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Chemical Looping Combustion of different types of biomass in a 0.5 kW_{th} unit

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ABSTRACT

Chemical Looping Combustion (CLC) using renewable solid fuels appears as an important option to reach negative carbon emissions. In this work, three types of forest and agricultural residues (pine sawdust, olive stone and almond shell) were tested between 900–980 °C in a 0.5 kW_{th} unit with an iron ore as oxygen carrier (Tierga ore) working under *In situ* Gasification-Chemical Looping Combustion (*i*G-CLC) mode. Specific solids inventories lower than 1000 kg/MW_{th} were tested as they were consider more representative of what can be used in a larger CLC unit. CO_2 represented about 70% in the fuel reactor outlet gas stream, followed by unburnt compounds: H_2, CO and CH_4. CO_2 capture efficiencies increased with the fuel reactor temperature achieving almost 100% of capture with the three biomasses at temperatures above 950 °C. In contrast, no clear trend with the fuel reactor temperature was observed for the total oxygen demand, achieving values about 25%. The major contribution to this value comes from the unburned volatiles with a small contribution coming from tar (≈ 1%). Regarding tar, naphthalene was the major compound found at the different operating conditions. The present results support the consideration of the CLC process with biomass (bio-CLC) as a promising Bio-Energy with Carbon Capture (BECCS) technology.

1. Introduction

Sustainability is becoming one of the most important challenges of present societies. One of the threats to the sustainability of our planet is climate change. In order to mitigate the effects of the changes in climate, different actions should be taken to restrict anthropogenic greenhouse gas (GHG) emissions. Based on the findings presented in the 5th Assessment Report of the International Panel on Climate Change (IPCC) [1], the Paris Agreement in 2015 set the objective of limiting the global average temperature increase to 2 °C by reducing the GHG emissions and within them, CO_2 emissions [2]. To reach this goal it becomes necessary to develop not only neutral but also negative carbon emission technologies (NETs) during the present century [3]. NETs comprise different types of technologies which actually reduce carbon concentration in the atmosphere, such as afforestation, agricultural land management, bio-char soil sequestration, ocean liming, enhanced weathering, ocean fertilization and Bio-Energy with Carbon Capture and Storage (BECCS) [4].

BECCS technologies are drawing increasing attention in the last years. They match both biomass combustion and Carbon Capture and Storage (CCS) and this combination reinforces their potential to generate heat and/or power, while removing CO_2 from the atmosphere [4]. Biomass carbon emissions are considered neutral because of their short life cycle. Moreover, biomass accessibility, simply sustainable management as well as relatively homogeneous world distribution must be considered as important characteristics of biomass compared to other fuels. In this way, including biomass technologies, the energy mix self-sufficiency and environmental protection in energy supply would be ensured [5,6]. The bio-energy concept associated with BECCS includes both biomass fuelled biochemical and thermochemical processes easily combinable with CCS [7]. An almost pure CO_2 stream should be produced during fuel conversion to make feasible its transportation and storage. Simply pre-treated biomass or even biomass derived liquid and gas fuels can be used.

CCS technologies allow CO_2 emission reduction from stationary point sources in energy production. In this context, chemical looping combustion (CLC) processes have demonstrated to be one of the most suitable alternatives for CCS because of the low cost of carbon capture and energy penalty [8]. This technology allows fuel combustion in nitrogen-free atmosphere. A solid oxygen carrier (OC) provides the oxygen needed for fuel oxidation via redox reaction while circulating between the so-called fuel and air reactors. CLC combustion of solid

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Nomenclature

C_nH_m	general formula for tar compounds
$F_{i,FR}$	i species molar flow in the fuel reactor outlet stream (mol/h)
$F_{CO2,AR}$	CO_2 molar flow in the air reactor (mol/h)
$F_{C,vol}$	carbon flow coming from the volatile matter (mol/h)
M_O	oxygen atomic weight (g/mol)
$\dot{m}_{OC}$	solid circulation rate (kg/h)
$\dot{m}_{SF}$	biomass mass flow (kg/h)
R_{OC}	oxygen transport capacity
X_{char}	char conversion (–)

Greek symbols:

η_{CC}	CO_2 capture efficiency (%)
Ω_{SF}	amount of oxygen to burn the solid fuel (kg oxygen/kg biomass)
ϕ	oxygen carrier to fuel ratio
Ω_T	total oxygen demand (%)
Ω_{tar}	oxygen demanded by the tar at the fuel reactor outlet (%)

fuels has reached an important development in the last decade [9]. Most of the knowledge has been gained using coal as fuel in prototypes in the range 0.5 kW_{th} to 3 MW_{th}. The majority of the CLC units operated under the *In Situ* Gasification-Chemical Looping Combustion (*i*G-CLC) mode. Fig. 1 shows the scheme of a typical *i*G-CLC unit for solid fuels. In this process, the solid fuel is gasified in the fuel reactor using steam as gasifying agent. Both the volatile compounds and the gasification products generated react with the oxygen carrier to produce CO_2 and H_2O. The possible unburnt compounds at the outlet of the fuel reactor would be further oxidised in an oxygen polishing step. This stream can be easily dried to obtain a CO_2 stream ready to be transported and stored. Finally, the oxygen carrier is re-oxidized in the air reactor.

Based on this experience, the biomass fuelled CLC became feasible as a BECCS technology. First results using biomass (pine sawdust) and iron ore as oxygen carrier were obtained by Shen et al. [10] in a 10 kW_{th} unit. They evaluated the influence of the fuel reactor temperature on the gas product composition. Pine sawdust was also used in the experiments performed at Instituto de Carboquímica by Mendiara et al. [11] with a Fe-based iron ore (Tierga ore) as oxygen carrier. The influence of the fuel reactor temperature on the CO_2 capture and combustion efficiency was assessed. Tar measurements were also performed. Moreover, no interaction of biomass ashes with the oxygen carrier was observed after 78 h of continuous operation. Several manganese ores were used as oxygen carriers by Schmitz et al. [12] for wood char combustion in a continuous 10 kW_{th} CLC unit at Chalmers University of Technology. Some of them presented low oxygen demands and high carbon capture efficiencies. Wood char was also used by Linderholm et al. [13] in a 100 kW_{th} CLC plant also located at Chalmers University of Technology. In this case, Tierga ore was used as oxygen carrier. The highest combustion efficiency observed in these experiments was 93%. It should be mentioned that high specific solids inventories (> 1000 kg/MW_{th}) were used in the previously described studies. According to the experience gained in experiments with coal in different continuous CLC units, the optimum value of this parameter would be lower to avoid high pressure drop in the fuel reactor [14]. This could affect the combustion efficiency reached. Recently, a new 10–50 kW_{th} scale CLC plant for biomass combustion was built at VTT Technical Research Centre in Finland an operated by Pikkarainen et al. [15]. They found high oxygen demands during the combustion of wood pellets due in this case to an insufficient bed temperature of the fuel reactor, as the unit was originally designed for gasification.

A big step in the scale-up of the biomass CLC process was recently presented by Berdugo-Vilches et al. [16]. Several experimental campaigns were carried out in a semi-commercial dual fluidized bed (DFB) unit at Chalmers University consisting of a 12 MW_{th} boiler coupled to a 2–4 MW_{th} bubbling bed gasifier. The gasifier can be assimilated to a fuel reactor of a conventional CLC unit and the boiler to the air reactor. More than 1000 hours of combustion were reported using commercial wood pellets as fuel and ilmenite and a manganese ore as oxygen carriers. Combustion efficiencies up to 60% were achieved although the temperature in the gasifier was not high, about 830 °C. Although this plant represents a non-optimized reactor design for CLC applications, these results highlight the strong potential of the CLC technology for biomass combustion and reinforce its possibilities as BECCS technology.

In this line, the present work aims at further contributing to the knowledge of biomass CLC. Commonly, pine or spruce tree pellets have been used as fuels. The objective of this work is to extend the study to other types of biomass (agricultural residues such as olive stones and almond shells) in order to identify possible differences during combustion. Besides, operation with specific solids inventories lower than 1000 kg/MW_{th}will be assessed. Experiments are performed in a continuous 0.5 kW_{th} unit operating under *i*G-CLC mode. The influence of the fuel reactor temperature on the results obtained is evaluated using specific solids inventories realistic for industrial CLC units.

2. Experimental

2.1. Oxygen carrier and biomass

Tierga ore was used as oxygen carrier in the present experiments. In a comparative study among Fe-based oxygen carriers, Tierga ore showed the highest reactivity in the combustion of coal [17,18] as well as stability and durability combined with its low cost. Thus, it was also selected to perform biomass combustion experiments. After receiving it from an hematite mine in Tierga (Zaragoza, Spain), the ore was crushed to 100–300 μm size particle and calcined at 950 °C during 12 hours for increasing its mechanical strength. The main properties of Tierga ore are summarized in Table 1. A detailed description of the techniques

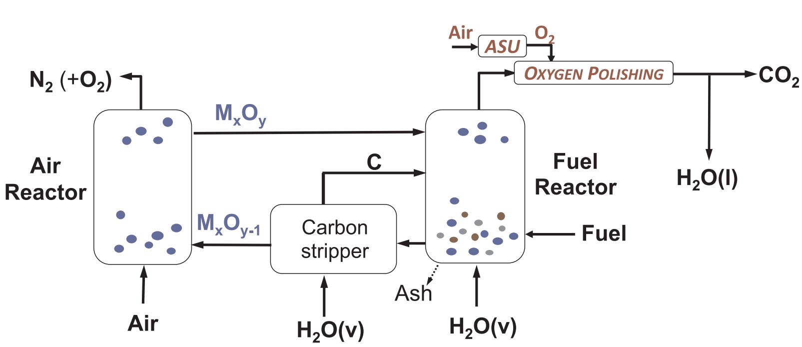

Fig. 1. Scheme of the *i*G-CLC process.