Advanced materials for Chemical Looping processes

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Objectives and novelty

The persistent increase in atmospheric greenhouse gas concentrations is primarily driven by anthropogenic activities, with CO_2 emissions constituting the predominant contributory factor. These emissions largely arise from the combustion of fossil fuels for energy generation. Among the various mitigation strategies proposed to address CO_2 emissions, Bioenergy with Carbon Capture and Storage (BECCS) has emerged as a promising approach, as it enables simultaneous energy production and the achievement of net-negative CO_2 emissions. Within this framework, Chemical Looping Combustion (CLC) represents an advanced carbon capture technology. CLC enables combustion through the transfer of oxygen from a solid metal oxide oxygen carrier (OC), which undergoes cyclic redox reactions between two interconnected reactors, namely the fuel reactor and the air reactor. A specific operational variant of CLC, particularly suitable for solid fuels, is Chemical Looping with Oxygen Uncoupling (CLOU). In the CLOU process, the oxygen carrier releases gaseous oxygen within the fuel reactor, allowing fuel conversion to proceed via mechanisms analogous to conventional combustion. This feature enhances reaction kinetics and improves overall system efficiency.

Despite these advantages, the development of CLOU technology remains limited to Technology Readiness Level (TRL) 4, indicating that significant challenges remain before its deployment at industrial scale. In particular, the identification and optimization of suitable oxygen carriers with effective oxygen uncoupling properties remain critical.

The objective of this doctoral thesis was to develop oxygen carrier materials for CLOU processes with magnetic properties and improved lifetime at TRL 5. Formulations were designed to combine high reactivity, redox stability, and magnetic response. Newly formulated materials were tested in a 50 kW_{th} CLC unit at Instituto de Carboquímica, achieving for the first time a technological readiness level TRL 5 for CLOU process. The results improve process efficiency and provide design criteria for industrial application in this type of CO_2 capture systems.

Results

To advance the CLOU process toward TRL 5, Cu-based oxygen carriers supported on magnetic MnFe spinels were developed with varying kaolin content to enhance mechanical stability using scalable granulation. Improved crushing strength was achieved only after calcination at 1100 °C. Screening of the synthesized oxygen carriers was conducted using thermogravimetric analysis, mechanical characterization, and batch fluidized bed testing. Cu30MnFekao7.5_1100, exhibited stable redox performance without agglomeration. Further investigation of the selected Cu30MnFekao7.5 oxygen carrier in a 1.5 kW_{th} continuous CLOU unit (TRL 4) confirmed robust performance across different biomass fuels. Several performance parameters were evaluated, including combustion efficiency, which quantifies the extent of fuel conversion within the fuel reactor, and the CO_2 capture efficiency which is defined as the fraction of carbon converted to gaseous products in the FR relative to the total amount of carbon converted to gas in the entire unit. Complete combustion was achieved even at 800 °C, while CO_2 capture efficiency reached 97.4% at 950 °C during combustion of pine sawdust in the 1.5 kW_{th} unit. After 80 hours of operation, the material showed no agglomeration and retained its magnetic properties, enabling efficient separation from ash. Ash–oxygen carrier interactions were studied at TRL4 by comparing Cu30MnFekao7.5 with a kaolin-free oxygen carrier, Cu30MnFe. While Cu30MnFe exhibited negligible ash interaction after 15 hours, Cu30MnFekao7.5 showed gradual accumulation of Mg and K, with concentrations doubling after 56 hours.

Despite similar reactivity and stability, the increased ash interaction and production challenges associated with kaolin-containing oxygen carriers led to the selection of Cu30MnFe as the preferred candidate for scale-up to TRL 5. This material was successfully tested in a 50 kW_{th} CLC unit, representing a significant advancement toward industrial deployment. During a 40h experimental campaign, high performance was maintained across three types of biomass as well as Taldinsky coal (the later used as reference for comparison with previous results). A CO_2 capture efficiency of 93% was achieved at 886 °C for pine sawdust, along with a low oxygen demand of 4.6%. Figure 1 illustrates one of the key findings of this study, namely the transition in combustion mechanism from in situ gasification chemical looping combustion (*i*G-CLC) to CLOU. This transition is particularly beneficial for enhancing combustion efficiency, especially at temperatures above 850 °C. The figure presents the relationship between total oxygen demand, defined as the amount of oxygen required during the oxygen polishing step to fully oxidize unconverted gaseous species, and CO_2 capture efficiency during the combustion of various biomass fuels and coal. In all cases, an increase in temperature leads to higher CO_2 capture efficiency. At lower temperatures, the results show that oxygen demand increases with CO_2 capture efficiency, which can be attributed to the enhanced generation of gasification products. Under these conditions, combustion predominantly proceeds via the *i*G-CLC mechanism, in which the products of char gasification react with the oxygen carrier following a gas-solid reaction. The interaction between gasification products and the oxygen carrier dominates the overall process, resulting in an increased oxygen demand. A similar trend is observed for CLOU materials operating at relatively low temperatures. However, as the temperature exceeds approximately 850 °C, a clear shift in combustion behavior is observed. In the cases of olive stone and pine sawdust, oxygen demand decreases despite increasing CO_2 capture efficiency, indicating that the oxygen uncoupling mechanism becomes dominant. In this regime, gaseous oxygen released from the oxygen carrier contributes significantly to biomass combustion, as in conventional combustion. As a result, under these conditions, CLOU oxygen carriers release a higher amount of gaseous oxygen, thereby reducing the overall oxygen demand.

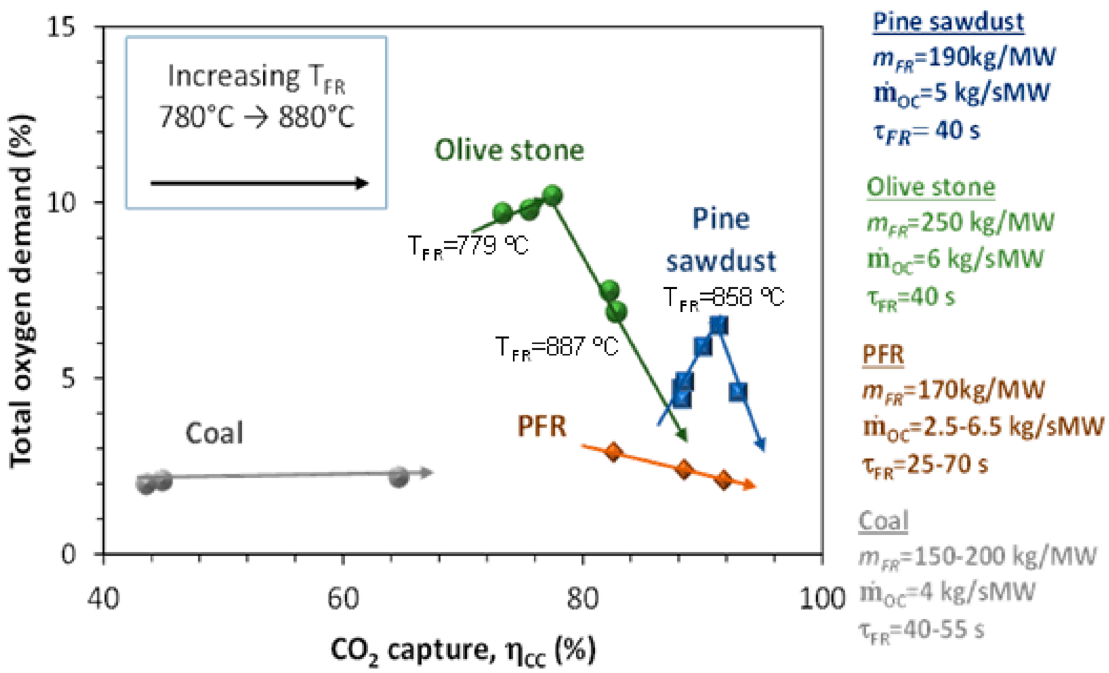

Figure 1. CO_2 capture efficiency and total oxygen demand for various fuels tested with Cu30MnFe oxygen carrier in the 50 kW_{th} unit at operating temperatures between 780–880 °C.

Comprehensive physicochemical characterization of the used OC was performed which yielded many novel conclusions regarding the reaction mechanism. Cu migration within the particle matrix led to crack formation and internal voids, increasing porosity and progressively reducing mechanical strength, ultimately causing particle fragmentation. Chipping was identified as the dominant attrition mechanism. Although ash elements, particularly Si, accumulated on the surface, no fluidization issues occurred. Despite the chemical stability of major components, notable changes in solid-phase composition were observed, including the formation of a CuMnFe spinel phase ($Cu_{0.5}MnFe_{1.5}O_4$), which persisted throughout the campaign as it can be seen in Figure 2. Importantly, the MnFe spinel structure retained its magnetic properties and reactivity, enabling efficient separation and reuse of both particles and fines.

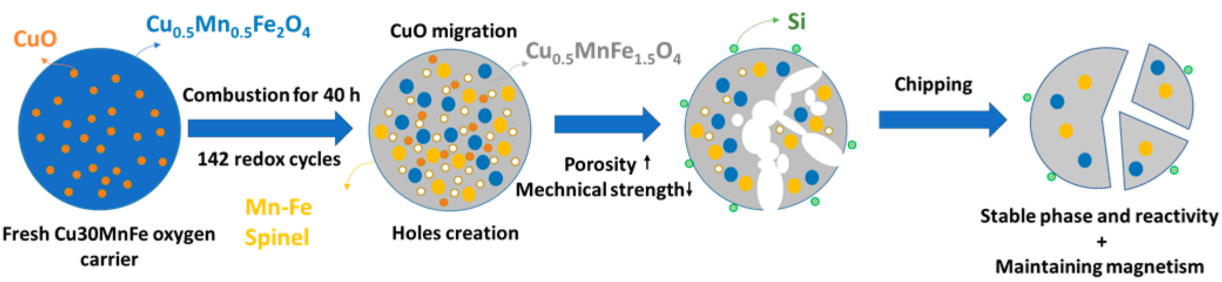

Figure 2. Scheme of the oxygen carrier transformation during CLOU operation.

Conclusion

The CLOU process was successfully demonstrated at TRL 5 for the first time using a 50 kW_{th} unit, with stable operation across biomass and coal fuels. The Cu30MnFe oxygen carrier showed high performance, achieving up to 93% CO_2 capture and low oxygen demand under optimized conditions. Although mechanical degradation due to chipping was observed, the material maintained its chemical stability, reactivity, and magnetic properties, enabling ash separation and reuse. Ash accumulation did not cause operational issues such as agglomeration. The formation of a stable CuMnFe spinel phase indicates a promising pathway for improving the durability of the oxygen carrier. Synthesizing the material to favor the formation of this spinel structure from the outset could be advantageous, as it may enhance mechanical integrity and mitigate chemical stresses during operation.

Related publications

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