The Development of a Novel Cu-Mn Oxygen Carrier for the Chemical Looping Gasification of Biomass

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THE DEVELOPMENT OF A NOVEL Cu-Mn OXYGEN CARRIER FOR THE CHEMICAL LOOPING GASIFICATION OF BIOMASS

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ABSTRACT
Circulating fluidized bed technology applied to combustion processes in which oxygen and fuel are fed into separate reactors is referred to as Chemical Looping Combustion. Typically, oxygen reacts with a reduced metal (oxide), then it is transferred to a second vessel where the metal oxide is reduced by a hydrocarbon. In chemical looping gasification, a fuel is contacted indirectly by oxygen and/or steam again with a metal oxide shuttling between two vessels reducing the contact between fuel and air. In this case, a concentrated stream of syngas exits the fuel reactor undiluted by nitrogen. The objective of this study is to develop a solids substrate capable of releasing oxygen in the fuel reactor. A bimetallic Cu-Mn oxygen carrier was synthesized by incipient wetness impregnation at ambient conditions over Al₂O₃. Copper-based oxygen carriers have superior oxygen transfer capacity and environmental and economical characteristics compared to nickel, iron and cobalt, but the operating temperatures are limited due to the low melting point of the metallic copper. Adding manganese to copper minimizes the formation of copper aluminate. Moreover, it inhibits copper agglomeration and carbon deposition. The developed oxygen carriers were characterized by BET, XRD and SEM analyzers. Also, oxygen transfer capacities of particles were tested using thermo gravimetric analysis (TGA). Results indicate that Cu-Mn is a superior carrier, which is suitable for the separation of oxygen in a chemical looping process. Also, adding manganese to copper allows working at high temperatures and improves the reactivity of copper.

INTRODUCTION
Energy-efficient practices are becoming more and more necessary as energy prices continue to rise and the impact of climate change emerges. Institutions that adopt measures to reduce energy and its associated greenhouse gas emissions will obtain financial, environmental, and social benefits. New opportunities for biomass energy are developing as environmental and economic concerns encourage governments, industries, and consumers to explore alternatives to fossil fuels.

Combustion and gasification are two processes, which convert hydrocarbons to energy. Gasification has some advantages over combustion, such as higher efficiency, treating with a lower volume of gas and low emission of toxic gases. Gasification also makes it possible to have synthesis fuels, which can be used for transportation. However, an
oxygen separation unit is needed before each gasification process, which can raise the capital and variable costs of the process. A chemical looping process is a relatively new technology for combustion and gasification processes. Figure 1 shows a schematic of a chemical looping combustion process.

![Chemical looping combustion](image)

Chemical looping combustion consists of two reactors. On the right side is the fuel reactor, where oxygen from a metal oxide ($M_yO_x$) reacts with fuel according to the following reaction:

$$(2n+m)M_yO_x + C_nH_{2m} \rightarrow (2n+m) M_yO_{x-1} + mH_2O + nCO_2$$

On the left side is the air reactor, where an oxidation reaction occurs between reduced metal oxide ($M_yO_{x-1}$) and air:

$$M_yO_{x-1} + 1/2O_2 \rightarrow M_yO_x$$

Consequently, CO$_2$ is separated from water by condensing the product stream. Both reactors should operate as circulating fluidized beds in order to supply the circulation of oxygen carrier between the two beds. It has been reported that chemical looping combustion is the most economical way to capture CO$_2$ compared to post capture and oxyfuel processes (1). Besides combustion, chemical looping is a suitable technology for gasification. It can provide the oxygen needed for gasification reactions. In this way a pure syngas can be obtained.

Mattison and Lyngfelt found that some oxide systems of the transition metals, Fe, Cu, Co, Ni and Mn could be used as oxygen carriers (2). Some researchers (3-5) reported that nickel is the best oxygen carrier in terms of reactivity, although there are thermodynamic restrictions in the presence of CO and H$_2$ (6). Hossain et al. (7-9) observed that carbon deposition is a major problem in dealing with nickel carriers.

In addition to nickel, copper deserves serious consideration due to its high reactivity and low cost. De Diego et al. (10) developed Cu-based oxygen carriers by mechanical
mixing, co-precipitation, and impregnation methods. They analysed the behaviour of CuO in a thermogravimetric analyser. Their results showed that carriers prepared by impregnation exhibited excellent chemical stability without sustainable decay of the mechanical strength in multicycle testing. Copper suffers from agglomeration due to its low melting point. Researchers have tried to improve the properties of copper by using promoters. Adanez et al. (6) prepared a nickel-copper oxygen carrier using the dry impregnation method. They showed that CuO is used for the reduction reaction before NiO. In addition, it was observed that NiO stabilized the CuO and allowed working at 950°C.

Pure manganese oxide is expected to release oxygen at 900°C, but there are thermodynamic limitations for the reoxidation of these materials at low oxygen concentration levels in the air reactor at elevated temperatures (11). Recently, Moghtaderi (12) studied the separation of oxygen from air in a chemical looping process and demonstrated that a 1:1 mixture of Mn/Co metal oxide systems has more favourable redox characteristics than its parent materials.

Considering the different properties of individual Mn- and Cu-based oxygen carriers, the objective of this work was to use manganese as a promoter for the copper oxygen carrier. It is claimed that manganese can enhance the thermal stability of copper as well as its reactivity.

EXPERIMENTS
Oxygen Carrier Preparation
The incipient wetness impregnation method was used for catalyst preparation. In the following order a specific amount of nitrate hydrate salt of the desired metal was mixed with distilled water. All salt should be dissolved in water. Then, activated alumina was added gradually as a binder to the nitrate solution until it makes a paste. The entire amount of water solution should be adsorbed by the pores of the binder. Drying, which is the next step, was performed at 140°C for 12 hours. Finally, prepared powders were calcined at 850°C for 5 hours in air atmosphere. In each impregnation step a specific amount of active phase settles on the support. Impregnation steps should be repeated in order to reach the desired concentration of the active phase. Stirring can be done at higher temperatures in order to increase the solubility of salt in water and, consequently, increase the amount of settling of the active phase on the binder during each impregnation step. Copper, manganese, nickel, and cobalt have been used as the active phase and activated alumina as the binder. Also, in the case of the bimetallic oxygen carrier 50-50% of each metal has been used. Table 1 shows the amount of loading of the active phase versus impregnation steps:
Table 1. Loading of active phase versus impregnation step

<table>
<thead>
<tr>
<th>Impregnation Step</th>
<th>%Metal loading ( \frac{\text{weight of metal}}{\text{weight of metal+weight of support}} \times 100 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.8</td>
</tr>
<tr>
<td>2</td>
<td>18.6</td>
</tr>
<tr>
<td>3</td>
<td>24.6</td>
</tr>
</tbody>
</table>

**CHARACTERIZATION**

Several techniques have been used to characterize the prepared oxygen carriers. A laser diffraction apparatus has been used to determine the particle size distribution of powders. The surface area of the oxygen carrier was measured by BET. The identification of the crystalline phases of the oxygen carrier was carried out using powder X-ray diffraction (XRD) analysis in an X-ray diffractometer using Cu-K\( \alpha \) radiation. Changes in morphology were determined in a scanning electron microscope (SEM). Table 2 shows the physical properties and the crystalline phases of the oxygen carrier.

Table 2. Properties of prepared oxygen carriers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size(( \mu )m)</th>
<th>Surface area ( (m^2/g) )</th>
<th>Density ( (kg/m^3) )</th>
<th>XRD phases (fresh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>109</td>
<td>67.49</td>
<td>2346</td>
<td>CuO, Cu(_2)O, CuAl(_2)O(_4), Al(_2)O(_3)</td>
</tr>
<tr>
<td>Cu-Co</td>
<td>127</td>
<td>45.92</td>
<td>2383</td>
<td>CuO, CoO, CuAl(_2)O(_4), Al(_2)O(_3)</td>
</tr>
<tr>
<td>Cu-Ni</td>
<td>140</td>
<td>61.25</td>
<td>2437</td>
<td>CuO, Cu(_2)O, NiO, CuAl(_2)O(_4), NiAl(_2)O(_4), Al(_2)O(_3)</td>
</tr>
<tr>
<td>Cu-Mn</td>
<td>102</td>
<td>58.99</td>
<td>2135</td>
<td>CuO, Cu(_2)O, MnO, Mn(_3)O(_4), MnAl(_2)O(_4), Al(_2)O(_3)</td>
</tr>
</tbody>
</table>

The reactivity of the oxygen carrier was determined using a thermogravimetric analyzer. For the reactivity test 20 mg of sample were exposed to alternating reduction and oxidation cycles. The particles were well spread out in the platinum basket (5 mm in diameter and 1 mm in height) forming a single layer, thus avoiding the inter-particle mass transfer resistance. Air (20 ml/min STP) was used as the oxidizing agent and nitrogen (20 ml/min STP) was used as carrying gas during the reduction step. The experiments were carried out at 800\(^\circ\)C and atmospheric pressure. Usually, the reactivity of the oxygen carrier will reach a constant value after the second cycle. However, the reactivity data related to the fifth cycle has been chosen for comparison purposes.
RESULTS AND DISCUSSION
The purpose of this study was to separate oxygen from air using a chemical looping process. The main step for commercializing the process is to develop an oxygen carrier with superior reactivity and stability properties. Besides having high reactivity duringoxidation and reduction reactions, an oxygen carrier should have sufficient thermal and mechanical stability and be environmentally friendly and inexpensive.

Copper is one of the candidates for the oxygen carrier in the chemical looping process. Its high reactivity, low cost, and friendly environmental properties make it one of the best materials, like metal oxide. However, copper suffers from agglomeration due to its low melting point (1083°C). In chemical looping processes, the oxygen carrier must pass around one hundred thousand cycles through circulating fluidized beds. As a result, agglomeration can be a huge problem. For this reason, it is suggested to use a bimetallic Cu-Mn oxygen carrier. It has been shown that besides increasing the agglomeration resistance, manganese can enhance the oxygen transport capacity of copper oxide. During calcination, which is one of the catalyst preparation steps, a solid-solid reaction takes place between copper oxide and alumina as the binder. During this reaction CuAl₂O₄ forms, which has a higher oxidation temperature compared to CuO. Consequently, it is trying to avoid the reaction between copper and alumina. During XRD experiments, it was investigated whether adding manganese can decrease the amount of copper aluminate, because between copper and manganese, the latter has a higher tendency to react with alumina. Thus, CuO remains as the active phase. The oxidation and reduction reactions are:

\[
\begin{align*}
\text{Cu} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CuO} \\
\text{CuO} & \rightarrow \text{Cu} + \frac{1}{2} \text{O}_2
\end{align*}
\]

Figure 1 shows SEM micrographs for Cu and Cu-Mn oxygen carriers before and after 20 oxidation-reduction cycles. It is evident that copper particles stick together at 800°C because of agglomeration. By adding manganese, copper particles can withstand higher temperatures without agglomerating.
Particle diameter will increase because of agglomeration and it can cause defluidization of the bed. Figure 3 compares the reactivity of various oxygen carriers, which were prepared in this study.

Cu-Mn has a high oxygen transport capacity as well as high oxidation and reduction rates compared to other carriers. Figure 4 shows the effect of a number of oxidation-reduction cycles on the reactivity of the Cu and Cu-Mn oxygen carrier.
In the case of pure copper, its reactivity will decrease as it is cycled and especially from the first to second cycle due to agglomeration and the formation of copper aluminate. Manganese can stabilize the reactivity of copper as can be seen in Figure 4(b).

CONCLUSION
Biomass as a renewable source of energy has been the focus of much interest in recent years. Gasification technology is very effective in terms of conversion of biomass, environmental aspects, efficiency, etc. However, the gasification process has some challenges, such as oxygen separation. In the present study, a chemical looping process was proposed for the separation of oxygen from air using a novel oxygen carrier. To achieve this, a Cu-Mn oxygen carrier was prepared via the incipient wetness impregnation method. The performance of the oxygen carrier to separate oxygen from air was tested in a thermogravimetric analyzer. Results showed that manganese can enhance the properties of copper. By increasing the agglomeration temperature of copper, it can withstand high temperatures. Also, adding manganese decreases the possibility of forming copper aluminate during the calcination process resulting in improved reactivity.

REFERENCES