldwide [1,14–17]. Among the OCs used, low-cost iron-based OCs are the preferred materials for solid fuel combustion. A Circulating Fluidized Bed (CFB) or Bubbling Fluidized Bed (BFB) is commonly adopted as the fuel reactor. Today, the largest solid-fueled CLC unit is Alstom's 3MW_{th} system in Windsor, USA, using Ca-based OCs [15]. 1 MW_{th} CLC facility using hard coal and iron-based OCs has been successfully demonstrated and operated in a continuous model without external heat sources [18]. A design of a 455 MWe CLC power plant with solid fuel has been developed within the project ENCAP [19]. Recently, an engineering design for a coal-fueled CLC boiler was also performed at a commercial-scale (1000 MW_{th}) with ilmenite OC as the circulating material for fuel combustion [20].

There are still significant challenges with the performance and the cost of solid-fueled CLC. Several issues contribute to these challenges, including OC cost and efficiency, kinetics, reactor configuration, and solid handling. The present cost for OC makeup and disposal are very close to that of fuels even when low-cost iron-based OCs are used [21]. Both solids circulating between the two reactors and the char-OC separation process (either as a stand-alone process or as part of the reducer), need to process a very large amount of solids. Presently, the FR is operated at a relatively low temperature, where coal gasification is very slow. As demonstrated by the solid-fueled CLC facilities worldwide, the FR off-gas contains a substantial amount of unconverted gas (H_2 and CO). Furthermore, the plant efficiency of the present CLC configuration (the first generation) is not as high as anticipated (35.1% for the iron-based CLC plant and 32.6% for the Ca-based CLC plant [21]).

At University of Kentucky Center for Applied Energy Research (UKy-CAER), a second generation of coal-fueled CLC plant has been proposed to significantly improve plant efficiency and CO_2 capture. The second generation system has a plant configuration similar to gaseous-fueled PCLC reported by Hamers [22] or Pressurized Fluidized Bed Combined Cycle. The direct coal-fueled PCLC unit serves as a combustor to generate a flue gas stream of high temperature and high pressure. This flue gas is used to drive a gas turbine and the following steam cycle for large-scale power generation. After water condensation and heat recovery steps, the CO_2 stream from the FR is compressed for sequestration. Cost–effective iron-based OCs from solid waste or natural ore are selected to increase the operational temperature and to reduce operational costs. The major driving forces for the development of the second generation CLC system are higher plant efficiency, low cost of electricity and CO_2 capture. Our thermodynamic analysis [23] predicted that the second generation system at the scale of 550 MWe could provide more than 90% CO_2 capture, greater than 95% CO_2 purity, and a net plant efficiency of more than 44.5% (LHV) with CO_2 pressurized to 2215 psi. A similar PCLC process was proposed by Southeast University (SEU), China, but no calculated plant efficiency was provided [24]. A 100 kW_{th} PCLC unit has been demonstrated using iron ore and coal by SEU [25].

Although the second generation of the solid–fueled PCLC is promising, almost no test data and experience are available to define initial operation conditions and design parameter selection, and further to project plant performance and cost. Very little information has been reported on kinetics of OCs at elevated pressure [26–30]. However, these data were collected for the understanding of the main characteristics of the gaseous fueled-CLC. The goal of this research was to gain an initial understanding of the reactions in the FR of the solid-fueled PCLC, and collect essential information to evaluate performance and design parameter selection. Experiments were conducted at pressures ranging from 1 to 6 bars in a fluidized bed reactor, and designed to study the effects of solid fuel reactivity and the roles of iron-based OCs. Two red mud OCs (RM OC) and ilmenite ore were selected as OC materials. RM OC was developed by UKy-CAER from Bauxite residuals of aluminum industry, which has been identified as a cost-effective OC for coal-fueled CLC. The flow regime of the FR was designed as a bubbling fluidized bed for both OCs and coal char. For the sake of simplicity, coal char and steam were used as fuel and gasification agent, respectively. Both H_2O and CO_2 have been proposed as gasification agents for solid-fueled CLC. CO_2 can be fed by recirculating a fraction of the product gas of the FR. Thus, to some extent the steam requirement and the energy penalty for steam generation can be reduced. The effect of using CO_2 with steam on solid-fueled CLC has been validated by Ana Cuadrat [12], showing that the increase of CO_2 fraction in gas mixture would significantly drop the gasification rate and combustion efficiency.

2. Experimental

2.1. Materials

Three iron-based OCs were used in this research, including activated ilmenite ore and two RM OCs. Ilmenite ore has been identified as a low-cost OC, and its behaviors in both gaseous- and solid-fueled CLC processes have been reported [31–33]. The raw ilmenite ore was primarily composed of $FeTiO_3$, TiO_2, with a small amount of Fe_2O_3. As a pretreatment, the ore was crushed into 125–355 μm particles, stabilized in air at 950 °C for 24 h, and activated by 10 redox cycles (20% CO in N_2 gas for 15 min oxidation, and diluted air for regeneration) in a fluidized bed reactor. The two RM OCs, S-RM OC and A-RM OC, were prepared from two different Bauxite residuals of aluminum industry by lab-scale freeze-granulation. The detailed methods can be found in our previous study [34]. Both RM OCs were calcinated at 1150 °C for 6 h to obtain the proper particle morphology and mechanical strength. These calcinated particles in the range of 125–355 μm were collected for experimentation.

Table 1 summarizes the chemical composition and physical properties of the OCs tested. SEM images of the fresh OC particles are included in the supporting information (S-Fig. 1). In the baseline experiment, fused Al_2O_3 particles (125–355 μm) were used as bed materials for coal char external gasification, and the physical properties are listed in Table 1. The XRD patterns, presented in Fig. 1, show that the active content of two RM OCs is Fe_2O_3, and Ca-Al-O, or Na-Al-Si-OC composites function as structural support. Previous research [34] showed that the active content (free Fe_2O_3 phase) in RM OCs can be completely reduced to metallic iron by dry syngas, and all iron-containing phases involved during the reduction and regeneration, i.e. Fe_2O_3, Fe_3O_4, FeO and Fe, did not react with the support material to form a new spinel phase. Therefore, the unique structure of RM OCs ensures the reaction with coal-derived syngas will be the reduction of free Fe_2O_3 to Fe_3O_4, FeO and further to metallic iron. The crystalline phases identified in the activated ilmenite OC include Fe_2TiO_5, TiO_2 and a small