Manganese minerals as oxygen carriers for chemical looping combustion of coal

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Abstract

In this paper, four different manganese minerals were tested in a batch fluidized bed reactor to evaluate their performance in the Chemical Looping Combustion (CLC) of solid fuels. The char gasification rate in the experiments with the manganese minerals tested was higher than the corresponding values for ilmenite and iron ore, which were taken as benchmark materials. This phenomenon was attributed to the deposition of K, Na and Ca from the manganese minerals on char particles so that they catalysed char gasification. The char gasification rate observed using manganese minerals decreased with the number of cycles until a stable value was reached. Under these conditions, one of the materials presented higher char gasification rates than those observed for benchmark materials even when most of the K was already released. An estimation of the CO$_2$ capture efficiency in a continuous unit using one of the selected manganese minerals showed that around 99% CO$_2$ capture efficiency could be reached at 1000 ºC with a solid inventory in the fuel reactor as low as 300 kg/MW$_{th}$ if an efficient carbon stripper was present.

Keywords: CO$_2$ capture; chemical looping; combustion; coal; manganese mineral
1. Introduction

Chemical Looping Combustion (CLC) technology is one of the carbon dioxide capture technologies with lower cost and energy penalties associated. Thus, research on the different aspects of this technology has received significant attention during the last years.

In CLC, combustion takes place without any contact between air and fuel. The oxygen required for combustion is supplied by a solid oxygen carrier which takes oxygen from air in the air reactor and then transfers it to the fuel in the fuel reactor, according to what is shown in Figure 1. This allows for a concentrated CO\textsubscript{2}-stream at the outlet of the fuel reactor, which facilitates CO\textsubscript{2} capture. Therefore, the search for an oxygen carrier reactive enough and with good mechanical properties, with low attrition and absence of agglomeration to withstand the successive redox cycles in the Chemical Looping system has turned into one of the main priorities for the scale up of this technology.

Materials based on oxides from different transition metals such as nickel, copper, cobalt, iron or manganese have been investigated and tested at different scales during last years. In the case of the combustion of a solid fuel, it is especially valuable that the oxygen carrier used in CLC was a low-cost material since part of the oxygen carrier can be lost during operation. As it can be seen in Figure 1, when a solid fuel (mainly coal) is combusted in a CLC system the ash generated should be periodically drained to avoid its accumulation. In the drainage process, part of the oxygen carrier can be lost together with the ashes. Thus, it would be desirable that the oxygen carrier was as cheap as possible.

Many works have been published in the last years following the objective of finding low-cost oxygen carriers. Most of them have been dedicated to iron-based materials from
different origins. Among the minerals, ilmenite, an iron titanate, has been intensively used in pilot units from 0.5 kW\textsubscript{th} to 1 MW\textsubscript{th} burning coal\textsuperscript{2-8}. Other authors evaluated different iron ores\textsuperscript{9-11} and also industrial residues\textsuperscript{12}.

According to recent literature studies, some manganese minerals have shown higher reactivity than ilmenite. A Brazilian manganese mineral was used as oxygen carrier in a 10 kW\textsubscript{th} unit with petcoke as fuel and the results showed that the char gasification rate was four times that obtained under similar conditions with ilmenite\textsuperscript{4}. The increase in the char gasification rate resulted in an increase of the CO\textsubscript{2} capture efficiency from around 70\% with ilmenite to 98\% with the Brazilian manganese mineral. The value of oxygen demand also decreased to a value of 10\% with this manganese mineral. Nevertheless, a high fine-production rate (1.6 \%/h) compared to ilmenite was observed for the Brazilian manganese mineral. Considering these results, different manganese minerals were selected and evaluated as oxygen carriers in a laboratory-scale fluidized-bed reactor in the temperature range 900-970\degree\textsuperscript{C}\textsuperscript{13}. Six manganese minerals from different origins (including the previously mentioned Brazilian mineral) were tested and all of them exhibited higher rates of char gasification than ilmenite. Several possible explanations were argued. The first explanation would point to a certain oxygen uncoupling effect in the material, i.e. a release of oxygen from the manganese mineral due to the transformation Mn\textsubscript{2}O\textsubscript{3} to Mn\textsubscript{3}O\textsubscript{4}, which would favour char combustion. The second explanation would correspond to the decreased importance of H\textsubscript{2} inhibition in char gasification due to a higher reactivity of the manganese minerals to the gases produced in char gasification (H\textsubscript{2} and CO) when compared to ilmenite. However, the experimental evidence presented by Arjmand et al.\textsuperscript{13} led to the conclusion that neither of the previous explanations was the determining mechanism behind
the higher rate of char gasification observed with the manganese minerals compared to ilmenite. A third explanation was then presented and discussed. These authors propose that manganese minerals have a catalytic effect on the char gasification. Carbonates, oxides and hydroxides of potassium and sodium present in different quantities in all the manganese minerals analysed have melting and boiling temperatures close to the temperature in the fluidized bed. A possible reaction mechanism would assume that these K and/or Na containing compounds were released in the gas phase and then bound to the surface of the char. The authors supported this mechanism based on the uniform distribution of K and Na elements found on the surface of partially gasified petcoke particles extracted from the fluidized bed when the manganese minerals with the highest amount of potassium and sodium were used. Moreover, these two samples had shown the highest rate of char gasification.

Considering all this, manganese minerals exhibit a great potential to be considered as oxygen carriers in CLC processes using solid fuels. Nevertheless, the extent of the effect of their presence on the char gasification rate should be analyzed as a function of the redox cycle number in order to consider their use in a continuous unit. In line with this, the objective of the present work is to further investigate the enhancement of the char gasification rate when manganese minerals are used as oxygen carriers and compare this behaviour with the performance of selected iron-based oxygen carriers taken as reference. The manganese minerals were selected considering they showed similar, or even higher, reactivity and even lower attrition rate values than those showed for a Brazilian Mn-ore taken as a reference Mn-based material 14.
2. Experimental

2.1 Manganese minerals and solid fuel used

Four different manganese minerals were tested in this work. The reactivity of these materials to the main gases involved in combustion processes (H$_2$, CO and CH$_4$) was already studied and presented in a previous publication from the authors$^{14}$. The same identification of the manganese samples used in this previous work will be used in the present work. The manganese minerals were named according to their origin as MnSA from South Africa (SA); MnGBHNE and MnGBMPB from Gabon (GB) together with the abbreviated name of the supplier, i.e. Hidro Nitro Española S.A. (HNE) and Mario Pilato Blatt S.A. (MPB); and finally, MnBR from Brazil (BR). Details about the treatment of the manganese minerals before being used in CLC experiments as well as the characterization of these materials can be found elsewhere$^{14}$. Here, Table 1 is included summarizing the main chemical and physical properties of all the manganese minerals used. In addition to the four manganese minerals, activated ilmenite and iron ore previously used in other works from the authors were also used here as benchmark materials for comparison purposes$^{6,9}$. The particle size of the oxygen carrier materials was in the range 100-300 µm in all the cases.

Char from South African bituminous coal was used as solid fuel in all the experiments. The use of char as fuel facilitated the evaluation of the influence of the presence of the different manganese minerals on the char gasification rate. Char was obtained from coal particles in the size range 200-300 µm. The procedure followed for char preparation from coal and characterization was described elsewhere$^{15}$. 
2.2 Batch fluidized-bed reactor

The manganese materials and reference iron-based materials were tested in a batch fluidized bed reactor adapted for the feeding of solid fuel batches. Figure 2 shows the scheme of the experimental setup used. Details about this set-up and the methodology used in the experiments can be found elsewhere\textsuperscript{15,16}. The bubbling fluidized bed consisted in all the cases of 300 g of the corresponding oxygen carrier. Steam was used as gasifying agent and fluidization medium during the reduction period and it was fed at the bottom of the fluidized bed. A total flow corresponding to a gas velocity of 0.1 m/s at 900ºC was introduced in the reactor. During the reduction period, 1 g of char was fed inside the bed and gasified. The gasification products reacted with the oxygen carrier particles to produce CO\textsubscript{2} and H\textsubscript{2}O. After a short purge period with nitrogen, the oxygen carrier in the bed was regenerated using a stream consisting of 10% oxygen in nitrogen. During both reduction and oxidation, the gases leaving the reactor were analysed after condensing the steam. Dry concentrations of the gases were determined in a non-dispersive infrared analyser (CO, CO\textsubscript{2} and CH\textsubscript{4}), a thermal gas conductivity analyser (H\textsubscript{2}) and a paramagnetic analyser (O\textsubscript{2}).

2.3 Data evaluation

To evaluate the performance of the different materials, several parameters were calculated from the experimental results. A carbon balance to the gaseous species in the reactor allowed calculating the rate of char conversion, \( r_C(t) \). Methane was not considered as it was never detected.

\[
r_C(t) = (y_{CO_2} + y_{CO}) \cdot F_{out}
\]  (1)
where the total dry basis outlet flow, $F_{out}$, was estimated from a nitrogen flow introduced in the outlet stream of the reactor prior to analysis, $F_{N_2}$:

$$F_{out} = \frac{F_{N_2}}{1 - \sum_i y_i}$$  \hspace{1cm} (2)

In equation (2), $y_i$ is the molar fraction of the component $i$ (CO$_2$, CO or H$_2$) at the outlet stream of the reactor.

Using the rate of char conversion, the value of char conversion at different reaction times, $X_{chars}$ can be calculated:

$$X_{char}(t) = \frac{\int r_C(t) \cdot dt}{N_{C, char}}$$  \hspace{1cm} (3)

where $N_{C, char}$ is the moles of carbon fed into the reactor.

The instantaneous rate of char conversion, $r_{C, inst}$, is defined as the rate of gasification referred to the amount of non-gasified carbon in the reactor.

$$r_{C, inst}(t) = \frac{r_C(t)}{N_{C, char} \cdot (1 - X_{char})}$$  \hspace{1cm} (4)

The oxygen balance to the gaseous species allowed to calculate the rate of oxygen transferred from the oxygen carrier to the gasification products, $r_O(t)$:

$$r_O(t) = F_{O, out} - F_{O, in} = F_{out} \cdot (2y_{CO_2} + y_{CO}) + F_{H_2O, out} - F_{H_2O, in}$$  \hspace{1cm} (5)

To calculate the flow of water at the reactor ($F_{H_2O, out}$) exit it was assumed that the flow of hydrogen either in H$_2$ or H$_2$O came only from the introduced steam:

$$F_{H_2O, out} = F_{H_2O, in} - F_{out} \cdot y_{H_2}$$  \hspace{1cm} (6)

Including equation (6) in equation (5), the rate of oxygen transferred is:
\( r_O(t) = F_{out} \cdot (2y_{CO_2} + y_{CO} - y_{H_2}) \) \hspace{1cm} (7)

Then the oxygen carrier conversion can be calculated from the integration of equation (7) with time as:

\[ X_O(t) = 1 - \frac{1}{N_{O,OC}} \int_0^t r_O(t) \cdot dt \] \hspace{1cm} (8)

where \( N_{O,OC} \) are the moles of oxygen in the oxygen carrier:

\[ N_{O,OC} = \frac{m_{OC} \cdot R_{OC}}{M_O} \] \hspace{1cm} (9)

where \( m_{OC} \) is the mass of oxygen carrier and \( M_O \) is the oxygen atomic mass.

3. Results and Discussion

3.1 Char combustion experiments

Several cycles of char combustion under CLC conditions using the four manganese minerals tested in this work were carried out at 950°C. Figure 3 shows the results using MnGBHNE as bed material as representative of a typical cycle. The char fed was gasified to CO and H\(_2\) after contacting with steam in the reactor. Afterwards, these gasification products reacted with the manganese mineral to produce CO\(_2\) and H\(_2\)O. In a previous study from the authors, the four manganese minerals used in the present work showed high reactivity to H\(_2\) and CO, thus no or small amount of CO and/or H\(_2\) were expected at the outlet of the reactor using char as fuel. As it can be seen in Figure 3, all H\(_2\) and most of CO were oxidized to H\(_2\)O and CO\(_2\), respectively, by MnGBHNE reaching a maximum dry concentration of CO\(_2\) of 13%. Figure 3 also shows both the char and oxygen carrier
conversion evolution with time during the reduction period. The combustion of gasification products consumed the oxygen in the manganese mineral, thus a decrease in the oxygen carrier conversion \(X_O\) was observed. After the purge with 100% \(N_2\), the manganese mineral was rapidly regenerated by oxidation with 10% \(O_2\) and increase in \(X_O\) with time was observed. It should be noted that no \(CO_2\) and/or \(CO\) were registered during the oxidation process, which suggested the complete char gasification during the reduction period, in accordance with the value of \(X_{char}=1\) reached at the end of reduction in Figure 3.

For the other three manganese minerals, i.e. MnSA, MnGBMPB and MnBR, similar behavior was observed.

### 3.2 Evaluation of the char gasification rate with different manganese ores

Figure 4 presents the instantaneous rate of char gasification \(r_{C,inst}\) in the first reduction period as a function of char conversion \(X_{char}\) for the four manganese minerals at 950ºC. The values in Figure 4 are compared with those obtained under similar conditions with activated ilmenite and iron ore previously used by the authors \(^6,9\). These two iron-based oxygen carriers showed good performance in continuous CLC operation with coal and this is the reason why they are here considered as reference for comparison. In order to facilitate the comparison, a stable stage corresponding to \(X_{char}=0.4-0.8\) was considered. According to the results in Figure 4, the rate of char gasification in the presence of the manganese minerals MnSA, MnGBHNE, MnGBMPB and MnBR was much faster than in the presence of ilmenite and iron ore. Actually, the values of \(r_{C,inst}\) using ilmenite and iron ore are around 20%/min, approximately half of the average value obtained using manganese minerals.
The higher rate of char gasification in the presence of manganese minerals could be ascribed to the following factors: (i) oxygen uncoupling effect; (ii) reactivity of the manganese mineral to \( \text{H}_2 \); (iii) solid-solid reaction between oxygen carrier and fuel; and/or (iv) catalytic effect of the manganese mineral on the char gasification. In the following sections each of these factors will be analyzed and discussed.

3.2.1 Oxygen uncoupling effect

In the present work, the char feeding to the bubbling fluidized bed was carried out after the bed was purged in nitrogen, so that most of the gaseous oxygen released was already lost during that period. Therefore, it seems that the release of oxygen from the manganese materials cannot be considered as an explanation for the high char gasification rate observed. This fact confirms the behavior observed in a previous work \(^{14}\), where the ability of these four manganese materials to release gaseous oxygen under successive redox cycles was evaluated in detail. In this previous study, the possible oxygen uncoupling effect was studied in a thermogravimetric analyzer and a fluidized bed reactor. The oxygen release only occurred in the first exposure to \( \text{N}_2 \) and then disappeared as \( \text{Mn}_3\text{O}_4 \) was not oxidized back to \( \text{Mn}_2\text{O}_3 \). Note that oxygen uncoupling capability was only available when \( \text{Mn}_2\text{O}_3 \) is reduced to \( \text{Mn}_3\text{O}_4 \) \(^{17}\).

3.2.2 Reactivity of the manganese minerals to \( \text{H}_2 \)

According to our previous tests with gaseous fuels (\( \text{H}_2 \), CO and \( \text{CH}_4 \)), the reactivity of these manganese minerals to \( \text{H}_2 \) was higher than that observed for ilmenite under the same conditions in a batch fluidized bed \(^{14}\). The rate index in the reaction with \( \text{H}_2 \) at \( 950^\circ \text{C} \) calculated for the manganese minerals was in the range 1.5-2.0 \%/min while the rate index
calculated for ilmenite was around 1.5 \% / \text{min}. Nevertheless, the \text{H}_2 concentration observed in all the present experiments was close to zero due to the high oxygen carrier to char ratio used. Therefore, high gas conversion was observed in all cases, and low inhibitory effect of \text{H}_2 on the gasification rate is expected regardless the oxygen carrier used. However, the char gasification rate observed in Figure 4 for any of the manganese minerals was at least 1.5 times that for ilmenite and iron ore, which was unexpected considering the \text{H}_2 inhibition effect. According to our results, the decrease in the \text{H}_2 inhibition in the presence of manganese materials cannot be considered the main mechanism to justify the rapid gasification observed. These results are in line to those reported in the investigations of Arjmand et al. \textsuperscript{13}.

3.2.3 Solid-solid reaction between manganese minerals and fuel

Another possible explanation to the higher char gasification rate in the presence of manganese minerals would come from a contribution to the total char consumption rate of the solid-solid reaction between the oxygen carrier and the char. However, clear indications of the slow rate of this solid-solid reaction in a fluidized bed reactor were already discussed in literature \textsuperscript{18}. More indeed, the present work also tested the solid-solid reaction between manganese minerals and char in nitrogen at 950\degree C. No combustion products were observed at the outlet of the reactor. According to the carbon balances performed, all the char introduced was already burned when 10\% oxygen was introduced during the oxidation period. Therefore, solid-solid reaction between manganese mineral particles and fuel cannot illustrate the fast char conversion observed.
3.2.4 Catalytic effect of the manganese mineral on the char gasification

It is a known fact already reported in literature that alkali metal elements K and Na have positive effects on the gasification of graphite and char\textsuperscript{19,20}. In addition to K and Na, Ca could also be considered as a catalyst for graphite gasification, although lower catalytic effects than K and Na were observed\textsuperscript{21}. Regarding the CLC process, the enhancement on char gasification by the presence of K and Na in Mn-ores was demonstrated by Arjmand et al.\textsuperscript{13} using six manganese minerals. They observed that the instantaneous rate of char gasification increased with higher contents of K and/or Na in the manganese minerals and proposed that these elements were transferred to the gas phase under the reaction conditions used and then deposited on the char surface.

Table 1 shows that the manganese minerals used in the present work also possess certain amounts of Na (MnSA), K (MnGBHNE, MnGBMPB and MnBR) and Ca in their composition. Therefore, the previously observed catalytic effect of K and/or Na from the manganese minerals on the char gasification rate can also be present in the results obtained in the current work. This possibility is further analyzed next.

In order to evaluate the possible catalytic effect of the Na, K and Ca in the manganese minerals on char gasification several cycles of char combustion with the four manganese minerals were performed in the fluidized bed reactor. It was found that the rate of char gasification decreased with the number of cycles for all these minerals. However, only results corresponding to MnSA and MnGBHNE will be shown in this analysis, as they were the materials with the lowest attrition rates and higher crushing strength after the
reactivity experiments with gases in the batch fluidized bed. This makes these materials more promising for further use than the MnGBMPB and MnBR minerals.

Figure 5 plots the values of the instantaneous char gasification rate \( r_{C,\text{inst}} \) as a function of \( X_{\text{char}} \) for MnGBHNE and MnSA during successive redox cycles and compares these values with those corresponding to the activated ilmenite and iron ore taken as reference. The values of char gasification rate decreased with the number of cycles and then became stable, both for MnGBHNE and MnSA. These stable values of the char gasification rate were achieved after 9th and 11th cycles for MnGBHNE and MnSA, respectively. Once the stable rate values were reached, MnGBHNE exhibited much higher char gasification rate than the iron ore and ilmenite, whereas MnSA showed similar values to those obtained with the iron-based reference materials. In order to clarify the different behavior observed for the MnSA and MnGBHNE materials, samples were extracted for different redox cycles to examine the evolution of K, Na and also Ca contents in the oxygen carrier for different reduction times using the EDX technique. The reason to include Ca in the analysis is that this metal can also act as a catalyst for char gasification and according to Table 1, the content of Ca in the MnSA sample is high. Figure 6 shows the results obtained in the SEM-EDX analysis to the MnGBHNE mineral. This material showed relevant K and Ca content. In this case, potassium was only detected in the beginning of tests and the intensity of the K pattern decreased with the number of redox cycles to become negligible at the end of the tests. In Figure 6 (A), it can be observed that the distribution of K is homogenous inside the calcined particle. However, after the use in the batch fluidized bed, potassium has almost completely disappeared from the manganese mineral, see Figure 6 (B). In the case of MnSA, Na was initially detected in particles, but no Na could be detected after the redox
cycles. It is assumed that all Na was released from the manganese mineral after the redox cycles were performed. In this case, only Ca was detected in the MnSA particles, although the intensity of the Ca pattern in the MnSA material also decreased with the number of redox cycles. The decrease of K, Na and Ca intensity indicates the lower contents of these elements in the used MnGBHNE and MnSA, respectively, which can contribute to explain the decrease in the char gasification rates with the number of cycles. Nevertheless, it should be pointed out that the stable rates of char gasification with MnGBHNE are higher than those observed for MnSA after similar number of cycles in Figure 5. This observation might be attributable to the fact that K has higher mobility than Ca during coal gasification which resulted in an easier and faster distribution of K on the basal plane of char than Ca\textsuperscript{21}. Therefore, although the amount of Ca in the MnSA mineral is larger than the amount of K in MnGBHNE, K results a more effective catalyst for char gasification once it reaches the char particles. This mechanism can contribute to explain the fact that MnGBHNE exhibited higher char gasification rates than MnSA.

Another fact that is interesting for future investigations is that after the loss of most of K in the MnGBHNE mineral, it presented higher char gasification rates than the reference materials (ilmenite and iron ore). An additional test was performed in order to corroborate the catalytic effect of the MnGBHNE material on char gasification even when the major part of the K present is lost. After being used in 18\textsuperscript{th} successive redox cycles, the MnGBHNE sample was completely reduced at 950ºC to MnO using a gaseous stream composed of 30% H\textsubscript{2} in nitrogen. With the bed completely reduced, no oxygen uncoupling effect, or contribution of the oxygen carrier to decrease the H\textsubscript{2} inhibition on char gasification was possible. Moreover, this reduced sample has a negligible content of
potassium, as it was shown in Figure 6. Therefore, the rate of char gasification using the
reduced MnGBHNE as bed material should be similar to that obtained using an inert bed,
e.g. sand. Thus, the same experiment was repeated using silica sand as bed material. Both
experiments were performed at 950ºC. Char was fed to a bed of sand or reduced
MnGBHNE and gasified using steam. Figure 7 compares the evolution of char conversion
rate with time in both experiments. As it can be observed in the Figure, the char conversion
rate is clearly higher in the presence of the reduced MnGBHNE when compared to a sand
bed. Moreover, the char gasification rate is closer to that observed in the last cycle (18th
cycle) performed with the MnGBHNE. Further research to clarify this behavior of the
MnGBHNE mineral needs to be undertaken.

3.3 Influence of temperature on the char gasification rate

Figure 8 presents the instantaneous rate of char gasification once stable reactivity was
reached as a function of temperature for MnGBHNE, MnSA and the benchmark materials
(ilmenite and iron ore). As expected, the char gasification rate increased with temperature
in all the cases. Little differences in the char gasification rate were observed for MnSA and
the iron-based materials at the different temperatures used. This fact agrees with the fact
that the high gasification rate initially observed for the MnSA mineral decreased with the
number of redox cycles. Nevertheless, the rate of char gasification with MnGBHNE was
approximately 1.5 times that observed for MnSA and the iron-based materials at the
different temperatures tested.
3.4 Analysis of the particles after use in the batch fluidized bed

The four manganese minerals were subjected to several redox cycles in the batch fluidized bed. In total, MnSA was tested during 10 h, MnGBHNE during 20 hours, MnGBMPB during 3 hours and MnBR during 3.5 hours. No problems of fluidization were observed during the whole experimental campaign with any of the materials. Nevertheless, after the experiments performed at the highest temperature tested (1000 ºC) with both the MnSA and MnGBHNE it was observed that particles tended to get stacked forming small agglomerates only visible using a microscope. Figure 9 shows SEM pictures of the particles extracted from the fluidized bed after experiments at 1000 ºC. According to these images, the number of aggregates formed under similar conditions seems to be larger in the MnSA sample than in the MnGBHNE and the size of the aggregates formed is less than 500 µm. It is necessary to note that these aggregates observed from SEM images did not lead to defluidization problems during the whole experimental campaign.

3.5 Estimation of the CO$_2$ capture efficiency for a continuous CLC unit

In order to analyze the potential performance of the MnGBHNE mineral in a continuous CLC system an estimation of the carbon capture efficiency for different solids inventories in the fuel reactor was performed. The methodology to estimate the CO$_2$ capture efficiency was already detailed in a previous publication from the authors$^{22}$. It is based on the char gasification rate determined in this work, and it takes into account for the properties of the oxygen carrier and solid fuel considered.

Figure 10 (A) presents the calculated CO$_2$ capture efficiency, $\eta_{CC}$, as a function of oxygen carrier inventory in the fuel reactor, $m_{FR}$. In this case, a carbon stripper is not considered in
the CLC unit. Char particles no converted in the fuel reactor reach the air reactor, they might be burned there producing CO$_2$ which will be therefore not captured. As a consequence, full CO$_2$ capture would not be reached in the CLC process. According to Figure 10(A), around 8000 kg/MW$_{th}$ of MnGBHNE would be needed to reach 90% CO$_2$ capture efficiency at 900 ºC. However, if the fuel reactor temperature is increased up to 1000 ºC, around 1600 kg/MW$_{th}$ would be enough to reach 95% CO$_2$ capture efficiency.

The use of carbon stripper can effectively decrease the oxygen carrier inventory required to obtain the same carbon capture efficiency, as it is shown in Figure 10(B). As it was shown in Figure 1, a carbon stripper is a unit placed between fuel and air reactors. The function of the carbon stripper is to recover unconverted char particles that might be leaving the fuel reactor. Thus, the char flow entering into the air reactor would be decreased and, hence, the CO$_2$ capture would be increased. Now, a carbon separation efficiency of the carbon stripper equal to $\eta_{CS}$=0.98 was assumed. This is a realistic value considering the carbon separation efficiencies reported in literature for currently operating carbon stripper systems$^{23}$. Under these conditions, an oxygen carrier inventory as low as 300 kg/MW$_{th}$ allows to reach a CO$_2$ capture efficiency of 99% at 1000ºC using the MnGBHNE mineral. Considering all the previous results, the MnGBHNE material has demonstrated to be a potential material to be used as oxygen carrier in CLC with coal.

4. Conclusions

Four manganese minerals (MnSA, MnGBHNE, MnGBMPB and MnBR) were tested in a batch fluidized bed reactor at different temperatures in the range 900-1000 ºC using char
from bituminous coal as fuel in order to evaluate their performance as oxygen carriers for CLC of coal.

Initially, all of the manganese minerals showed values of instantaneous char gasification rate \( (r_{C,\text{inst}}) \) higher than those obtained under the same experimental conditions with iron-based reference materials already used in continuous CLC units (i.e. ilmenite and iron ore). This result was attributed to the presence of K, Na and Ca in the manganese minerals that were released during gasification to the gaseous atmosphere and then bound to the char particles, where they acted as catalysts for char gasification.

The values of char gasification rate obtained with the manganese minerals decreased with the number of redox cycles until they reached a stable value as catalytic elements such as Na and K were lost. In the case of the MnGBHNE material the stable value of char gasification rate was still higher than ilmenite or the iron ore, although in this case most of the K in the manganese mineral had already been released and its catalytic effect on the gasification of char particles would no longer be of relevance.

The effect of temperature on the char gasification rate obtained using MnGBHNE and MnSA minerals was relevant, especially in the case of MnGBHNE. At the different temperatures used, the rate of char gasification with MnGBHNE was approximately 1.5 times that observed for MnSA and the iron-based materials.

Finally, an estimation of the CO\(_2\) capture efficiency that could be reached in a continuous CLC unit using MnGBHNE as oxygen carrier was done. According to the calculations presented, an oxygen carrier inventory of MnGBHNE as low as 300 kg/MW\(_{th}\) would allow to reach a CO\(_2\) capture efficiency of 99% at 1000°C.
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Nomenclature

- \( F_{H_2O, in} \): steam molar flow fed to the reactor (mol/s)
- \( F_{H_2O, out} \): steam molar flow exiting the reactor (mol/s)
- \( F_{N_2} \): nitrogen molar flow introduced before mineral analysis (mol/s)
- \( F_{out} \): total dry flow exiting reactor (mol/s)
- \( F_{O,in} \): oxygen molar flow entering the reactor (mol/s)
- \( F_{O,out} \): oxygen molar flow exiting the reactor (mol/s)
- \( M_O \): oxygen molar weight (kg/mol)
- \( m_{OC} \): mass of oxygen carrier (kg)
- \( N_{c,char} \): moles of carbon fed into the reactor
- \( N_{O,OC} \): moles of oxygen in the oxygen carrier active for CLC process
- \( r_c(t) \): rate of char conversion (mol/s)
- \( r_{c, inst}(t) \): instantaneous rate of char conversion (s\(^{-1}\))
- \( r_o(t) \): rate of oxygen transferred from the oxygen carrier to the fuel gas (mol/s)
- \( R_{OC} \): oxygen transport capacity
- \( X_{char}(t) \): char conversion
- \( X_o(t) \): oxygen carrier conversion
$y_i$: molar fraction of the component $i$ at the outlet of the reactor


List of Figure captions

Figure 1. Scheme of the Chemical Looping Combustion process

Figure 2. Batch fluidized bed reactor setup

Figure 3. Product distribution, as well as char and oxygen carrier conversion with time in experiments with MnGBHNE at 950°C.

Figure 4. Instantaneous rate of char gasification ($r_{\text{C,inst}}$) as a function of char conversion ($X_{\text{char}}$) for the four manganese minerals at 950°C

Figure 5. Instantaneous rate of char gasification ($r_{\text{C,inst}}$) in the reduction period as a function of char conversion ($X_{\text{char}}$) for the four manganese minerals at 950°C after successive redox cycles

Figure 6. EDX mapping of the MnGBHNE showing K distribution inside the solid particle in calcined particles and used particles (after 18th redox cycles)

Figure 7. Char conversion ($X_{\text{char}}$) with time at 950°C and using steam as gasifying agent in the presence of: i) sand ii) reduced MnGBHNE iii) MnGBHNE after 18th redox cycles as bed materials

Figure 8. Influence of temperature on the instantaneous rate of char gasification ($r_{\text{C,inst}}$) for the MnSA and MnGBHNE minerals

Figure 9. SEM pictures of the (A) MnSA and (B) MnGBHNE samples after experiments at 100°C
Figure 10. Estimation of the CO$_2$ capture efficiency for different solid inventories in the fuel reactor at different temperatures in the range 900-1000 ºC using MnGBHNE (A) without and (B) with a carbon stripper system. Fuel: South African bituminous coal.
**Figures**

![Chemical Looping Combustion process diagram]

**Figure 1.** Scheme of the Chemical Looping Combustion process.
Figure 2. Batch fluidized bed reactor setup.
Figure 3. Product distribution, as well as char and oxygen carrier conversion with time in experiments with MnGBHNE at 950°C.
Figure 4. Instantaneous rate of char gasification ($r_{C,\text{inst}}$) in the first reduction period as a function of char conversion ($X_{\text{char}}$) for the four manganese minerals at 950°C.
Figure 5. Instantaneous rate of char gasification ($r_{C, \text{inst}}$) in the reduction period as a function of char conversion ($X_{\text{char}}$) for the four manganese minerals at 950ºC after successive redox cycles.
Figure 6. EDX mapping of the MnGBHNE showing K distribution inside the solid particle in calcined particles and used particles (after 18th redox cycles).
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Tables

Table 1. Composition and physical properties of the manganese minerals

<table>
<thead>
<tr>
<th>Element distribution (wt.%)</th>
<th>MnSA</th>
<th>MnGBHNE</th>
<th>MnGBMPB</th>
<th>MnBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>39.8</td>
<td>46.6</td>
<td>53.0</td>
<td>44.6</td>
</tr>
<tr>
<td>Fe</td>
<td>14.6</td>
<td>5.1</td>
<td>3.6</td>
<td>5.2</td>
</tr>
<tr>
<td>Si</td>
<td>3.3</td>
<td>4.2</td>
<td>1.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Al</td>
<td>0.2</td>
<td>3.8</td>
<td>2.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Ca</td>
<td>5.3</td>
<td>0.9</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Mg</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Na</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>0.8</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>O&lt;sup&gt;a&lt;/sup&gt;</td>
<td>36.2</td>
<td>38.4</td>
<td>37.5</td>
<td>38.9</td>
</tr>
</tbody>
</table>

| Bulk density (kg/m<sup>3</sup>) | 3510 | 2570 | 2900 | 2230 |
| BET surface area (m<sup>2</sup>/g) | 0.6  | 10.1 | 7.4  | 12.2 |
| Porosity (vol.%)               | 12.3 | 35.7 | 30.2 | 47.3 |
| Crushing strength (N)          | 4.6  | 1.8  | 2.4  | 1.0  |
| Oxygen transport capacity (wt.%) | 4.7  | 5.0  | 5.8  | 5.2  |

<sup>a</sup>Oxygen was determined by difference