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Full Length Article

Assessment of low-cost oxygen carrier in South-western Colombia, and its use in the *in-situ* gasification chemical looping combustion technology

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ABSTRACT

In Chemical Looping Combustion (CLC), the Oxygen Carrier (OC) is key element of the process. Most OCs have been developed synthetically, using an active metal oxide combined with an inert material. When solid fuels are used, a loss of OC is expected as it mixes with the ashes generated during the CLC process making the costs elevated. As a result, there is a growing interest in using low-cost OCs based in Mn and Fe.

In this research, a by-product derived from manganese ore purification is studied. This material has a high silicon content and it is composed of rhodonite as the main specie and wustite as the minority specie. The material, a Mn mineral from the Nariño department in the Southwest of Colombia, was selected in a previous work based on its good properties such as appropriate crushing strength, an oxygen transport capacity of 3.4%, and a relatively high reactivity.

Here, tests in a batch fluidized bed reactor were carried out with the selected material with CH_4, CO, and H_2 at 950 °C during 50 cycles. A good behaviour was observed with CO and H_2, with a moderate attrition, and lifetime of 2950 h. The material presented a trend towards agglomerating with CH_4, and no agglomeration with CO and H_2. The possible oxygen uncoupling effect due to the presence of combined oxides of manganese and silicon was also evaluated, but there was no evidence in the 950–1040 °C interval when the material was oxidized with a 10 vol% O_2.

Due to its good performance with CO and H_2, the material was evaluated for the *in-situ* Gasification Chemical Looping Combustion (*i*G-CLC) technology, using a Chilean reactive coal as fuel at temperatures from 900 °C to 1000 °C.

Its good behaviour with H_2 and CO makes it a promising OC for *i*G-CLC technology.

1. Introduction

Nowadays, the increase in greenhouse gas concentration (GHG) is evident. This has led to an increase in global temperature, which in turn as led to climate change [1]. An option to avoid this is through the use of CO_2 capture and storage (CCS).

Chemical Looping Combustion technology (CLC) has emerged as a very attractive option for the capture of carbon dioxide because it inherently separates itself from the other components of the flue gases, i.e. N_2 and O_2 that are not used, so no additional energy is required for their separation [2].

A key element for the development of CLC is the oxygen carrier (OC). When solid fuels are used there are losses of OC because they mix with the ashes of the process. This is the reason why there is a growing interest in low-cost OCs [3]. In this context, the use of minerals in their natural state or industrial waste seems to be very promising because they a have good reactivity with the solid fuel gasification products (H_2 or CO). Low-cost materials are being considered for use with gaseous fuels [4,5].

Several authors [6,7] studied Fe-based materials and industrial waste for carbon gasification in situ with CLC (*i*G-CLC), finding that the gasification rate of char decreases when the O/C molar ratio decreases

Abbreviations: GHG, greenhouse gases; CLC, chemical looping combustion; IPCC, intergovernmental panel on climate change; OC, oxygen-carrier; OCs, oxygen-carriers; *i*G-CLC, *in-situ* gasification chemical-looping combustion; CLOU, chemical-looping with oxygen uncoupling; XRF, X-ray fluorescence; XRD, X-ray diffraction; BET, Brunauer-Emmett-Teller surface area analysis; TGA, thermogravimetric analyzer; SCM, shrinking core model; bFB, batch fluidized bed; Me_xO_y, óxido metálico; ICP, inductively coupled plasma

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as the concentration of H_2 and CO increases. Bauxite waste (red mud), such as hematite ore was able to burn the gasification products with a high combustion efficiency. These efficiencies are comparable to those obtained under the same conditions using the Fe-based synthetic material.

Fe, Mn oxides are becoming important because they are inexpensive and non-toxic, and their oxygen transport capacity is higher when compared to Fe [8].

The highest oxidation state of Mn is MnO_2 and it decomposes at 500 °C [9]. However, at temperatures above 800 °C only the Mn_3O_4 is present as a stable material [10]. Therefore, only the transformation between Mn_3O_4 and MnO is considered for CLC applications. Mn_2O_3 may be an alternative for the Chemical-Looping with Oxygen Uncoupling process (CLOU), which is based on the decomposition of the metal oxide to Mn_3O_4 and O_2 in reducing atmospheres. Because the CLOU process presents greater efficiencies of CO_2 capture and combustion than the CLC with conventional carriers, it would be extremely interesting to achieve oxidation Mn_2O_3 with air, but the re-oxidation of manganese oxides to Mn_2O_3 is restricted to comparatively low temperatures, around 800 °C, which makes using the CLC technology difficult [11]. The formation of combined oxides can overcome the mechanical and thermodynamic limitations that can present Mn oxides as reported by some authors [5,11,12].

Ryden et al. [12] provide an overview of the feasibility of developing OCs from combined oxides, that is, oxides with crystalline structures that include several different cations. Since the manganese ions may be present in a large number of oxidation states, the Mn forms oxides with a large number of elements, which may allow the development of OCs from combined oxides that release O_2 in conditions suitable for the CLOU process.

Jing et al. [13] studied synthetic combined oxides by mixing Mn_3O_4 and SiO_2 from which manganese silicates are produced, such as: braunite (Mn_7SiO_{12}) and rhodonite ($MnSiO_3$), depending on the SiO_2 content and the calcination temperature. They have found that these species are very important in CLOU behaviour, which was thermodynamically predicted and experimentally tested.

Also, they observed a total conversion with syngas (50% CO–50% H_2) for the materials with low content of SiO_2 and the attrition rate of the tested oxygen carriers was very high and varied from 3.9 wt%/h to 40.2 wt%/h.

With respect to natural minerals, different lifetimes have been reported in literature for Fe ore (1600 h) [14], Ilmenite (700 h) [15] and Mn ore (284 h) [16] when used in CLC due to their attrition during CLC. Mei et al. [17] studied different Mn minerals in *i*G-CLC with bituminous coal as the fuel finding instantaneous char gasification rates higher than Ilmenite and iron ore.

In a previous study [18] of 8 Fe and Mn minerals found in Colombia, a screening of different materials was made and its reaction kinetics was studied using thermogravimetric analysis, a Mn mineral, from the Nariño department in the Southwest of Colombia was selected (OXMN010A) due to its good properties. The main component identified in this mineral is rhodonite ($MnSiO_3$) with one small fraction of wustite (FeO). Reduction and oxidation reactions for this mineral are shown in Table 1 [12].

The objective of this work is to study the behaviour of a mineral of Mn (OXMN010A) in a batch fluidized bed (bFB) with gaseous (CLC) and solid (iG-CLC) fuels to know its suitability as oxygen carrier material.

2. Experimentation

2.1. Oxygen carrier

The OXMN010A material, from the department of Nariño-Colombia, was selected through a previous study [18]. Sampling is performed according to the ASTM D2234 norm [19]. The characterization is performed by: crushing strength analysis, surface area analysis (BET), X-ray fluorescence analysis (XRF) and X-ray diffraction (XRD) using Thermo Scientific equipment, model ARL9900 Workstation with an X-ray tube for fluorescence with rhodium anode. In Table 2 the results obtained for the mineral's characterization are shown.

OXMN010A is subjected to a thermal treatment (heating at 1050 °C for 4 h with air at atmospheric pressure) and the crushing strength is measured before and after this in order to verify its improvement with the thermal treatment. A crushing strength greater than 1 N is considered acceptable [20] within the screening processes that allow the selection of an OC with the appropriate mechanical properties. The result of the crushing strength after the heat treatment is 3 N, which is equivalent to a 29% increase. This result is in agreement with that reported by some authors [13,21].

In the bFB experiment with coal, a subbituminous coal from Mina Invierno in Riesco Island (Chile) was used. The proximate and ultimate analyses are shown in Table 3.

2.2. Experimental facilities

The realization of several reduction–oxidation cycles in a batch fluidized bed reactor (bFB) are an approximation to the continuous

Table 1
Reduction-oxidation Reaction for OXMN010A.

Sample	Reactive	Reactions
OXMN010A	CH_4	$2Mn_7SiO_{12} + 12SiO_2 + \frac{3}{2}CH_4 \rightarrow 14MnSiO_3 + \frac{3}{2}CO_2 + 3H_2O$
	CO	$Mn_7SiO_{12} + 6SiO_2 + 3CO \rightarrow 7MnSiO_3 + 3CO_2$
	H_2	$Mn_7SiO_{12} + 6SiO_2 + 3H_2 \rightarrow 7MnSiO_3 + 3H_2O$
	O_2	$14MnSiO_3 + 3O_2 \rightarrow 2Mn_7SiO_{12} + 12SiO_2$

Table 2
Characterisation of OXMN010A mineral used in tests for Chemical Looping Combustion (CLC) and *in-situ* Gasification Chemical-Looping Combustion (*i*G-CLC).

Particle diameter (μm)	Oxygen transport capacity (% w/w)	Crushing strength (N)	Surface Area BET (m^2/g)	Elementary composition (XRF) [a]							Crystalline phases (XRD) [b]	
				Si	Al	Fe	Ca	Mg	Ti	Mn	MnSiO3 (Rodonite)	FeO (Wüstite)
100–300	3.4	2.3	23.3	13	2.5	3.5	1.9	0.8	0.2	35.7	85.4	6.1

[a] Percent in % w/w. Values less than 0.1 are negligible.
[b] Percent in % w/w.