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Defluidization of the oxygen carrier ilmenite – Laboratory experiments with potassium salts

Maria Zevenhoven*, Christoffer Sevonius, Patrik Salminen [1], Daniel Lindberg, Anders Brink, Patrik Yrjas, Leena Hupa

Åbo Akademi University, Faculty of Science and Engineering, Piispankatu, 820500 Turku, Finland

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ABSTRACT

Use of biomass in combustion and subsequent CO_2 capture ideally lead to negative CO_2 emissions. New techniques for biomass conversion are Chemical Looping Combustion of Biomass (Bio-CLC) and Oxygen Carrier Aided Combustion (OCAC). In both techniques, the ash-forming elements of biomass, mainly consisting of potassium, calcium, sulfur, phosphorus, and chlorine, may interact with the oxygen carrier bed material, causing agglomeration and defluidization, and thus inhibit the oxidation/reduction reactions. The detailed mechanisms behind this effect are not properly understood. Ilmenite, an iron-titanium mineral, is used as an oxygen carrier in both CLC and OCAC.

In this study, the interactions between ilmenite and potassium compounds, typical for biomass ashes, were studied. Mixtures of ilmenite with different potassium compounds were thermally treated in a crucible in an oxidizing environment at 850 and 950 °C. These conditions are relevant for OCAC and in the parts of CLC where oxidation of the oxygen carrier takes place. The interactions between potassium compounds, KCl, KH_2PO_4, K_2CO_3 and K_2SO_4 and the carrier material, were studied using DTA-TGA, XRD, and SEM-EDS. Thermodynamic equilibrium calculations were carried out to verify the reactions.

Results from the crucible tests were used to explain the behavior of ilmenite in the presence of potassium salts in a lab-scale fluidized bed conversion. The bed agglomeration mechanisms depend on the potassium salt: KCl glued the particles together, whereas K_2CO_3 reacted with the bed particles. KH_2PO_4 reacted with the bed material and glued the particles together. K_2SO_4 remained non-reactive and did not influence the agglomeration of ilmenite bed particles.

1. Introduction

In the Nordic countries, an abundance of wood-derived fuels is available that can be used for energy conversion in a sustainable way. Commonly, biomass fuels are considered being nearly CO_2 neutral. If combined with CO_2 capture, energy conversion using biomass may even reduce CO_2 in the atmosphere referred to as negative CO_2 emissions, so-called Bio-energy with carbon capture and storage (BECCS) [1].

Biomass fuels are often fired in fluidized beds (FB's) that provide good heat transfer and flexibility. However, fluidized bed combustion of biomass also has drawbacks, such as bed agglomeration leading to defluidization [2] and a low efficiency if good mixing in the bed is not achieved. Although the fluidizing air mixes the bed material and fuel, oxygen transfer between the gas phase and fuel can often be improved [3].

Recently, oxygen carriers have been introduced as additional bed materials in fluidized bed combustion, so-called oxygen carrier aided combustion (OCAC). These oxygen carriers are well-known bed materials used in chemical looping combustion (CLC) where they are the sole source of oxygen in the fuel conversion. In OCAC, oxygen carriers provide oxygen to the fuel through a series of oxidation and reduction reactions providing oxygen to regions in the FB with slightly sub-stoichiometric conditions. The bed can consist partly of traditional bed material such as sand and an oxygen carrier or be replaced entirely by an oxygen carrier [4–7].

When traditional or alternative bed materials, such as oxygen carriers, are used ash compounds may interact with bed material leading to agglomeration and subsequent defluidization. Ash could even inhibit the oxygen transfer or catalyze other reactions taking

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* Corresponding author.
E-mail address: maria.zevenhoven@abo.fi (M. Zevenhoven).

[1] Currently at Thermo Fisher, Sweden.

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place in the process [8].

In CLC the fuel is converted in such a way that it produces a gas stream rich in CO_2 but low in other gases, thus greatly facilitating CO_2 capture. Instead of air, a solid oxygen carrier provides oxygen to the fuel. The focus of CLC for biomass, currently mainly wood conversion, may be an interesting option facilitating negative CO_2 emissions.

In CLC the combustion set-up uses two separate reactor vessels, an air reactor, and a fuel reactor, often both fluidized beds (Fig. 1). The fluidized bed reactors provide excellent contact between the bed material and gas and enable good heat transfer. In the air-reactor, heat is produced when the oxygen-carrying material is oxidized in air. In the fuel reactor, the fuel is oxidized through reactions with the oxidized bed material, which is consequently reduced. As the bed material consists of redox metal oxides, the shift between the different oxidation states of the metals enables the transport of oxygen between the two reactors (Reaction 1).

$$2Me_XO_{y-1}(s) + O_2(g) \rightleftarrows 2Me_XO_y(s) \qquad (1)$$

Due to the exothermic reaction associated with the oxidation of the metal from a lower oxidation state to a higher state, heat is released into the air reactor. The temperature in the air reactor in CLC is in the range of 850–1000 °C. Since the flue gas from the air-reactor consists of oxygen-depleted air only, high steam temperatures can be reached.

In the fuel-reactor, the hot oxygen carrier is reduced by gaseous fuel components. If a solid fuel is used, the fuel is pyrolyzed, and the formed pyrolysis gases react with the bed material. Steam can be used as a fluidizing agent in the fuel reactor. The char produced in the pyrolysis process is gasified by the fluidizing media. CO and H_2 produced in the gasification process can then react with the bed material to CO_2 and H_2O. In the fuel reactor, the temperature is slightly lower than in the air reactor. The high temperature ($\approx 950\,°C$) in the air reactor is caused by the exothermic oxidation of the oxygen carrier in air, whereas endothermic reactions cause the lower temperature in the fuel reactor ($\approx 850\,°C$). In contrast to traditional combustion, the produced CO_2- rich flue gas is not diluted with N_2, This CO_2- rich stream facilitates carbon capture and storage without active separation of flue gas components.

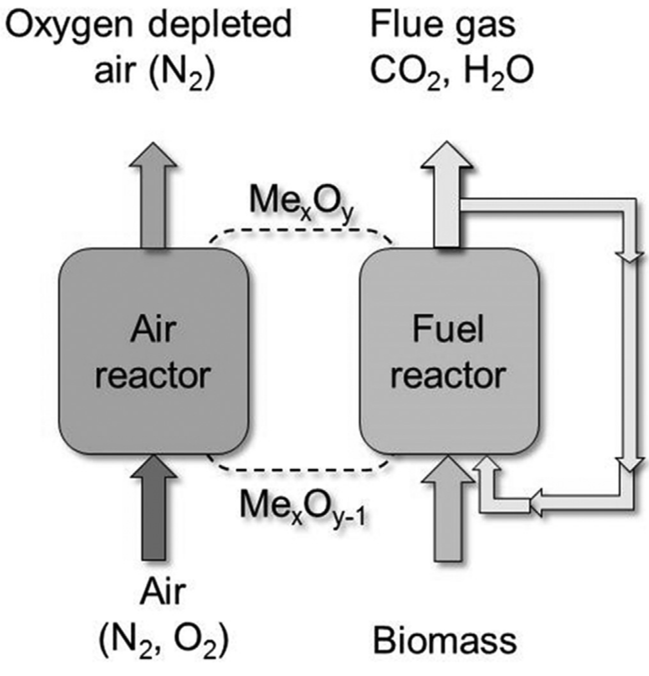

Fig. 1. Principle of CLC.

The general concept of CLC was patented by Lewis and Gilliland [9] in 1954 and reintroduced as a possible way to mitigate CO_2 emissions by Ishida and Jin [10] some 40 years later. The process was demonstrated by Lyngfelt and Thunman [11] in sustained operation in a 10 kW prototype unit for gaseous fuel. Until today hundreds of different oxygen carrier materials have been tested and the technique has been successfully demonstrated in chemical-looping combustors in the size range of 0.3–50 kW. The practical use of oxygen carriers based on iron oxides, manganese oxides, and nickel oxides, as well as natural minerals, such as ilmenite, and combined oxides, such as $CaMnO_3$, for conversion of both solid and liquid fuels, was demonstrated [12–16].

As of 2016, CLC has been demonstrated for coal and gas in >24 pilot units during >7500 h of operation. The largest pilot unit operated has a thermal power of 3 MW. Essentially 100% fuel conversion and 100% CO_2 capture could be reached when a manganese-based oxygen carrier was used [17]. More recently biomass fuels are used in CLC. Firstly, biomass chars were used, since chars have similar properties when compared to coal [18,19]. Recently the fuel choice has been extended to wood and wood chars as well [20–23].

Using oxygen carriers in fluidized beds puts specific demands on their properties:

- High reactivity of the bed material with fuel and oxygen, combined with the ability to convert the fuel fully to CO_2 and H_2O is needed;
- Low fragmentation and attrition, as well as a low tendency for agglomeration, is preferred;
- Low production costs and an environmentally friendly material is preferred as well.

Oxygen carriers may also be present on supporting materials. For example, a natural ore may contain a non-reactive compound that helps maintain the structure of the particles and increases the porosity and activity of the oxygen carrier [12]. Whereas pure chemicals have high reactivity, their high price makes them less suited for solid fuels. When compared to gaseous fuels, solid fuels contain ash-forming matter that may deposit on the oxygen carrier affecting its activity. Therefore, low-cost materials with sufficient reactivity towards H_2 and CO are of interest for solid fuels used in CLC and OCAC. An example of such an oxygen carrier is the natural mineral ilmenite. Leion et al. [24] found that ilmenite is an inexpensive and attractive oxygen carrier material. Ilmenite is a mineral consisting of iron and titanium oxides, FeO and TiO_2. It is the most abundant of all titanium minerals and mined in large quantities. These factors make ilmenite a low-cost material. According to Leion et al. [24], the intermediate species between the oxidized and reduced form are Fe_2O_3 and $Fe_2O_3 \cdot TiO_2$.

In a quartz bed, alkali metal and alkaline earth metal compounds are usually involved in agglomeration [25]. These compounds are the main ash forming matter in wood. In the Nordic countries, wood is the most abundant fuel available for energy conversion, besides municipal waste and agricultural residues. Fig. 2 shows the average composition of the main ash-forming elements in wood, agricultural residues, and algae. The data was based on fuel analyses of 21 different kinds of wood, 30 different kinds of agricultural residues and five algae taken from the Åbo Akademi University Chemical fractionation database. The ash forming matter of wood mainly consists of potassium, calcium and low amounts of sulfur and chlorine, while its silicon content is low. The ash forming matter of biomass mainly consists of potassium,