Reseña Tesis. Coal combustion by chemical looping with oxygen uncoupling (clou) using cu-based oxygen carriers

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OBJETIVES AND NOVELTY

The main objective of this thesis is to demonstrate the coal combustion with CO_2 capture with a Cu-based oxygen carrier in a continuous system with different solid fuels (coals of different rank and biomass). In this case, it is intended to use the capability of CuO to generate gaseous oxygen in contact with fuel at high temperature, according to the process called CLOU (Chemical Looping with Oxygen Uncoupling). This process is based on the Chemical Looping Combustion (CLC) technology but using oxygen carriers that can release gaseous O_2 at the operation conditions.

In 2009, first investigation on oxygen carriers with CLOU properties based on copper and manganese oxides were published. Initial results focused the interest of several research groups in developing new materials with properties suitable for the CLOU process. The number of publications in this field has been growing over the last 5 years. However, the experimental work was mainly carried out in a TGA or in a batch fluidized bed reactor. Evaluations of developed materials in continuous system (interconeted fluidized beds) are scarcely found in literature and the works where the CLOU concept is demonstrated with solid fuels are carried out within this thesis.

RESULTS

Initially a screening of materials was carried out to select a suitable Cu-based oxygen carrier for CLOU process. More than 50 oxygen carriers were prepared by different methods and with different compositions (using as inert: $MgAl_2O_4$, Al_2O_3, MgO, ZrO_2, SiO_2, TiO_2 and sepiolite), and CuO as active phase. The reactivity of these oxygen carriers was studied in a TGA and a batch fluidized bed reactor. Moreover, the resistance to agglomeration of the different particles, mechanical strength and attrition rate were also analyzed. Among the different materials evaluated an oxygen carrier with a 60 wt.% of CuO and a 40 wt.% of $MgAl_2O_4$ as inert prepared by spray drying (referred as Cu60MgAl_SD from now) was selected for further testing in the CLOU process. This material fulfils all the requirements for CLOU process: high reactivity, high oxygen release rate, high agglomeration resistance and low attrition rate.

The capacity of Cu60MgAl_SD material to burn solid fuels was analyzed in a batch fluidized bed reactor for coal combustion. Several redox cycles between 900 and 950 ºC were done lasting 31 h. The oxygen carrier to coal ratio was varied in order to analyze the O_2 generation rate, and three different operation regimes were identified in a CLOU process. Complete combustion was obtained with solids inventory higher than 58 kg/MW_{th}, 955 ºC. Between 32 and 58 kg/MW_{th}, CO_2 is the main product and CO and O_2 were present in the flue gases. Below 32 kg/MW_{th} CO and CO_2 were present in the flue gases without O_2.

The proof of the CLOU concept was carried out during 18 h of bituminous coal combustion with the Cu60MgAl_SD oxygen carrier in a continuous 1.5 kW_{th} CLOU unit system consisting in two interconnected fluidized bed reactors. The effect of the operating conditions –such as temperature of the fuel reactor, solids circulation rate and the coal feeding rate– on the CO_2 capture efficiency and the combustion efficiency were investigated. In all cases, unburnt compounds were not present at fuel reactor outlet, being CO_2 and H_2O the only products of combustion even if the oxygen carrier particles were highly converted. Also, high CO_2 capture efficiencies were measured. Moreover, the performance of the CLOU process for combustion of coals of different rank (one lignite, three bituminous coals and one anthracite) was determined in the 1.5 kW_{th} a continuous CLOU unit with this oxygen carrier. A total of 40 h of operation were carried out with the fuel reactor temperature varying from 900 ºC to 950 ºC. With all the coals used, unburnt compounds were not present in the fuel reactor outlet. CO_2, H_2O and O_2 were the only products present at the fuel reactor outlet. The coal rank showed an important effect on the CO_2 capture efficiency. Very high CO_2 capture efficiencies were obtained with the lignite and the medium volatiles bituminous coals, reaching values of 99% with the lignite at 950 ºC, see Figure 1.

Also, combustion of biomass by CLOU process to obtain negative CO_2 emissions (Bio CCS) was demonstrated for the first time in the continuous CLOU unit of 1.5 kW_{th} during 10 h of operation. A fuel reactor temperature higher than 900 ºC was required to exploit the oxygen uncoupling benefits and resulting in no unburnt compounds at the fuel reactor outlet. Complete combustion and 100% CO_2 capture efficiency were achieved at a fuel reactor temperatures higher of 935 ºC using a solids inventory in the fuel reactor as low as 650 kg/MW_{th}.

The fate of sulphur during coal combustion in the CLOU process was analyzed for 15 h of continuous operation in the 1.5 kW_{th} unit with a high S content lignite (5.2 wt.% S) using the oxygen carrier Cu60MgAl_SD. Most of the S present in the coal was released as SO_2 in the fuel reactor. A minor fraction was transferred to air reactor and emitted as SO_2,

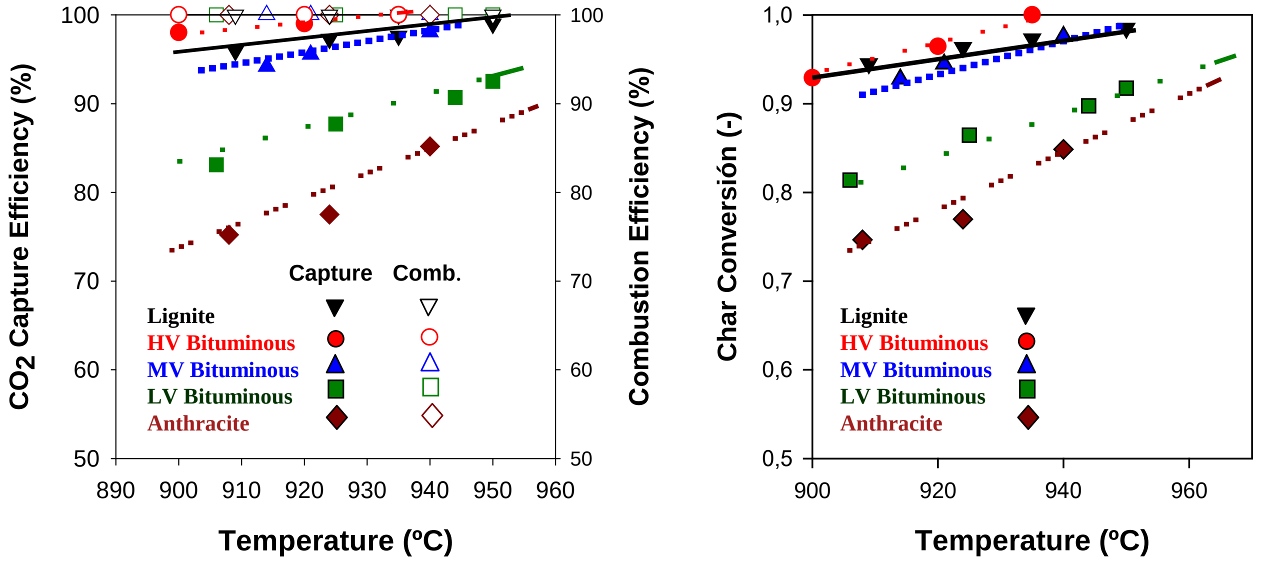

Figure 1. (a) Combustion efficiency in the fuel reactor and CO_2 capture efficiency, and (b) char conversion, as a function of the fuel reactor temperature obtained with different coals.

although emissions higher than legal limit were found with this lignite with high S content. However, no additional actions would be required for other coals with lower S content. The emissions may have been due to a non-uniform S release during char combustion resulting from the presence of pyritic S in this coal (2 wt.%).

A final characterization of physical and chemical properties of the oxygen carrier particles after 40 h of continuous operation burning coals of different rank was carried out. An important decrease in the crushing strength of the particles related to an increase in the porosity with the operation time in the CLOU unit was found. This fact indicates the need of an improvement in the lifetime of the particles. However, the oxygen carrier particles had a stable reactivity and oxygen transport capacity.

A comparison between CLC and CLOU process for the solid fuels combustion was carried out. It was found that higher combustion and CO_2 capture efficiencies were obtained with the CLOU mode. This behaviour it is due to two causes: the better combustion of the volatiles with the gaseous O_2 generated by the CLOU oxygen carrier, and the faster char conversion with the gaseous O_2 in front of the slower char gasification with H_2O required in CLC mode. The char conversion rate was between 3 to 4 times higher in the CLOU mode than in CLC for biomass and 1.5-5 times for coals. At 920ºC the CO_2 capture efficiency obtained in CLC mode with lignite was 93% but it decrease to 58 and 40% for the bituminous coal medium in volatiles and anthracite respectively. On the other hand, with the same fuels the CO_2 capture efficiency obtained in the CLOU mode was 97% at 935 ºC for lignite and bituminous coal medium volatiles and 84% with anthracite.

To develop a model of the CLOU process, the reaction rates of decomposition of CuO to Cu_2O and oxidation of Cu_2O to CuO of the Cu60MgAl_SD oxygen carrier for CLOU process were measured by TGA to determine the redox kinetic. A nucleation model for the variation of the solid conversion with time and a Langmuir-Hinshelwood surface kinetic control together with Freundlich's isotherm was valid to predict the experimental data in a broad range of O_2 concentration and temperatures, even at O_2 concentrations very close to equilibrium conditions. The solids circulation fluxes and solids inventories needed on each reactor of a CLOU process to get full combustion were calculated using the kinetic data of the oxygen carrier and different coals. A minimum solids inventory of 160 kg/MW_{th} in the fuel reactor and 95 kg/MW_{th} in air reactor were determined to transfer the oxygen flow demanded for full combustion of lignite

RELATED PUBLICATIONS

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