Fuel 232 (2018) 693–703

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

# Oxygen release from manganese ores relevant for chemical looping with oxygen uncoupling conditions

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ARTICLE INFO

*Keywords:*
Manganese ore
Chemical looping
Oxygen release
Char
Solid fuel

ABSTRACT

The use of manganese ore as oxygen carrier has recently gained interest, primarily due to the combination of low cost and moderate to high reactivity. The possibility of an oxygen uncoupling reaction enhancing reactivity may be an additional advantage. In this paper, six manganese ores (Gloria, Tshipi, Gui Zhou, Metmin, Sibelco Calcined and SinAus) were evaluated with respect to their ability to release oxygen with a devolatilized wood fuel (char) using a small batch fluidized bed reactor. The char was used in order to establish the rate of the oxygen release i.e. oxygen uncoupling. The manganese ore samples were heat treated for 24 h at 950 °C and sieved to a size fraction of 125–180 µm prior to experiments. The oxygen release was evaluated at four temperatures (850, 900, 950 and 1000 °C). Moreover, comparisons were made with the reactivity of these ores with gaseous fuels made in previous works. All six investigated ores showed a small $O_2$ release (CLOU effect), which increased with temperature. Still, the oxygen uncoupling effect is likely not the dominating reaction when using gaseous fuels, as the overall oxygen transfer via CLOU is considerably smaller compared to the oxygen transfer when gaseous components react directly with the particle. For example, at 1000 °C the Gloria ore had the highest mass-based reduction rate, dω/dt, was 0.047 wt%/s for methane and 0.36 wt%/s for syngas, which should be compared with the much lower dω/dt of 0.0073 wt%/s for char, which is a measure of the CLOU effect. The best performing ores were Gloria and Tshipi, which showed the highest uncoupling capacity and rate of oxygen release. It is interesting to note that these two ores had significantly higher Ca and Mg fractions compared to the other four ores with lower reactivity. This suggests that combined Mn-Ca phases may be active for the oxygen release reaction. The ores were analyzed with XRD and SEM-EDX to establish which phases were present in the ores. It was found that the bulk of the ores are very heterogeneous, while the individual particles are much more homogeneous in composition.

## 1. Introduction

Metal oxide systems evaluated for use as oxygen carriers in chemical looping combustion are normally based on oxides from the metals Fe, Cu, Ni and Mn [1,2] and most of the research done has focused on the use of the first three of these metal oxides. However in recent years Mn based oxides, pure or combined with other oxides, have gained a lot of attention as potential oxygen carriers [3–26]. Combined manganese oxides are mainly of interest because of their potential ability to release gaseous oxygen by chemical-looping with oxygen uncoupling (CLOU) [3]. Pure manganese oxides are thermodynamically capable of releasing oxygen to the gas phase and the fuel is thus partially or totally converted by normal combustion [4]. This is show in Reactions (1) and (2).

$$3\ Mn_2O_3 =>2\ Mn_3O_4 + 1/2\ O2 \qquad \text{(reaction 1)}$$

$$CxHy + (\ x+\ y/2)\ O_2 => y/2\ H_2\ O+\ x\ CO_2 \qquad \text{(reaction 2)}$$

But the re-oxidation of the $Mn_3O_4$ (Reaction (3)) requires a temperature below around 800 °C in 5% $O_2$, and at these low temperatures the rate of reaction is too low for practical use [4,5].

$$2\ Mn_3O_4 + 1/2\ O_2 => 3\ Mn)2O_3 \qquad \text{(reaction 3)}$$

Thus, chemical-looping combustion with manganese oxide uses a system of lower oxidation state, i.e. $Mn_3O_4$/MnO, which does not involve any oxygen release, Reactions (4) and (5).

$$CxHy + 2(\ x+\ y/2)Mn_3O_4 => xCO_2 + (y/2)H_2\ O+\ 3(2\ x+\ y)Mn_2O_3 \qquad \text{(reaction 4)}$$

$$3MnO + 1/2\ O_2 => Mn_3O_4 \qquad \text{(reaction 5)}$$

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https://doi.org/10.1016/j.fuel.2018.06.024
Received 16 October 2017; Received in revised form 31 May 2018; Accepted 6 June 2018

However, the thermodynamics of manganese oxide when combined with other oxides may change to give a higher oxidation state of the manganese oxide. Thus, the ability to both release and re-oxidize becomes possible at higher temperatures. Consequently, these combined manganese oxides attain properties for CLOU, albeit less pronounced as compared to the more simple monometallic systems. In a real process these combined manganese materials can be expected to use a combination of the normal CLC, i.e. direct reaction with fuel, and CLOU, i.e. oxygen release. Thus, the more or less pronounced property of CLOU may enhance the use of the materials in a normal CLC system [6]. Both synthetic and natural ore based manganese materials have been studied as oxygen carriers for use with different fuels. Mattisson et al. has recently presented an overview of the combined manganese oxide systems which have been investigated in the literature [7]. Here, also some new binary and ternary systems were explored. Manganese ore contains a number of elements forming different manganese oxide systems that are capable of $O_2$ release. Some of these systems have been investigated separately. Extensive investigations have been done with respect to the Fe-Mn system, including investigations of the effect of composition, fuel and support [8–11]. In the Fe-Mn system Fe partly substitutes some of the Mn which increases the temperature where re-oxidation is possible. Excellent CLOU properties have been attained in laboratory with pure Mn-Fe oxides, with release of almost all oxygen in 30 s. However, these materials showed low physical stability and when tested in continuous operation turned into dust in a few hours,[3]. Adding Ca to Mn is interesting since this results in a perovskite $CaMnO_3$ with very prominent uncoupling properties [12–16,27]. $CaMnO_3$ has been investigated with gaseous fuels in both a laboratory scale 300 W CLC unit [17], a 500 W unit [28], two 10 kW units [18,29,30] as well as in two other units of 120 kW [31] and 1 MW [32,33], as well as with liquid fuel [34].

In the operation in these different units complete gas conversion has been possible to attain in some cases, although with some slight excess of oxygen. Also low loss of fines have been shown, suggesting lifetimes of up to thousands of hours. Further, improved conversion has been found when used with solid fuels in another 10 kW unit, albeit the material shows difficulties with sulphur-containing fuels [35,36].

Other combined oxides studied include the Mn-Si [19] and Mn-Mg combinations [20], the latter comprehensively investigated by Jing et al. [21]. Furthermore, ternary manganese oxide systems have been studied, thus Frick et al. investigated oxygen carriers based on Mn-Si-Ti [22] and Arjmand et al. studied the Mn-Fe-Si system [23]. Hanning (former Källén) et al. studied the following synthetic materials including silica: Mn-Si [24], Mn-Fe-Si [25], and Mn-Si-Ti [26] in a 300 W laboratory scale CLC system. Most stable of these materials was silica with addition of Ti, which was subsequently also used with solid fuels in a 10 kW unit [35,36].

While synthetic particles are reactive, they may also be expensive to produce, which requires longer lifetimes and smaller losses in operation to be economically attractive. One option to reduce costs is to use low cost materials based on Mn, such as manganese ores or waste products [3]. Manganese ores may present opportunities with respect to possible CLOU behavior, as they often contain many of the metals/metal oxides which can enhance this uncoupling effect.

Natural manganese minerals are likely a more cost viable option compared to the expensive manufactured particles, especially when using solid fuels where losses of carrier is expected during ash separation. Research with these types of materials include screening studies of manganese ores in batch fluidized reactors [37–40], with the ambition to evaluate both reactivity and the CLOU effect. Most of the studies have used gaseous fuel although there has been some research on solid fuel conversion, as well as the catalytic effect of alkali metals in the ore on the char gasification reaction [41,42]. Ksepko et al. studied the redox reactions of manganese ore in a TGA using 10–25 vol.% $CH_4$ as the reducing agent between 750 and 950 °C [43]. Manganese ores have also been investigated in continuous operation, including tests in a 300 W reactor [3] and with solid fuels in two 10 kW CLC reactors [44–47] and with biomass in a 20 kW unit [48].

In these works, manganese ores were evaluated during continuous operation, and the effect on the gas conversion, carbon capture efficiency and lifetime of the oxygen carrier were evaluated. It was found that manganese ores could be used successfully in continuous operation generally had better performance as compared to ilmenite, albeit with higher attrition. In a few cases ores formed agglomerates and were discarded as potential oxygen carriers, but those that did not form agglomerates, had lifetimes of up to 284 h based on production of fines [44]. Linderholm et al. investigated a sintered manganese ore in operation in a 100 kW unit [49], as well as ilmenite mixed with manganese ore. The manganese ore content was up to 8 wt% of the bed in these experiment and it was seen that there was a significant increase in gas conversion as manganese ores were mixed in with the ilmenite [50]. Manganese ores have also been modified with copper attempting to enhance the reactivity of the oxygen carrier as shown in operation in a 1 kW unit, [51].

In summary, manganese based oxygen carriers have been studied with regards to their composition, as both natural and synthetic particles. A range of materials have been evaluated in units of different sizes. Most work has been done on synthetic materials prepared in the laboratory, although there is some work which has been done on manganese ores, as described above. From these experiments it has been seen that manganese based oxygen carriers can have significant oxygen release and high $CO_2$ yield from $CH_4$ and CO. The Mn-ores studied in this work have similar price and possibly also similar lifetime as other ores such as ilmenite [52]. It also has been shown that the manganese ores are more reactive than ilmenite [39]. They have CLOU properties, but with significantly less $O_2$ release than highly reactive CLOU materials like CuO [4]. On the other hand they are by far less costly as compared to CuO.

In this work, the reactivity of six manganese ores was evaluated as oxygen carriers for CLOU with wood char at four temperatures to determine the oxygen release rate. It has previously been shown that it is possible for naturally occurring manganese ores to release minor amounts of oxygen to the gas phase. This is because of presence of various metals together with which Mn may form combined Mn-oxide systems as discussed above. It has also been shown that oxygen is released much faster when char is added to a bed of oxygen carriers with uncoupling properties. This is because the char removes the oxygen that effectively hinders the decomposition and has been investigated using a range of synthetic oxygen carrier materials [10,14]. The effect is due to the rapid removal of oxygen from the bulk gas phase by the char, which enhances the driving force for oxygen release from the carrier. Up until now, there has been no study of the rate of oxygen release from manganese ores at fluidized bed conditions, and thus the aim of this investigation is to obtain more information regarding this reaction pathway using a series of promising ores.

## 2. Experimental

Manganese ores were selected for testing based on the results from two previous studies [38,39].

### 2.1. Material

From the previously tested ores a total of six ores were selected [38,39]. Gui Zhou and Metmin were selected because they had the highest oxygen release in an inert atmosphere. Gloria and Tshipi were selected because they achieved the highest $CO_2$ yield with methane and syngas. The last two ores Sibelco Calcined and SinAus were included because they had been used in large units, one in 100 kW CLC unit and the other in a 12 MW boiler. These two had also been pretreated by calcination, i.e. before reaching Chalmers. Before the experiments, pretreatment of all the manganese ores was conducted by calcination in a box furnace for 24 h at 950 °C in air. This was done to remove