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Chemical looping combustion of low-ash and high-ash low rank coals using different metal oxides – A thermogravimetric analyser study

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ABSTRACT

Multiple redox experiments have been performed in a thermogravimetric analyser with well characterised iron and nickel oxide to assess their reactivity with low-ash Victorian brown coal as fuel, and nitrogen, air, CO_2 and steam as combustion and gasification atmosphere. In addition, a high-ash lignite was used as fuel to compare its performance with the Victorian brown coal. The results show good performance of iron oxide as oxygen carrier over multiple cycles. However, NiO, a good oxygen carrier for gaseous fuel, shows progressively less reactivity over the multiple cycles. It has been observed that both the metal oxides can initiate the reduction reaction as low as 400 °C under different experimental condition. Five reductions and oxidations (Re-dox) cyclic experiments reveal 87% combustion of Fe_2O_3 and coal mixture under CO_2 atmosphere at the end of the 5th cycle. However, the same for NiO is 67%. Metal oxide and coal solid mixture mass during re-dox experiments have been compared with thermodynamic predictions in similar experimental conditions. A continuous mass loss trend for NiO has been observed different from the thermodynamic predictions.

1. Introduction

Conventional coal based power generation involving combustion and gasification requires direct contact between air and coal. This dilutes the resulting gases due to the presence of nitrogen (N_2) in air. So the concentration of CO_2 is reduced in flue gases which make CO_2 separation and capture energy intensive. Chemical looping combustion and gasification (CLC/G) is one of the promising technologies to achieve potentially easier CO_2 capture. In chemical looping combustion, an oxygen carrier; preferably metal oxide, is used to transfer oxygen from combustion air to fuel. In this way direct contact between air and fuel is avoided which essentially prevents CO_2 from being mixed with combustion gases.

The CLC system is composed of two reactors: an air reactor and a fuel reactor. In the fuel reactor, the fuel particles are reduced by oxygen from metal oxide and reduced metal oxide is re-oxidised in the air reactor to be used in the next cycle. The main advantage of this system is a concentrated stream of CO_2, free from dilution with nitrogen and its oxides can be obtained from fuel reactor after condensing the water vapour. A generalised description of the overall system is given in Fig. 1. Reaction stoichiometry is given by the equations below:

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

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

where Me stands for metal and MeO as metal oxide.

Chemical looping concept has been widely studied and important progress has been made for combustion of natural gas [1]. The chemical looping methodology has been investigated previously with synthesis gas, derived from coal, as feedstock [2–4]. Lyngfelt et al. [3] tabulated a number of studies on chemical looping combustion using coal derived syngas as fuel with different oxygen carriers. However, only a few studies have been conducted on the combustion of solid fuels, such as coal [5]. Alstom Power Inc. used Limestone ($CaSO_4$) as oxygen carrier in the development of chemical looping technology for three different purposes explicitly for combustion with CO_2 capture, syngas production and H_2 production with CO_2 capture [6]. The reactivity of a batch of NiO/Al_2O_3 oxygen carrier in a relatively long term (100 h of operation) chemical looping experiment for combustion of Bituminous coal was investigated in a 10 kW_{th} continuous interconnected fluidized bed metallic reactor by Shen et al. [7]. The reactivity deterioration of the nickel-based oxygen carrier was observed during the experimental period. The effect of temperature on gas composition of both fuel and air reactor, carbon content of fly ash, carbon conversion and CO_2 capture efficiency were also investigated using the same reactor. Coal gasification was observed to be the main factor which controlled the contents of CO and CH_4 concentrations in the fuel gas and carbon conversion efficiency in the process of CLC using bituminous coal with NiO oxygen carrier. Carbon loss due to elutriation of fine char particles limited the carbon conversion efficiency to 93% at 970 °C temperature [8]. Dennis et al. [9] and Scott et al. [10]

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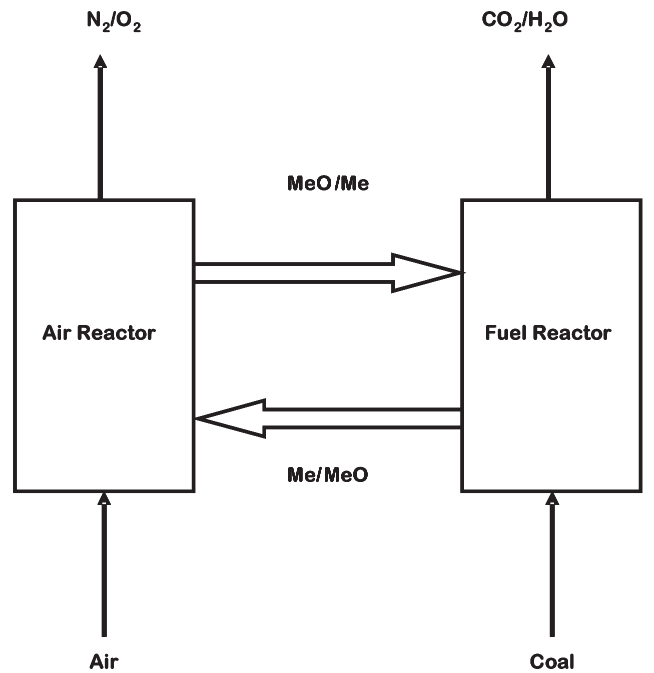

Fig. 1. Schematic of chemical looping combustion.

reported in situ gasification of Hambach lignite and its char in presence of gasification agents (steam and CO_2) in fluidized bed reactor with Fe_2O_3 as oxygen carrier. Dennis and Scott [11] also investigated in situ gasification of the same solid fuel and its char using CO_2 in presence of copper oxide in an externally-heated fluidized bed. There was little evidence to suggest a direct reaction between carbonaceous and carrier solids, other than via a gaseous intermediate. Kinetics of gasification was observed to be faster in presence of the oxygen carrier and no agglomeration between carrier particles and ash was observed. Performance of Cu-based oxygen carrier for in situ chemical looping gasification of two bituminous coals from Russia and USA were investigated by Dennis et al. [12] and compared with Hambach lignite [11]. The bituminous coal produced char which was less reactive as compared to the lignite char. Since the kinetics of gasification by CO_2 of the chars from both bituminous coals were slow, their rates were controlled by intrinsic chemical kinetics and were not affected by the ability of the oxygen carrier to alter the rates of external mass transfer when gasification is rapid [12]. The combustion and re-oxidation properties of direct coal chemical looping combustion with a number of metal oxide as oxygen carrier has been investigated using thermogravimetric analyser and bench scale fixed bed reactor by Siriwardane et al. [5]. Among various metal oxides evaluated, CuO showed the best reaction properties. CuO was able to initiate the reduction reaction as low as 500 °C and completed the full combustion at 700 °C. In addition the reduced Copper was fully re-oxidised by air at 700 °C. Surface morphology changes of used CuO were observed as compared to the fresh one but without significant surface sintering. Cao and Pan [13] and Cao et al. [14] discussed the chemical looping combustion process analysis and redox reaction kinetics of different solid fuels in a series of two publications. The first one presented the concept of CLC process for solid fuels using a circulating fluidized bed. Tests on the reduction of CuO with coal and some opportunity solid fuel such as biomass were conducted by differential scanning calorimetry and thermogravimetric analyser to simulate the chemical looping combustion and reported in the second publication. Results strongly supported the feasibility of using CuO as oxygen carrier for solid fuel CLC. CuO reduction by solid fuel was initiated at the same temperature as observed by Siriwardane et al. [5]. Leion et al. [15–18] investigated the feasibility of using a number of different solid fuels (Mexican petroleum coke and coals from South Africa, China, Indonesia and Taiwan and France) in chemical looping combustion in a laboratory fluidized bed reactor system with different oxygen carriers–synthetic particles of 60% active material of Fe_2O_3 and 40% $MgAl_2O_4$, natural mineral Ilmenite, NiO, and unprocessed iron ore . The effect of steam and SO_2 concentration in the fluidizing gas was investigated as well as effect of temperature. The presence of an oxygen carrier was shown to enhance the conversion rate of the gasification reaction. Only minor agglomeration for the oxygen carrier was observed [15,16]. Compared to the other oxygen carriers the reactivity of the used NiO particles was considerably lower for the high-sulphur fuel such as petroleum coke and higher for the low-sulphur fuel. Much more unconverted CO was released and the fuel conversion was much slower for high-sulphur fuel, suggesting that the nickel-based oxygen carrier was deactivated by the presence of sulphur. For all experiments NiO showed good fluidizing properties without any signs of agglomeration [17]. In case of oxide scale and unprocessed iron ore the results showed that both oxygen carrier worked well and increased their reactivity with time [18]. Chemical looping combustion and gasification of petroleum coke, Mexican Pet coke and South African coal were investigated by Berguerand and Lyngfelt [19–22] using Ilmenite, iron titanium oxide ($FeTiO_3$), as oxygen carrier in a 10 kW_{th} chemical looping combustor. The CO_2 capture for different fuel ranged between 60% and 96% and average solid fuel conversion ranged between 65% and 70%. Incomplete gas conversion led to an oxygen demand averaging at 25%.

From the above literature it is evident that only limited numbers of investigations have been performed on chemical looping using lignite or brown coal. Chemical looping has never been tested with Victorian brown coal.

Victoria has large resources of brown coal (>500 years at current consumption rate) and therefore there is a strong incentive for development of efficient technologies, such as chemical looping, for power generation from Victorian brown coal with potentially easier CO_2 sequestration. However, there are issues which need to be identified and addressed for CLC application of Victorian brown coal. Much is unknown about the yield of products (such as H_2, CO_2, CO, and Char) and their rates from this process as a function of time, temperature, particle size and type of brown coals. The fate of externally added oxygen carrier particles through the reaction process is unknown. The durability of oxides to sustain repeated cycles through oxidation and reduction in presence of solid residues is another area of concern. Issues related to agglomeration of solid particles over the period of time with variation in temperature during reduction and re-oxidation in real reactor situation is also unknown.

The major objective for application of chemical looping technology with Victorian brown coal is to achieve a concentrated stream of CO_2 and H_2. There can be three alternative pathways to achieve this goal. These are:

(i) Ex situ gasification of coal to syngas followed by combustion [23].
(ii) In situ gasification of brown coal, that is, to gasify a mixture of oxygen carrier and coal with CO_2 or H_2O to syngas followed by combustion [15,20] and
(iii) Chemical looping with oxygen uncoupling (CLOU) method [24].

However, investigations pertaining to any of the approaches mentioned above have not been explored with Victorian brown coal. This is a rationale for this study.