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ScienceDirect

Energy Procedia 114 (2017) 387 – 394

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Chemical looping combustion in a bed of iron loaded geopolymers

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Abstract

The chemical looping combustion allows for inherent CO_2 separation when burning fossil fuels in presence of a suitable oxygen carrier. The choice of the material to be used should take into account not only chemical/physical properties but also economical, environmental, and safety concerns, addressing for more common materials, like Fe oxides. In this research a geopolymeric oxygen carrier, based on Fe_2O_3, was tested for the first time in a laboratory CLC plant operated at high temperature for the combustion of a CO rich gas from char gasification in CO_2. The CLC plant reliably performed in repeated cycles without decay of the CO conversion during the chemical looping combustion. The maximum CO content in the flue gas was around 1% vol. and carbon monoxide conversion achieved 97%. The calculated oxygen transport capacity was 0.66%. The plant results were confirmed by the XRD analysis that proved the presence of reduced phases in samples after chemical looping stage and by significant peaks obtained during H_2 reduction in TPR equipment.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: chemical looping combustion; oxygen carrier; geopolymers; hematite; gasification

1. Introduction

The chemical looping combustion (CLC) is a promising two-step combustion method enabling inherent CO_2 sequestration, so that low extra energy is needed for its separation from the rest of flue gases [1]. The process is based on the use of a solid oxygen carrier, usually a metal oxide, which performs the task of transporting the oxygen required for combustion from an air reactor to a fuel reactor, designed as two interconnected fluidized beds [2, 3]. This method, may result more economically advantageous than others (e.g. wet absorption, calcium loop). In this process, indeed, the fuel is introduced to the fuel reactor where it reacts with the oxygen carrier (the metal oxide), at high temperatures, subsequently being reduced to a lower oxidized form [4]. Since both reduction and oxidation

Peer-review under responsibility of the organizing committee of GHGT-13.
doi:10.1016/j.egypro.2017.03.1180

steps may be exothermic, heat can be recovered from both reactors and no large temperature differences can be expected between each other.

Usually the metal oxides chosen to act as oxygen carriers are embedded in a high temperature stable and porous matrix which, eventually, may increase the abrasion resistance of the oxygen carrier itself and improve the oxygen diffusion ability. The extent of the oxidation-reduction reactions involved in the process may vary depending on the reaction conditions and the chemical nature of the adopted metal oxide. Fe, Mn, Ni and Cu oxides have been widely proposed in literature as potential candidates for CLC, in form of pure oxides or in combination [3, 5]. Ni and Cu oxygen carriers have been demonstrated to be very effective, achieving up to 21% of theoretical O transport capacity in the case of NiO reduction to Ni, but they are toxic [6, 7].

Among the different metal oxides that have been proposed so far, iron oxide has a great potential, as it shows relevant advantages, such as the no-toxicity, the large availability, the good resistance to agglomeration and the low-price. Iron oxide can be available in three oxidized forms, FeO (wüstite), Fe_3O_4 (magnetite) and Fe_2O_3 (hematite). It usually behaves by reduction/oxidation of the Fe_2O_3/Fe_3O_4 pair, with a theoretical oxygen carrier capacity equal to 3.34% wt.

In a previous work by the authors [8], a novel oxygen carrier based on iron oxide has been successfully synthesized embedding Fe_2O_3 in a geopolymer matrix. Geopolymers are quasi-amorphous, three-dimensional, and nanostructured ceramic materials that can be produced at low to moderate temperature (25-100 °C) by alkaline activation of alumino-silicate precursors [9] through an easy, low-cost and green process. This class of materials is characterized by a diffused meso-porosity, a rather high surface area, associated with substantially high mechanical strength, abrasion resistance and high temperature stability up to 1000 °C [10-11], properties which make them optimal candidates for fluidized bed operations in CLC systems.

Tests on a granulated metakaolin-based geopolymers added with iron oxide were performed in thermogravimetric equipment and in a lab-scale fixed bed reactor cyclically operated at temperature of 900 °C and atmospheric pressure with a flow rate of reducing and oxidizing gas mixtures (Ar, Ar/CH_4) [8]. The Fe_2O_3-doped geopolymer exhibited promising results in terms of higher kinetics, being the geopolymer O carrier more efficient than a commercial Fe oxide in specific operating conditions (short times of reduction and oxidation cycles) and showing higher rate index.

The coal/biomass gasification is a well-developed process for producing a synthetic gas to be converted in further stages. When the gasifying agent is H_2O or CO_2, external heat is required in order to sustain the reactor temperature in the operation range 800-900 °C. If a CLC step is accomplished in sequence to gasification for zero emission combustion, the recirculated hot oxygen carrier can sustain, at least partly, the gasification reactor with benefits for the plant intensification and economics.

The present article reports on a combined gasification-CLC process for the combustion of wood char, with the utilization of an oxygen carrier based on geopolymeric matrix. The results of the experimental tests in a laboratory scale CLC plant and the characterization of the samples from the reactor were presented and discussed in the paper.

2. Experimental

2.1. Experimental equipment

A laboratory scale plant for CLC was used in tests aimed at checking the performance of the oxygen carrier for the conversion of a CO rich gas. As shown in Figure 1, the plant includes two tubular reactors in AISI 316 (22 mm ID and 500 mm length), which are vertically installed inside an electric furnace Carbolite 1200. The first tube (CLC reactor) is filled with alumina wool at both ends and granular oxygen carrier at center (20-30 g), whilst the second tube (gasification reactor) is filled at center with wood char (2-5 g). A system of tubes and control valves (Fig. 1) allows for periodic switching of the operation in the two tubes. A multi-component continuous gas analyzer (mod. GEIT GAS 3160) is used to measure CO, CO_2 and O_2 concentrations in the gas streams from the plant, after the separation of dust and water. A digital manometer monitors the pressure at the base of the gasification reactor. A mass-flow controller (mod. Brooks F21780-001) regulates the flow rate of CO_2 from a bottle, whilst a volumetric pump provides the air for the regeneration.

The plant was initially heated up to the desired temperature in inert atmosphere for the gasification reactor and air for the CLC reactor. Afterwards, three operation modes are feasible by purposely switching the control valves. In a