RELEVANCE OF PLANT DESING ON CLC PROCESS PERFORMANCE USING A CU-BASED OXYGEN CARRIER

Alberto Abad*, Pilar Gayán, Francisco García-Labiano, Luis F. de Diego, Juan Adánez

Dept. of Energy and Environment, Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, Zaragoza 50018, Spain

*Email: *abad@icb.csic.es*

Abstract – Previously validated mathematical CLC models were used to simulate the process performance of CLC methane combustion using an impregnated Cu-based material and to analyze the effect of the fuel reactor design (being either a bubbling fluidized bed or a circulating fluidized bed). The CLC models consisted on the coupling of individual fuel and air reactor models to simulate steady state of a CLC unit. Individual models considered both the fluid dynamic of the fluidized beds at the each specific regime and the corresponding kinetics of oxygen carrier reactions. From the model outputs, the performance of the different systems were assessed by calculating the methane conversion in the fuel reactor and the solids conversion at both the fuel reactor and air reactor outlet. An analysis of the different CLC units with the mathematical model tool showed the feasibility to analyse the strong dependence of the process performance on the CLC plant design and oxygen carrier characteristics. Main results highlights that the selection of a suitable particle size of the oxygen carrier is a key factor to achieve complete combustion with low solids inventory in the fuel reactor. Thus, when the fuel reactor is operated in the bubbling fluidized bed regime, the required solids inventory would be 130 kg/MW$_{th}$ using an average particle size of 0.3 mm. However, with a circulating fluidized bed fuel reactor, complete combustion was predicted with 140 kg/MW$_{th}$ using an average particle size of 0.15 mm, while uncomplete combustion would be obtained if an average particle size of 0.3 mm was chosen. Conclusions for the optimization design of a CLC unit using the impregnated material will be drawn based on the results of the modeling and simulation.

INTRODUCTION

Chemical Looping Combustion, CLC, is one of the most promising processes to capture CO_2 at a low cost. It is based on the transfer of the oxygen from air to the fuel by using a solid oxygen carrier that circulates in dual fluidized bed systems. The CO_2 capture is inherent to this process, as the air does not get mixed with the fuel. The reactor scheme of the CLC process is shown in Fig. 1. The CLC process has been successfully demonstrated for gaseous fuels with a wide variety of oxygen carriers in multiple prototype plants, most of them with the configuration of two interconnected fluidized-bed reactors (Adanez, et al. 2012). In the fuel reactor, the oxygen carrier is reduced while the fuel is oxidized. In the air reactor, the oxygen carrier is oxidized again with air to its original state. The net chemical reaction and combustion enthalpy is the same as in a conventional combustion, where the fuel is burned in direct contact with oxygen from air.

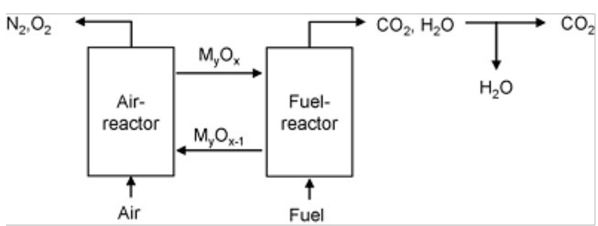

Fig. 1. Reactor scheme of the CLC process.

Up to now, CLC technology for gaseous fuels has been successfully demonstrated with more than 4000 hours of operational experience in continuous CLC plants up to 140 kW$_{th}$ using more than 40 different oxygen carriers (Adanez, et al. 2012). Among them, promising Cu-based oxygen carriers have been tested in several CLC facilities. These materials were prepared by the impregnation method, which is adequate for production of large amounts of solid particles at low cost. Our research group at Instituto de Carboquímica (ICB-CSIC) has optimized the impregnation method to develop highly reactive Cu-based oxygen carriers materials to be used during the scale-up of the CLC process (Cabello, et al. 2016). The next challenge is to upscale this technology from 140 kW_{th} to 10 MW_{th} since there is a promising niche application in on-field steam generation with CCS. Successful upscaling of this technology is highly dependent on the upscaling of two aspects in parallel, namely 1) upscaling of reactor system and 2) upscaling of oxygen carrier manufacture. Most efforts are being allocated to upscale the CLC system designs to the desired power of 10 MW (Sit, et al. 2013).

An interesting number of works can be found in the literature for the modelling of the reactors involved in a CLC system, as is presented in Adanez, et al. 2012. Modelling of fluidized-bed reactors can be divided into three main fields, which are closely connected: fluid dynamics, reaction scheme and kinetics, and heat balance. Fluid dynamics, mass balances and heat balances in the reactor must be solved simultaneously because of the variation of reaction rates and gas properties. Validation of the models against experimental results obtained in continuously operated CLC system is an important step before use them for design, optimization and scale-up purposes. However, few models have been validated against experimental results in continuously operated CLC units (Adanez, et al. 2012).

In this work, two validated CLC models are being used to analyze the relevance of the FR design in the performance of the process. In this way, a CLC model was developed for a bubbling fluidized bed, BFB, fuel reactor operated and validated against experimental results obtained during CH_4 combustion in a 10 kW_{th} CLC unit (Abad 2010). The second CLC model was developed and validated against experimental results obtained in a 120 kWth unit at TUV burning natural gas with a Cu impregnated oxygen carrier (Abad 2014a,b) and a circulating fluidized bed fuel reactor, CFB. Moreover, both the fuel and air reactor performance should be considered to optimize the operating and design conditions of a CLC unit. The CLC models consisted on the coupling of individual fuel and air reactor models to simulate steady state of a CLC unit. Individual models considered both the fluid dynamic of the fluidized beds at the each specific regime and the corresponding kinetics of oxygen carrier reactions. The reaction mechanism and reactivity depends on the pair gas-oxygen carrier considered, whereas the fluid dynamics is linked to the design and operating conditions of the reactor. The oxygen carrier considered was an impregnated Cu-based oxygen carrier.

MATHEMATICAL MODEL

To analyze and to optimize the performance of the CLC process, the CLC models were used. The required solids inventory in each reactor will depend on the oxygen transport capacity and reactivity of the oxygen carrier as well as the mass transference processes in the reactor. This last will be affected by the fluid dynamics properties of the air and fuel reactors, bubbling or circulating fluidized beds, as well as the oxygen carrier particles characteristics. Therefore, a reactor model should include both fluid dynamics and reaction kinetics in order to obtain the solids inventory needed to complete combustion of the fuel in a CLC unit.

Fluid dynamics. The BFB fuel reactor model includes both dense bed and freeboard regions. The hypotheses considered for the model were: steady state, isothermal bed at macroscopic level, perfect mixing of the solids in the dense bed and freeboard, no existence of particle fragmentation or attrition, and no elutriation. The model is one-dimensional and it considers lateral exchange of gas between bubbles and emulsion in the dense bed. The freeboard region starts from the upper limit of the dense bed, and it is characterized by a decrease in the solids concentration with the reactor height as proposed by Kunii and Levenspiel.

The CFB fluid dynamic model considers the reactor divided into two vertical regions with respect to axial concentration and backmixing of solids: a dense region in the bottom bed with a high and roughly constant concentration of solids; and a dilute region, where there is a pronounced decrease in the concentration of solids as height increases. Gas distribution and mixing between the emulsion and bubbles in the dense region was taken into account. Thus, the gas flow in the dense region was shared between the emulsion and bubble phases, with gas mixing between them controlled by diffusion. The dilute region had a cluster phase and a transport or dispersed phase. Both the cluster and transport phases were superimposed but with different mixing behaviour. The cluster phase had a strong solids backmixing with solids in the dense region. The transport phase was characterized by a core/annulus flow structure. It is worth noting that there is not a proper dense region in the air reactor because the high gas velocity and low solids inventory. Therefore, only the transport phase is considered for the air reactor. The global solids distribution in the reactors was calculated by fitting the total pressure drop in every reactor from the predicted solids concentration profile.

Mass balances

Mass balances for the different reacting compounds and products were developed for each phase in the different regions. The reaction for CH_4 conversion in the fuel reactor is shown in Equation (1) and the corresponding reaction in the air reactor is shown in Equation (2).

$$4\,CuO + CH_4 \rightarrow 4\,Cu + CO_2 + 2\,H_2O \tag{1}$$

$$2\,Cu + O_2 \rightarrow 2\,CuO \tag{2}$$

Oxygen carrier reduction and oxidation kinetics were determined by TGA and included in the models. The oxygen carrier particles were assumed to be composed by grains of metal oxide with a plate-like geometry on the porous surface of the support material, which react following a shrinking core model. The reaction rate was supposed to proceed by control of the chemical reaction in the gas-solid interphase.

Integration of the fuel reactor with the air. Each model is developed to simulate steady state conditions. But the solids conversion obtained from one reactor affects to the performance of the other reactor. Thus, conversion of the fuel is improved when the oxidation of oxygen carrier in the air reactor was increased. But for a high oxidation degree in the air reactor, the average reactivity of particles in the air reactor may be as low that the required value of conversion to transfer oxygen from air to fuel could not be reached. The consequence for this is that the CLC unit reach a steady state when the flow of oxygen transferred in the air reactor is equal to the oxygen transferred in the fuel reactor. This situation is given for determined values of solids conversion both in the fuel and air reactors. Therefore, the fuel and air reactor models are run consecutively until auto-convergence is reached, considering initially that all the oxygen carrier in the CLC unit is completely oxidized. Then, the solids conversion in every reactor progressively decreases until convergence is reached and results for steady state of the CLC unit are predicted.

The main outputs of the CLC models were: the fluid dynamics structure of the reactor, e.g. height of the dense bed and profiles of concentration and flow of solids in the freeboard; the axial profiles of gas composition and flows; the axial profiles of average conversion for the oxygen carrier; and the gas composition and solids flow in the reactor exit to the cyclone. From these outputs, the performance of the CLC system was assessed by calculating the CH_4 conversion in the fuel reactor and the solid conversions at both the fuel reactor and air reactor outlets. The performance of the CLC system was assessed by calculating the CH_4 conversion in the fuel reactor and the fraction of required oxygen taken by the oxygen carrier in the air reactor. Methane conversion was calculated by:

$$X_{CH_4} = \frac{F_{in,CH_4} - F_{out,CH_4}}{F_{in,CH_4}} \tag{3}$$

The fraction of oxygen taken by the oxygen carrier, Ω_{AR}, was calculated as the ratio of the amount of oxygen taken in the air reactor by the oxygen carrier to the oxygen demanded by the fuel for complete combustion.

$$\Omega_{AR} = \frac{F_{in,O_2} - F_{out,O_2}}{2F_{in,CH_4}} \tag{4}$$

RESULTS

The influence of the solids inventory, the circulation rate of solids, the oxidation degree of particles at the reactor inlet, the load of fuel gas, the reactor temperature, and the size of the oxygen carrier particles were analysed on the methane conversion. A key parameter for the design of a CLC system is the solids inventory in the fuel and air reactors, which are linked and dependent on the reactivity of the oxygen carrier and fluid dynamics of the reactor. The effect of mass transference processes and solids distribution in the air and fuel reactors can increase the actual solids inventory required in each one. The fluidization regime influences these issues, which mainly depends on particle properties and gas velocity.

As an example of simulation, Fig. 2 shows the axial profiles of gas and solids concentration in the fuel-reactor for a reference case for each BFB and CFB models of CLC process. Fig. 2(a) shows the axial profiles of molar flows of gases in the fuel reactor. The separation of the dense bed and the dilute region can be easily observed. The dense bed is stretched out to a height of H_b = 1.2 m, being characterized by a roughly constant solids concentration. Above the dense bed, the solids concentration decreases with the reactor height. In the dense bed, methane is slowly converted because the chemical reaction is restricted by the slow diffusion of methane from the bubbles to the emulsion phase, where reaction with the oxygen carrier happens. The major flow of methane goes through the bubble phase and the methane conversion in the dense bed is only 39%. In the dilute region above the dense bed, methane is converted faster than in the dense bed because an improved contact between gas and solids is found in this region. However, complete combustion is not reached because of the low solids fraction at the upper part of the reactor. This fact is because solids in cluster phase are more effective than solids in the dense bed converting methane. Fig. 2(b) shows gas and solid concentrations for the BFB fuel reactor CLC model. As it can be seen there is an important change in the profiles between the bottom bed and the freeboard regions. This fact is mainly due to the differences in the fluid dynamics of these two regions.

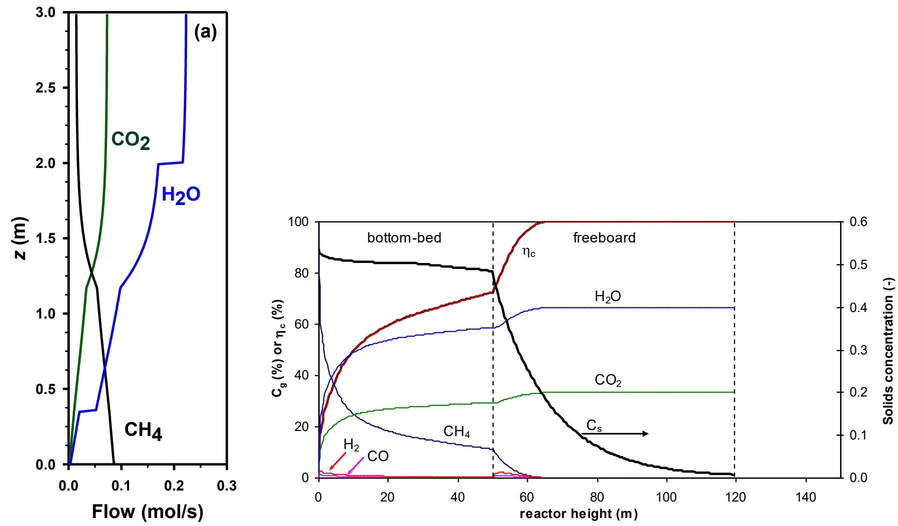

Fig. 2. Longitudinal profiles of gas and solids concentration in the fuel-reactor. (a) CFB fuel reactor model (b) BFB fuel reactor model.

Regarding the effect of the oxygen carrier particle size in BFB model, some increase in the methane conversion were found for higher particle size of the carrier (from 0.2 to 0.3 mm). This difference can be attributed to the different contact efficiency between gas and solids in the bottom bed. An increase in the particle size produces an increase in the minimum fluidization velocity and, thus, a decrease of gas flow in the bubble phase. On the other hand, the inventory of solids as a function of the ratio of oxygen carrier to fuel ratio, ϕ, and the conversion of the oxygen carrier at the fuel reactor inlet have been also analyzed. The inventory of solids predicted was lower than 80 kg/MW$_{th}$ when the ϕ value was > 2 at 800 ºC . However, the inventory of solids increases rapidly when the temperature decreases or the ϕ value approach the unity. For ϕ = 3, the solids inventory should be increased up to 280 kg/MW$_{th}$ at 750 ºC and 1200 kg/MW$_{th}$ at 700 ºC to reach a combustion efficiency of 99.9%.

In case of the CFB fuel reactor CLC model, a sensitivity analysis was done to the particle size of the oxygen carrier. The model predicts that a higher fraction of solids is in the dilute region as the particle size decreases, increasing the amount of particles both in the cluster and transport phases. The fuel conversion is higher when lower particle sizes are used due to the improved gas-solid contact in the dilute region compared to the dense bed. As a consequence, complete combustion of the fuel was predicted when the particle size of the oxygen carrier was lower than 0.14 mm. Moreover, the solids inventory in fuel reactor is a basic parameter that has to be defined, which may be modified by changing the pressure drop in the reactor. Fig. 3 shows the methane conversion predicted by the model as a function of the particle size of the oxygen carrier for several pressure drops in the reactor (which corresponds to different solid inventories). An increase in methane conversion was predicted as the particle size decreased; complete combustion can be reached for a particle size of 0.14 mm when the pressure drop in the reactor was 20 kPa, which corresponded to 130 kg/MW$_{th}$. Higher particle sizes would require higher pressure drops in the reactor.

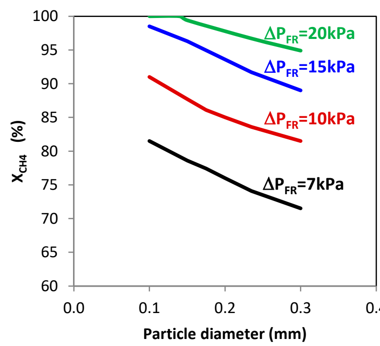

Fig. 3. Methane conversion predicted by the CFB fuel reactor CLC model as a function of the particle size of the oxygen carrier for different pressure drops in the fuel reactor.

The effect of solid inventory on both methane conversion in fuel reactor, X_{CH_4} , and oxygen fraction taken from the air reactor, Ω_{AR}, was investigated for different particle sizes. CFB model predictions showed an increase of X_{CH_4} and Ω_{AR} with an increase in solid inventory; see Fig. 4. However, the effect of particle size in the fuel reactor was different than in the air reactor. Thus, for low solids inventories in the air reactor, the effect of particle size on Ω_{AR} was negligible due to the air reactor only consist of dilute region at these conditions. But at high solid inventories, Ω_{AR} was lower with a particle size of 0.235 mm, due to the occurrence of the dense bed, which is less effective transferring oxygen from air to oxygen carrier. Thus, complete combustion can be reached with a particle size of 0.15 mm if solids inventory is 140 kg/MW$_{th}$ in fuel reactor and 350 kg/MW$_{th}$ in air reactor. Note that, the fuel and air reactor model were coupled to simulate steady state operation of the whole CLC pilot.

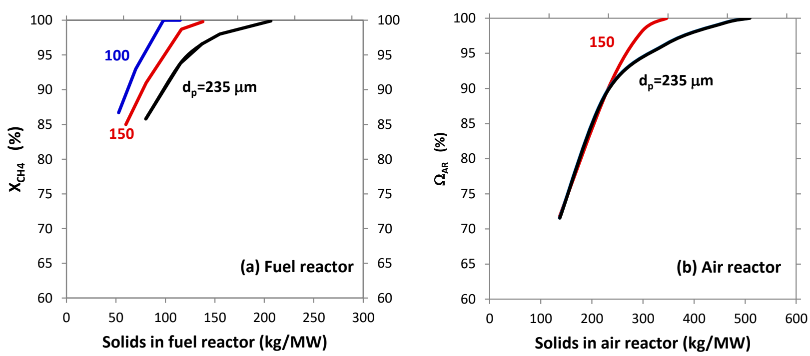

Fig. 4. (a) Methane conversion in fuel reactor, X_{CH_4} , and (b) oxygen fraction taken by the oxygen carrier in the air reactor, Ω_{AR}, predicted by the CFB fuel reactor model as a function of solids inventories in fuel and air reactors for different oxygen carrier particle size.

CONCLUSIONS

Two basic parameters must be considered in the design of a CLC system: the solids inventory in the fuel and air reactors, and the solids circulation flowrate between both reactors. As it was above shown, the solids inventory depends not only on the reactivity of the oxygen carrier but also on the fluid dynamic characteristics of the reactors. The solids inventory in the air reactor is higher than solids in the fuel reactor in most of cases. This fact shows the relevance of a proper design of the air reactor, in addition to the fuel reactor. In most of CLC units currently built, the air reactor was oversized to assure a high oxidation degree of the oxygen carrier. But if it is desired to decrease the amount of solids necessary, the air reactor must be evaluated in combination with the fuel reactor. Moreover, the required solids in CLC units are always higher than the minimum solids inventory, which were calculated considering uniquely the reactivity of materials. Restrictions related to mass transference processes in the reactors are responsible of the necessity for higher solids inventory, which affect in a complex way depending on the fluid dynamic characteristics of the fluidized bed reactors. To roughly, the required solids inventory can be between 1.5 and 4 times the calculated minimum solids inventory. Differences on solids inventory are also evident when different designs of CLC units are considered. Therefore, design parameters and operational conditions must be taken into account to determine the basic performance of a CLC unit.

It was found that in a BFB fuel reactor CLC process, the inventory of solids for a high conversion of the fuel was sensitive to the reactor's temperature, the solids' circulation rate and the extent to which the solids entering to the reactor had been regenerated. The optimal ratio of oxygen carrier to fuel was found to be 1.7 to 4 for a Cu-based oxygen carrier particle size of 0.3 mm. In this range, the fuel reactor solids inventory to obtain a complete methane conversion at 800 ºC was less than 130 kg/MW_{th}. On the other hand, in a CFB fuel reactor CLC process, complete combustion of methane could be reached with 140 kg/MW in the fuel reactor and 350 kg/MW in the air reactor with a particle size of 0.15 mm.

ACKNOWLEDGMENTS

This paper is based on the work performed in the frame of the European Commission Seventh Framework Program under the grant agreement N° 608571 (Project acronym SUCCESS).

REFERENCES

Abad, A, Adánez, J., García-Labiano, F, de Diego, LF, Gayán, P. Modeling of the chemical-looping combustion of methane using a Cu-based oxygen-carrier. 2010. Combustion and Flame 157, 602-615.

Abad, A, Gayán, P, de Diego, LF, García-Labiano, F, Adánez, J, Mayer, K, Penthor, S. 2014a. Modelling a CLC process improved by CLOU and validation in a 120 kW unit. 11th Int. Conference on Fluidized Bed Technology, Beijing.

Abad, A, Gayán, P, García-Labiano, F, de Diego, LF, Adánez, J. 2014b. Relevance of oxygen carrier characteristics on CLC design for gaseous fuels. 3rd International Conference on Chemical Looping, Goteborg.

Adanez, J., Abad, A., García-Labiano, F., Gayán, P., de Diego, L.F. 2012. Progress in Chemical-Looping Combustion and Reforming technologies. Prog. Energ. Combust 38, 215-282.

Cabello, A. Gayán, P. Abad, A. de Diego, L. F. García-Labiano, F. Izquierdo, M. T. Scullard, Williams, G. Adánez J. 2016. Long-lasting Cu-based Oxygen Carrier Material for Industrial Scale in Chemical Looping Combustion. International Journal of Greenhouse Gas Control, 52, 120-129.

Sit, SP, Reed, A, Hohenwarter, U, Horn, V, Marx, K, and Proell, T. 2013. Energy Procedia, 37, 671.