Operational feasibility of biomass combustion with *in situ* CO₂ capture by CaO during 360 h in a 300 kW_{th} calcium looping facility

M.E. Diego^{*1}, M. Alonso

National Institute of Coal - Spanish Research Council (INCAR-CSIC), Francisco Pintado Fe 26, 33011 Oviedo, Spain

ABSTRACT

Simultaneous biomass combustion and CO₂ capture using CaO, namely *in situ* calcium looping, has been proposed as a potential energy generation option with negative CO₂ emissions. Previous pilot plant trials have already proven the technical feasibility of this process concept in pilot plants of up to 300 kW_{th}. However, this study goes a step further and analyses the operational feasibility of these systems. For this purpose, a 360 h *in situ* calcium looping experiment was conducted in La Robla 300 kW_{th} facility in continuous mode, which is the longest calcium looping test so far conducted at pilot plant scale, to the best of our knowledge. Operational stability was achieved and maintained throughout the entire experiment. Control of the facility was easily kept by performing slight modifications to the biomass and air feeding rates in order to ensure adequate temperatures and active bed inventories within the reactors, as well as sufficient solid circulation rates. As a result, high CO₂ capture efficiencies of over 70% were achieved during most of the test. The successful results obtained not only confirm the technical viability but also prove the operational feasibility of the *in situ* CO₂ capture concept using CaO at high temperature at the 300 kW_{th} plant scale, which is crucial for the future development of this type of CO₂ capture technology.

^{*}Corresponding author. E-mail: marlen@incarcsic.es

KEYWORDS

BECCS, Bio-CCS, Calcium Looping, Biomass combustion, Negative emissions, CO₂ capture

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¹ Present address: Energy 2050, Energy Engineering Group, Department of Mechanical Engineering, University of Sheffield, Western Bank, Sheffield, United Kingdom. E-mail: m.diego@sheffield.ac.uk

23 1. INTRODUCTION

24 Biomass energy generation processes coupled with carbon capture and storage technologies
25 (BECCS) possess great potential for reducing the global concentration of CO₂ in the atmosphere [1], since
26 they are closely associated with the concept of negative emissions [2, 3]. It is foreseen that the deployment of
27 these carbon-negative technologies will play a key role in the most demanding scenarios of climate change
28 mitigation, as they can contribute greatly to meeting the challenging CO₂ reduction targets by reversing the
29 emissions of CO₂ [4, 5]. It is for this reason that they are currently attracting a great deal of attention
30 worldwide and large efforts are being devoted to developing such systems [1, 3, 4, 6-8]. The present work
31 deals with a carbon-negative energy generation option that combines biomass combustion with *in situ*
32 calcium looping as a technology for CO₂ capture.

33 The *in situ* calcium looping process is schematically outlined in Figure 1. It is based on the reversible
34 reaction between CO₂ and CaO and involves the use of two interconnected circulating fluidized bed
35 combustors (CFBCs), i.e., the combustor-carbonator and the combustor-calciner. The combustor-carbonator
36 operates as an air-fired biomass combustor at moderate temperatures of around 700°C, and the CO₂
37 generated is simultaneously captured inside the reactor by a flow of CaO particles ~~that arrives continuously~~
38 ~~from the combustor calciner~~. The CaCO₃ formed is circulated to the oxy-fired combustor-calciner, which
39 operates ~~as an oxy-fired combustor~~ at temperatures of around 840-900°C, typical of CFBCs [9]. As a result,
40 the CaCO₃ is decomposed into CaO particles that are circulated back to the combustor-carbonator, and into a
41 highly-concentrated CO₂ gas stream that, after undergoing purification and compression processes, is finally
42 stored. In addition, a CaCO₃ flow is introduced into the system (leading to an equivalent purge, as shown in
43 Figure 1), which serves to compensate for gradual loss of CaO activity towards CO₂ as a result of the
44 carbonation-calcination cycles, and for any small losses of solids that may occur in the cyclones. Similar
45 calcium loops are also employed in post-combustion calcium looping technology, which has already been
46 successfully tested in a number of pilot plants at the MW_{th} scale [10-12]. Unlike these post-combustion
47 systems, the *in situ* calcium looping concept takes advantage of the high operating temperatures of calcium
48 looping systems that allow biomass combustion and efficient CO₂ capture processes to take place
49 simultaneously inside the combustor-carbonator [13]. A recent cost analysis highlighted the potential of *in*
50 *situ* calcium looping systems [14]. The study concluded that such systems may be more favourable than oxy-

51 fired biomass plants alone in terms of CO₂ avoided cost, especially when the effect of the carbon price
 52 (emission trading system) and/or the availability of green certificates have to be taken into account. Further
 53 cost benefits can be achieved if biomass plants equipped with *in situ* calcium looping are integrated in larger
 54 systems [14].

55
 56 Figure 1. Scheme of the *in situ* calcium looping process for CO₂ capture.

57 The process of Figure 1 has been proven to be technically feasible at the INCAR-CSIC 30 kW_{th}
 58 facility [15] and at La Robla 300 kW_{th} pilot plant [16]. Reproducible results were obtained in both facilities
 59 despite the increase in scale [17], with CO₂ capture efficiencies in the range of 70-95% and a highly effective
 60 combustion in the combustor-carbonator [15, 16]. The aim of the present work is to go a step further and
 61 prove the operational feasibility of the *in situ* calcium looping process at the 300 kW_{th} scale. For this
 62 purpose, a continuous, long-duration experiment was carried out in La Robla pilot plant, the results of which
 63 are discussed and analyzed below.

64 2. EXPERIMENTAL

65 The experimental campaign presented in this work was conducted in La Robla 300 kW_{th} calcium
 66 looping pilot plant, property of Gas Natural Fenosa, which is located in León (Spain) inside the premises of a
 67 655 MW_e pulverized coal power plant that belongs to the aforementioned company. This facility (shown in
 68 Figure 2a) has been described in detail elsewhere [16, 17], but its main features will be outlined here for the
 69 sake of clarification. As indicated in Figure 2b, it employs two interconnected CFB reactors, a combustor-
 70 carbonator and a combustor-calciner, which are 12 m high and have an internal diameter of 0.4 m. These

71 reactors ~~are interconnected by means of bubbling bed loop seals and they~~ operate at temperatures of around
 72 700°C and 840-930°C, respectively. ~~Biomass is used as fuel in the facility and is fed through water-cooled~~
 73 ~~screw feeders to both the combustor-carbonator and the combustor-calcliner. Biomass C~~ombustion takes
 74 place inside both reactors using air ~~provided by two blowers~~ (although the calcination of CaCO_3 in the
 75 calcium looping process is carried out using a mixture of O_2/CO_2 , no oxy-calcination takes place in this pilot
 76 plant for the sake of simplicity). Limestone can ~~also~~ be continuously fed to the combustor-carbonator ~~using a~~
 77 ~~screw feeder~~. This facility is equipped with primary cyclones which close the main loop. A secondary
 78 cyclone is installed at the exit of the combustor-carbonator primary cyclone in order to retain finer solids that
 79 escape with the flue gas, contributing to a more accurate closure of the mass balance. Due to the certain
 80 specific features of this facility (lack of proper insulation after the primary cyclone of the combustor-
 81 calciner), no secondary cyclone was installed for the gas exiting the combustor-calcliner. Instead, a fan
 82 which blows air into the combustor-calcliner gas stream and increases the velocity of the gas flow through the
 83 duct is employed for the long-duration experimental campaign described in this work (see Figure 2b). This
 84 prevents the deposition of carbonate in this region, as the injection of air at this point produces a sharp
 85 decrease in temperature and in CO_2 concentration at the exit of the primary cyclone, and ensures a reduction
 86 in the residence time of the CaO particles in the duct. All the elements in the facility are refractory-lined or
 87 thermally insulated to minimize heat losses. However, water jackets are installed along the line that carries
 88 the solids from the combustor-calcliner to the combustor-carbonator (see black-shaded area in Figure 2b) ~~it is~~
 89 ~~necessary~~ to extract a fraction of the combustion and the carbonation heat from the combustor-carbonator ~~to~~
 90 and maintain the reactor at $\sim 700^\circ\text{C}$. ~~This is achieved by means of water jackets that are installed along the~~
 91 ~~line that carries the solids from the combustor-calcliner to the combustor-carbonator (see black-shaded area in~~
 92 ~~Figure 2b). Moreover, a 100 kW_{th} propane burner is placed in each reactor for start-up purposes. The pilot~~
 93 plant is equipped with T(i) temperature and pressure taps are distributed throughout the facility so that the
 94 ~~process can be to continuously monitored and the bed inventories inside the reactors can be accurately~~
 95 ~~estimated the process.;~~ (ii) ~~T~~two gas analysers ~~are located at the exit of the reactors for the continuous~~
 96 measurement that continuously measure of the CO_2 , O_2 and CO content (C_xH_y ~~measurement as CH_4 is also~~
 97 ~~present in one of the analysers)~~ composition of the exiting gases. (iii) ~~O~~xygen probes ~~are~~ located at the
 98 bottom of the combustor-calcliner and at the central part and at the outlet of the combustor-carbonator to
 99 follow the combustion reaction. ~~and (iv) These probes serve to detect possible leakage of fluidization air on~~

its way from the combustor-carbonator loop seal to the cyclone. Isokinetic probes are placed at the exits of the reactors to experimentally estimate the solid circulation rate and periodically extract solid samples. The solid circulation rate is also calculated by performing an energy balance at the point where the water jackets are placed.

Figure 2. (a) View and (b) schematic of La Robla 300 kW_{th} calcium looping pilot plant.

With the gas composition measurements obtained above it is possible to estimate the CO₂ capture efficiency inside the combustor-carbonator by means of the following equation:

$$E_{\text{carb}} = \frac{F_{\text{CO}_2, \text{comb}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{comb}}} \quad (1)$$

where $F_{\text{CO}_2, \text{out}}$ is the molar flow of CO₂ that exits the combustor-carbonator and $F_{\text{CO}_2, \text{comb}}$ is the CO₂ molar flow rate generated by the combustion of biomass in this reactor. $F_{\text{CO}_2, \text{comb}}$ in equation 1 is calculated by means of an oxygen balance and the elemental analysis of the biomass as described elsewhere [18].

The experimental CO₂ capture efficiency can be compared with the maximum CO₂ capture efficiency allowed by the equilibrium, E_{eq} , which is highly dependent on temperature. The calculation of E_{eq} performed by means of equation 2 makes use of the equilibrium molar flow of CO₂ at the exit of the combustor-carbonator, $F_{\text{CO}_2, \text{eq}}$, which can be obtained from the CaO-CaCO₃ equilibrium curve.

$$E_{\text{eq}} = \frac{F_{\text{CO}_2, \text{comb}} - F_{\text{CO}_2, \text{eq}}}{F_{\text{CO}_2, \text{comb}}} \quad (2)$$

As mentioned elsewhere [16, 17], the tests in this pilot plant begin by feeding the system with approximately 300 kg of fresh limestone. The start up process progresses with a gradual increase in temperature in all the elements of the pilot plant due to propane fired burners. The gas velocity in the reactors is kept at low values during this period to avoid the circulation of a large stream of low temperature solids and thereby, favouring the heating up process. When the bed temperature in the reactors is around 400°C and that of the secondary cyclones is above 100°C (to avoid water condensation), biomass is fed at a low rate to the combustor carbonator and the combustor calciner. As soon as the solid beds of both reactors reach 550°C, the propane burners are switched off and more biomass is fed in in compensation. Once this temperature is close to 650°C, the air and biomass feeding rate is increased to favour the circulation rate of the solids between the reactors. As a result, the temperature of the facility rises, and water is fed through the cooling jackets located in between the combustor calciner and the combustor carbonator when these jackets achieve a maximum temperature of 300°C to minimize thermal stresses. Once the combustor carbonator reaches 700°C, the biomass fed to this reactor is limited, while the air-biomass mixture fed to the combustor calciner is gradually increased to attain the targeted calcination temperatures.

Table 1. Key operating conditions during the experimental test.

Biomass composition	47.23% C, 40.01% O, 0.19% N, 6.87% H ₂ O, 5.69% H, 0.01% S
Biomass LHV (MJ/kg)	19.2
Combustor-carbonator temperature (°C)	660-730
Gas velocity within the combustor-carbonator (m/s)	1.3-1.8
Inventory of solids in the combustor-carbonator (kg/m ²)	150-345
CO ₂ concentration in the combustor carbonator due to combustion (% vol)	8.4-13.6
Solid circulation rate (kg/m ² s)	1.0-2.5
CO ₂ capture efficiency (%)	60-86
Combustor-calciner temperature (°C)	835-930

The tests carried out in this pilot plant followed the start-up procedure described in detail elsewhere [16, 17]. After the start-up this initial period, La Robla 300 kW_{th} pilot plant was operated under the conditions summarized in Table 1. Pine pellets were used as biomass in both reactors, with a composition and heating values as summarized in Table 1. As can be seen, biomass used has negligible sulfur content (as it is usual in biomass fuels) and therefore, no deactivation of the sorbent takes place in the *in situ* capture systems due to

137 reaction between active CaO particles and SO₂, unlike other calcium looping systems [19]. Limestone with
138 an initial mean particle diameter of 93 μm was fed to the combustor-carbonator to ensure sufficient active
139 bed inventories in both reactors and to maintain stable solid circulation rates. Continuous operation was
140 achieved in the pilot plant for 360 hours, the longest continuous steady state test conducted so far in a
141 calcium looping facility to the best of our knowledge.

142 3. RESULTS AND DISCUSSION

143 The results of the test discussed in this work are depicted in Figure 3. It shows that the pilot plant
144 functioned with an exceptional degree of stability for 360 hours. The combustor-carbonator operated steadily
145 at an average temperature of 700 °C, whereas the combustor-calciner operated at between 835 and 930 °C.
146 The solids inventory in the combustor-carbonator was maintained at an average value of 240 kg/m², as can
147 be seen in Figure 3a. The average gas concentrations measured by the gas analysers at the exit of the
148 combustor-carbonator were 9.5%vol O₂, 3.7%vol CO₂ and 0.2%vol CO (see Figure 3b), and no unburnt
149 hydrocarbons were detected. The aim of the excess of air used in the combustor-carbonator, compared with
150 the stoichiometric ratio of 5.67, was to increase combustion efficiency given the limited inventory of solids
151 in the reactor. The high CO concentration at the exit of the combustor-carbonator can be mainly attributed to
152 the relatively high temperature profiles between the lower and upper zones in this reactor (around 30-60°C-
153 since the solid circulation rates during the experiments were low), and possibly to the low bed inventory
154 [16]. Under these experimental conditions CO₂ capture efficiency was high and very close to that of
155 equilibrium as shown in Figure 3c, resulting in a normalized CO₂ capture efficiency value (i.e. E_{carb}/E_{eq} ratio)
156 of over 80%. During the last 30 hours of the experiment, the loss of solids from the primary cycle (i.e., after
157 the primary cyclones) increased substantially due to mechanical issues, as these pilot rigs are not usually
158 designed for continuous operation over such long periods. In order to compensate for this and maintain the
159 solid circulation flow between the reactors, the gas velocity in the combustor-calciner was increased. This
160 led to a lower degree of calcination inside this reactor (since the residence time of the particles in the
161 combustor-calciner was reduced), and a decrease in the active fraction of CaO present in the combustor-
162 carbonator inventory. As a result, the normalized CO₂ capture efficiency fell to values close to 70% (CO₂
163 capture efficiency of around 65%).

Figure 3. Representation of the main results and key operating conditions of the 360 h continuous experiment in La Robla 300 kW_{th} pilot plant.

The results shown in Figure 3 are of great importance. They demonstrate the stable operation of this *in situ* calcium looping process at the 300 kW_{th} scale under conditions of high CO₂ capture efficiency over a period of more than two weeks of continuous operation. Control of the pilot plant during the test was easily maintained with only small variations in key parameters, such as the temperature inside the reactors and the solid circulation rate (i.e., changes in the air and biomass feeding rate), and the solids inventory in the combustor-carbonator. Therefore, the long-duration experiment described in this work not only corroborates the technical viability but also demonstrates the operational feasibility of this calcium looping process with

simultaneous biomass combustion and CO₂ capture at the 300 kW_{th} scale, which provides confidence for the scale-up of this type of capture systems.

4. CONCLUSIONS

Continuous and stable operation has been achieved in an *in situ* calcium looping CO₂ capture facility of 300 kW_{th} for 360 h, resulting in high and constant CO₂ capture efficiencies in the range of 60-85%. Operational control was easily implemented and managed by the operators of the pilot plant. The simplicity of the operating process, together with the stability maintained over such a long period with a high CO₂ capture efficiency in the pilot testing facility, demonstrate the technical and operational feasibility of the CO₂ capture concept discussed in this work. The successful results presented in this study constitute an important contribution to the scale-up and future deployment of this technology among other BECCS options.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Prof. Juan Carlos Abanades for his valuable suggestions. The support received from Gas Natural Fenosa, especially from John Chamberlain and Carlos Pérez is also gratefully acknowledged. The work of David Muelas, Eli Pasalodos, Alberto Fernández, Francisco Velado, Jesús García and Armando Fernández, who were excellent operators during the experimental campaigns carried out in La Robla 300 kW_{th} pilot plant is also greatly appreciated.

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