CaLby2030

Decarbonising industrial processes with Calcium Looping

D3.1

Deliverable D3.2: Results of the experimental campaigns in the 1.7 MW_{th} pilot plant, I

Date: 30 of September 2024

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D3.2: Results of the experimental campaigns in the 1.7 MWth pilot plant, I

Deliverable title	Results of the experimental campaigns in the 1.7 MWth pilot plant, I
Work Package	WP3 - Pilot demonstration of advanced CFB-CaL in residual-biomass power plants (including WtE)
Lead beneficiary	CSIC
Due Date	30/09/2024 (M24)
Actual delivery date	30/09/2024 (M24)
Dissemination level	Sensible
Abstract	This deliverable presents the experimental results obtained to date in experimental campaigns carried out in la Pereda CFB-CaL pilot, under Task 3.2 of the CaLby2030 project. Progress in all sub-tasks has been achieved thanks to these results, including some key objectives of WP3. About 720 hours of additional operations on the pilot have been executed, accumulating more than 1320 hours since the beginning of CaLby2030. Successful initial tests achieved calcination efficiencies of between 96-98% when operating the calciner under oxy-combustion conditions burning biomass pellets. After solving issues linked to the solid circulation between reactors, tests with CO_2 capture in the carbonator demonstrated the stability and controllability of the pilot when using biomass as a fuel in the calciner, reaching in some dedicated tests CO_2 capture efficiencies over 99%. Interpretation of the results is consistent with basic models of the reactors and will supply information for the tuning of more advanced, dynamic and scalable models under development in WP4, supporting also design decisions for WP1-WP2. Preliminary tests on the la Pereda pilot, feeding plastics containing F and Cl as a proxy of WtE plants, indicate an extreme efficiency of the CFB-CaL system to capture in the solid phase Cl and F acid gases. These results are to be confirmed in future tests involving more realistic conditions (i.e. $Ca(OH)_2$ powder injection to the carbonator, gas recycle in the calciner, full operation with flue gases in the carbonator) and in independent analysis of solid samples (Task 3.3 ongoing), to be reported in D3.3.
Project Acronym	CaLby2030
Project Call	**HORIZON-CL5-2021-D3-02-13**
Type of Action	**HORIZON EUROPE - Research and Innovation Action**
Project Start Date	01/10/2022
Project duration	42 months
Grant Number	101075416

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HISTORY OF CHANGES

VERSION	DATE	MODIFICATION	PREPARED BY	APPROVED BY
1.0	12/09/2024	Initial full version	Borja Arias, Alberto Mendez, Paula Fernández, Yolanda Álvarez, Roberto García, Loreto Suarez, Javier Camús, Mónica Alonso, Marlén Diego, Juan Carlos Abanades, Igor Finca, María Lorenzo, Eduardo de Llera, Martin Haaf, Mais Baqain	Coordination team

EXECUTIVE SUMMARY

The DoA describes in Task 3.2 a series of subtasks that imply extensive pilot testing of CFB-CaL system at TRL6 in "la Pereda" pilot, to supply information for model validation purposes (WP4 and WP5) and support design activities in WP2 and WP1. This deliverable D3.2 represents a major step in the achievement of all WP3 project objectives because virtually all the targeted test campaigns anticipated have been initiated and/or even completed. As discussed in D3.1, the task in WP3 will be completed when additional retrofits are implemented on the pilot to allow $Ca(OH)_2$ feeding to the carbonator and a full flue gas recycle in the calciner to resemble realistic gas atmospheres in future commercial CFB oxy-fired calciners using biomass as a fuel.

This deliverable presents the experimental results from experiments that add about 700 hours of additional operation experience on the pilot, accumulating more than 1320 hours since the beginning of CaLby2030. The CFB-CaL pilot has demonstrated again the capability to operate CFB-CaL systems under stable and rather predictable steady state conditions. The oxy-calcination tests (Task 3.2.1), carried out after the retrofits that made the pilot functional again (see D3.1), have confirmed the capability of the pilot to reach intense oxy-calcination conditions when using biomass pellets as a fuel in the CFB-calciner, with calcination efficiencies between 96-98%. These have also demonstrated the possibility of operating the calciner under low excess of oxygen (i.e. below 1%v O_2) with moderate emissions of CO and unburnt carbon, positive impacts on NOx emissions (<200 ppm_v).

Due to operational and regulatory issues, most of the tests reported in this deliverable had to be carried out operating the CFB-CaL pilot in stand-alone mode (i.e. with the main power plant of la Pereda off) and no supply of flue gases. However, tests with CO_2 capture (Task 3.2.3) in the carbonator using air-CO_2 mixtures demonstrated the stability and controllability of the pilot when using biomass as a fuel in the calciner, reaching in some dedicated tests CO_2 capture efficiencies over 99%. These were obtained when the make-up flow of limestone was sufficiently high (to ensure CO_2 carrying capacities of the circulating solids over 0.4) and the temperature at the top of the calciner was maintained below 550ºC (by introducing the four bayonet tubes with cooling water circulating in its interior). These results were useful to plan for the future retrofit of a $Ca(OH)_2$ solid injection line, that should be able to reach similar CO_2 capture rates also with standard make up flows of limestone in post combustion applications.

Another achieved objective in these tests was linked to the task to generate a database of dynamic experimental information (Task 3.2.1 referring to WP2, WP4-5) on how the CFB-CaL reactor system behaves to step-changes or gradual changes in some of the operating conditions. Thus, some tests dedicated to dynamic experiments by modulating changes in the CO_2 concentration and gas velocities to the carbonator were carried out in la Pereda pilot plant. Closure of the carbon balances (by frequent sampling of solids with isokinetic probes) and general qualitative trends were in agreement with known impacts of and relationships of the key variables in the CFB-CaL system. The interpretation of the steady state periods is consistent with basic models of the reactors and will supply information for the tuning of more advanced, dynamic and scalable models under development in WP4, supporting also design decisions for WP1-WP2.

Finally, preliminary tests on the la Pereda pilot, feeding plastics containing F and Cl as a proxy of WtE plants, indicate an extreme efficiency of the CFB-CaL system to capture in the solid phase Cl and F acid gases. These results are to be confirmed in future tests involving more realistic conditions (i.e. $Ca(OH)_2$ powder injection to the carbonator, gas recycle in the calciner, full operation with flue gases in the carbonator) and in independent analysis of solid samples (Task 3.3 ongoing), to be reported in D3.3.

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1 INTRODUCTION AND SCOPE

As described in D3.1, the pilot plant of la Pereda has been retrofitted and made functional again after a long period of inactivity since 2018. This has allowed rapid progress in Task 3.2 on the objectives set up for WP3 in the CaLby2030 DoA. This deliverable D3.1 represents progress towards the following objectives:

1) *To demonstrate a CFB-CaL system for WtE and Bio-CHP power plants in a 1.7 MW_{th} CFB-CaL.* This has been partially achieved by carrying out oxy-combustion calcination test in the calciner using biomass as a fuel (see section 3 below) and by conducting experiments using as a proxy of WtE polymers containing Cl and F (see section 6).
2) *To demonstrate CO_2 capture rates over 99%*. This has been partially achieved (see section 5) by feeding high make up flows of limestone to ensure highly active circulating material and by cooling the top section of the carbonator. The results have been published in a peer reviewed paper (Arias et al 2024). The use of using $Ca(OH)_2$ as an additional sorbent is pending.
3) *To demonstrate the oxy-fired calcination of $CaCO_3$ with solids conversions efficiencies over 99%, using residual biomass and solid recovered fuels*; This has been completely achieved (see section 3 below) using biomass and a partially achieved using proxies of alternative fuels by injecting polymers containing F and Cl to the oxy-fired calciner (see section 6).
4) *To generate a database of experimental information useful for modelling/scaling up purposes in WP4, including dynamic operation data for WP2*; This has partially been completed as all the results (including Annex and datalogs) are made available to relevant project partners in WP2, WP4-5 for modelling and scale up purposes.
5) *To validate the circularity of CaO-rich purges in industrial uses of lime/hydrated lime and cement.* This has been initiated by gathering a large number of solid samples for future analysis as relevant for Task 3.3.

To facilitate the reading of the deliverable, understanding the limitations of the pilot at any point in time during the description of the results, this report has been organised in close-to-chronological Sections (3-6), with a first introductory section describing the pilot and the methodology to extract the maximum empirical information from the experiments (Section 2), test involving oxy-combustion of biomass in the calciner including close-to-stoichiometric combustion conditions (Section 3), dynamic test in support of WP2 and other dynamic modelling activities (Section 4), test results from experiments targeting CO_2 capture efficiencies over 99% (Section 5) and new test results involving combustion of a proxy fuel containing F and Cl in characteristic concentrations in Waste to Energy plants (Section 6). In addition to the qualitative and semi-quantitative interpretation of results provided in sections 3-6, there is an Annex and associated data-logs and lab results from solid characterization tests available to relevant partners in reactor modelling activities in WP2 and WP4-5.

2 DESCRIPTION OF THE PILOT AND THE EXPERIMENTAL METHODOLOGY TO ANALYZE THE EXPERIMENTAL INFORMATION

This section presents a brief description of the experimental facility (for more details on the pilot and its functionalities see D3.1) and the methodology used to interpret the experimental information obtained from the pilot plant. The CFB-CaL pilot of La Pereda remains the largest Calcium Looping pilot in the world and the one that has produced and published the most results (Arias et al. 2013, Diego et al. 2016, Diego et al. 2017, Arias et al. 2018, Diego et al. 2020) from over 5000 hours of operational experience. The pilot is integrated with the existing 50 MWe CFB power plant of HUNOSA, that is going to undergo a major retrofit to allow biomass firing and completely face out coal combustion from 2025. A general scheme of the interconnected carbonator and calciner reactors at the core of the la Pereda pilot facility is shown in Figure 1. The reactors are manufactured with an inert core of refractory and external steel walls. They have a total height of 15 m and the internal diameter of the carbonator and calciner is 0.65 and 0.75 m, respectively. Each reactor is equipped with a high efficiency cyclone at the gas exit. The solids leaving each reactor are separated from the gas phase and are directed by gravity trough two standpipes to a loop seal. The design of the loops seals includes two exits, that allows to split the flow of solids coming from each cyclone to the same reactor (internal circulation) and/or to the opposite (external circulation). The carbonator can be fluidized using air, flue gas from the existing power plant or a synthetic flue gas produced by mixing air with CO_2 coming from a cryogenic tank. The calciner can be fluidized using air or a mixture of O_2 and CO_2 for oxy-combustion-calcination tests. The calciner is equipped with a fuel and limestone feeding system composed of two independent dosification silos. Also, there is a continuous solid extraction system (a water-cooled screw) installed in the calciner that allows the control of the total solid inventory in the system (see below). On the other hand, the carbonator is equipped with a heat extraction system using bayonet water-cooled tubes, in order to control the reactor temperature as will be discussed below.

The instrumentation of the La Pereda pilot plant allows to manually control the system and also to obtain the maximum experimental information (pressure drops, solid samples, gas composition, temperature...). Most of this information, specially the data affecting the gas characteristics, is continuously measured and recorded with a data logging system. Regarding the solids, there are several pressure measurements along the risers in order to determine the distribution of solids and the total inventory. There are also pressure measurements in the stand pipes to follow the circulation of solids and to detect their accumulation. There are three gas analyzers to measure the composition of the gas entering the carbonator and leaving the reactors. These allow to measure the O_2, CO_2, CO, SO_2 and NO_x concentration. Also, a new gas analysis system composed by a FTIR gas analyzer able to measure the composition of acid gases (HCl, HF, NOx, SO_2, etc.) and unburnt hydrocarbons at the inlet of the carbonator and the exit of the reactors has been installed in the pilot within Calby2030 project (see D3.1). Another important part of the experimental information related to the inventory of solids (composition, carbonation conversion and reactivity towards CO_2) is determined using samples taken periodically from the reactors (up to three samples per hour in some experiments as noted below).

Concerning the methodologies used to assess the performance of the pilot, the following paragraphs refer to the methods applied to treat data from carbonator and calciner reactors. In the case of the carbonator, the main variables that affect the performance of the reactor are:

- The inventory of solids in the carbonator (n_{Ca} in Figure 1). This variable can be estimated continuously using the measurement of the pressure difference between the plane above the distributor and the exit of the riser.

- The average carbonator reactor temperature (T_{carb} in Figure 1). The carbonator reactor has a certain axial temperature profile due to the effect of the bayonet tubes, the exothermic character of the carbonation reactor (more intense in the dense bottom part of the carbonator) and the arrival of high temperature solids from the calciner (at between 830ºC-920ºC). As discussed in Section 5 of this deliverable, this temperature axial profile facilitates to enhance the CO_2 capture efficiency in the carbonator. However, increasing internal solid circulation (within the reactor through solid convective flows and through the recirculating solids from the cyclone-double loop seal system) can drastically reduce this difference of temperature to just 20-30ºC.
- The molar flow of CO_2 entering the carbonator with the flue gas ($F_{CO2, in}$ in Figure 1). The composition of the flue gas entering the carbonator and the mass flow rate are measured continuously.
- The average composition of the solids arriving to the carbonator and CO_2 carrying capacity (X_{ave} in Figure 1). Frequent solid sampling from suitable entry and exit ports is feasible with an isokinetic probe system. Chemical analysis, (CaO, $CaCO_3$, $CaSO_4$, ashes), CO_2 carrying capacity and carbonation reaction rates are determined from the samples taken periodically during the tests by thermogravimetric techniques, as these are needed to close the carbon mass balances in the system as described below.
- The molar circulation rate between carbonator and calciner reactors (F_{Ca} in Figure 1). This variable can be estimated by two methods in parallel when the system operates in steady state: the closure of the carbon balance and the closure of the heat balance in the carbonator. The total solid circulation rate through the risers can also be measured using a suction probe in isokinetic conditions at the exit of the riser. The carbonator riser is 15 m height and solids are largely disengaged from the gas at this height. Therefore, upwards solid circulation at that point is close to total solid circulation between reactors.

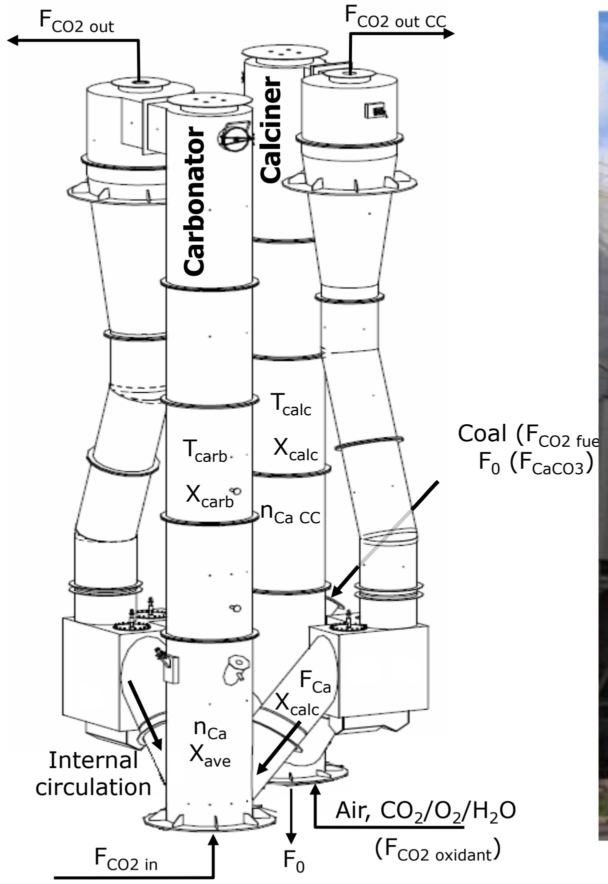

Figure 1. Schematics of the pilot plant facility and the main mass flows and operating variables involved in the test campaigns (left) and a photo of the pilot building (right).

The CO_2 capture efficiency in the carbonator (E_{carb}) is defined as the amount of CO_2 captured respect to the CO_2 fed to the carbonator and can be calculated as follows:

$$E_{Carb} = \frac{F_{CO_2 in} - F_{CO_2 out}}{F_{CO_2 in}} \qquad \text{Equation 1}$$

where F_{CO2} is molar flow of CO_2 (mol/m^{2}s). In a steady state, the overall CO_2 mass balance of the system can be written and calculated using three approaches.

$$\begin{pmatrix} CO_2 \text{ reacting} \\ \text{with CaO in the bed} \end{pmatrix} = \begin{pmatrix} CaCO_3 \text{ formed in the} \\ \text{circulating stream of CaO} \end{pmatrix} = \begin{pmatrix} CO_2 \text{ removed} \\ \text{from the gas phase} \end{pmatrix} \qquad \text{Equation 2}$$

Each term of this mass balance can be calculated independently using experimental measurements available in the pilot plant. Then, the values can be compared to analyse the steady state of the system and confirm the consistency of all involved measurements. The CO_2 removed from the gas phase is the most reliable term to evaluate capture efficiencies, as it can be determined directly from the continuous measurements of flue gas fed into the carbonator and the gas composition entering and leaving the reactor. An aspect to be considered when determining the CO_2

captured is a possible source of CO_2 in the carbonator from the solid fuel used in the calciner. If some unconverted fuel solids (i.e. char) reach the carbonator with the CaO stream, they can partially be burnt in the carbonator bed, thus producing additional CO_2. Determining the oxygen mass flow after and before the carbonator allows to evaluate if combustion is taking place in the carbonator, calculating the amount of CO_2 produced to correct the carbon balance in Equation 1.

Under steady state conditions, when there is no accumulation of CO_2 in the carbonator bed, the amount of CO_2 captured from the gas phase has to be the same as the $CaCO_3$ formed in the circulating stream of CaO. Thus, the following condition should be fulfilled:

$$E_{Carb}\, F_{CO_2\,in} = F_{Ca} \times (X_{carb} - X_{calc}) \qquad \text{Equation 3}$$

where F_{Ca} is the molar flow (mol/ m^{2}s) of CaO entering into the carbonator, X_{carb} is the carbonate content of the solids leaving the carbonator and X_{calc} is the carbonate content of the solids coming from the calciner and entering the carbonator. Considering the calciner and carbonator as perfect mixed reactors, it can be assumed that the composition of the solid in the bed is the same as the solids leaving the riser. Then, the molar flow of CaO (F_{Ca}) can be estimated from Equation 3 knowing carbonate composition of the solids extracted from carbonator and calciner during the experiment.

As was indicated above, another approach to calculate the mass flow of solids between reactors can be used by solving the energy balance in the carbonator. Since the pilot is refractory lined, heat losses are modest and can be calibrated when a steady state has been reached respect to heat transfer. Therefore, it is possible to determine during such steady state conditions the total solid circulation rate of solids arriving to the carbonator (G_s) from the calciner loop seal with this heat balance equation:

$$G_s = \left(\frac{Q_{refrig} + Q_{heatloos} + Q_{leangas} + Q_{CO_2\ capt} - Q_{carb} - Q_{comb} - Q_{fluegas}}{T_{s\,incarb} - T_{s\,out\,carb}} \right) \frac{1}{c_{ps}\, A_{carb}} \qquad \text{Equation 4}$$

where Q_{refrig} is the heat removed with the bayonet tubes, $Q_{heatloss}$ is the heat loss though carbonator walls, $Q_{leangas}$ is the heat leaving the carbonator with the flue gas, $Q_{CO2\ capt}$ is the heat leaving the carbonator with the CO_2 captured, Q_{carb} is the heat released due to carbonation reaction, Q_{comb} is the heat released due to the combustion of the small amount of coal arriving the carbonator, $Q_{flue\ gas}$ is the heat entering the carbonator with the flue gas fed, c_{ps} is the heat capacity of the solids and A_{carb} is the section of the carbonator. All the terms in the energy balance can be calculated continuously from instrumentation available in the pilot plant. If the solid circulation rate is known, the molar flow (F_{Ca}) can be obtained from the analysis of the samples taken from the reactors.

$$F_{Ca} = \frac{G_s\,(1 - X_{ash})}{PM_s} \qquad \text{Equation 5}$$

The Ca molar circulation rates can be calculated using Equation 5 can be compared with that obtained using Equation 3 and the experimental measurement if this is available. This allows to check the reliability of the experimental information.

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Another CO_2 mass balance expressed in Equation 2, particularly useful for data interpretation and reactor design, is the comparison of the flow of CO_2 captured from the gas phase and the flow of CO_2 reacting with the CaO particles present in the carbonator bed inventory at any particular time. This second term can be estimated as the product of two parameters, the amount of solids present in the bed and the average reaction rate of the solids.

$$F_{CO2in}E_{carb} = n_{Ca,active}\left(\frac{dX}{dt}\right)_{reactor} \qquad \text{Equation 6}$$

To close this mass balance, the carbonator model proposed by Alonso et al. (2009) and methodology used by Charitos et al. (2011) can be applied to interpret the experimental results from the pilot. The reactor model considers the CFB carbonator as a perfect mixed reactor for the solid phase and a plug flow reactor for the gas phase. For the average reaction rate of the solids, Alonso et al. (2009) assumed that the particles react at a constant rate until they reach their maximum carbonate conversion (X_{ave}) and after that the reaction rate stops. This simplification of the reaction rate is consistent with the experimental data available (see for example (Grasa et al. 2008)) and it has been shown to be accurate enough for the interpretation of the experimental data in la Pereda pilot plant (Arias et al. 2013). According to this assumption, the reaction rate of the particles depends on the CO_2 carrying capacity of the sorbent (X_{ave}) and the average CO_2 concentration in the carbonator and can be expressed as follows:

$$\left(\frac{dX}{dt}\right)_{reactor} = k_s\,\varphi X_{ave}\left(\overline{v_{CO2} - v_{CO2eq}}\right) \qquad \text{Equation 7}$$

where k_s is a constant reaction rate that depends on the limestone used and ϕ is a gas-solid contacting factor defined by Rodriguez et al. (2011). Once defined the reaction rate term, the active inventory of calcium can be defined taking into account the assumption of a perfect mixing reactor. According to this, the fraction of active solids in the carbonator (f_a) is that corresponding to the fraction of particles with a residence time lower than the time needed to increase the carbonate content from X_{calc} to X_{ave} (t^*).

$$n_{Ca,active} = n_{Ca}f_a = n_{Ca}\left(1 - e^{\frac{-t^*}{n_{Ca}F_{Ca}}}\right) \qquad \text{Equation 8}$$

The characteristic time (t^*) can be calculated by determining X_{calc} and X_{ave} from the solid taken and using the reaction rate define in Equation 7 (see references Alonso et al. 2009, Charitos et al. 2011). By combining Equation 6, Equation 7 and Equation 8, a design parameter named active space time (τ_{active}) can be defined that links all the operating parameters in the Ca-looping with the CO_2 capture efficiency (Charitos et al. (2011)):

$$E_{carb} = \frac{n_{Ca}}{F_{CO2in}}k_s\,\varphi f_{active}X_{ave}\left(\overline{v_{CO2} - v_{CO2eq}}\right) = \tau_{active}k_s\,\varphi\left(\overline{v_{CO2} - v_{CO2eq}}\right) \qquad \text{Equation 9}$$

The apparent constant rate ($k_s\phi$) in Equation 9 can be calculated as a fitting parameter by comparing the CO_2 capture from the gas phase and the CO_2 reacting with the CaO in the carbonator bed using Equation 6.

Regarding the calciner reactor, the most important variables are:

- The inventory of solids in the calciner ($n_{Ca\ CC}$ in Figure 1). Similar to the carbonator, this variable can be estimated continuously using the measurement of the pressure difference between the plane above the distributor and the exit of the riser.
- The average reactor temperature (T_{calc} in Figure 1), as the CO_2-CaO equilibrium imposes a minimum calcination temperature needed to ensure the calcination of $CaCO_3$ arriving the reactor.
- The molar flows of CO_2 involved in the calciner. There are several inputs or sources of CO_2 in the calciner (as depicted in Figure 1): the CO_2 entering with the oxidant ($F_{CO2\ oxidant}$), the CO_2 produced due to the $CaCO_3$ in the solids arriving from the carbonator ($F_{Ca}\ X_{carb}$ in Figure 1) and the make-up flow of limestone (F_{CaCO3} in Figure 1) , the source of CO_2 generated during the combustion of fuel ($F_{CO2\ fuel}$ in Figure 1).
- The average composition of the solids arriving to the calciner and the molar circulation rate between carbonator and calciner ($F_{Ca\ in}$). These can be determined in a similar way to the case of the carbonator.

The calcination efficiency (E_{Calc}) in the calciner can be defined as:

$$E_{Calc} = \frac{\text{moles of } CaCO_3 \text{ calcined}}{\text{moles of } CaCO_3 \text{ entering the calciner}} = \frac{X_{Carb*} - X_{Calc}}{X_{Carb}} \qquad \text{Equation 10}$$

where X_{Carb*} represents the average $CaCO_3$ content of the solid entering the calciner considering the solids arriving from the carbonator and the make-up flow of limestone. During a steady state, the following CO_2 mass balance should be fulfilled:

$$\begin{pmatrix} CO_2 \text{ increased} \\ \text{in gas phase} \end{pmatrix} = \begin{pmatrix} CaCO_3 \text{ disappeared} \\ \text{from the solid phase} \end{pmatrix} = \begin{pmatrix} CO_2 \text{ disapearing from} \\ \text{the solid phase} \end{pmatrix} \qquad \text{Equation 11}$$

The first term of Equation 11 can be calculated directly from the continuous measurements of CO_2 fed into the calciner with the oxidant (measured continuously), the CO_2 produced during fuel combustion (calculated continuously from the composition of the fuel used and the oxygen flow at the inlet and outlet of the calciner) and the gas composition leaving the reactor.

$$\begin{pmatrix} CO_2 \text{ increased} \\ \text{in gas phase} \end{pmatrix} = F_{CO_2\ out} - F_{CO_2\ Comburent} - F_{CO_2\ Fuel} \qquad \text{Equation 12}$$

The second term of this equation can be calculated periodically from the solids samples taken from the reactor and the molar circulation rates:

$$\begin{pmatrix} CaCO_3 \text{ disappeared} \\ \text{from the solid phase} \end{pmatrix} = F_{Ca} \times (X_{Carb} - X_{Calc}) + F_{CaCO3}(1 - X_{Calc}) \qquad \text{Equation 13}$$

During a steady state, the closure of the energy balance in the calciner can be solved by applying the following equation:

$$Q_{comb} + Q_{oxidant} = Q_{solids} + Q_{CO2fluegas} + Q_{lossCC} + Q_{calc} \qquad \text{Equation 14}$$

where Q_{comb} is the heat released due to the combustion of coal, $Q_{oxidant}$ is the heat input with the oxidant, Q_{CO2} flue gas is the heat output with the concentrated CO_2 flue gas, Q_{lossCC} are the heat losses through the reactor walls, Q_{calc} is the calcination heat and Q_{solids} is the heat input needed to heat up the stream of solids circulating between the reactors. Typically, the heat losses through the reactor wall are modest due to the refractory lining. The terms of Equation 14 can be estimated continuously from experimental measurements in the pilot plant.

The third term in Equation 11 (CO_2 disappearing from the solid phase) can be estimated following a methodology proposed by Martinez et al. 2013 that considers calcination conditions (temperature and CO_2 concentration) and the residence time of the solids in the reactor (mainly related with the inventory of solids and the molar flow of $CaCO_3$ entering the calciner).

With the previous methods, and after completing all retrofits needed to make the pilot functional again (see D3.1), test campaigns were carried out to progress with the Task 3.2 (Experimental campaigns for biomass-fired and WtE power plants) and its sub-tasks. In the following sections, the results of such test are reported in a summarised manner, with more details on the experiments available in the ANNEX section.

3 TESTS INVOLVING OXY-COMBUSTION OF BIOMASS IN THE CALCINER

Oxy-calcination tests using biomass as fuel in the calciner

One of the objectives of WP3 is to demonstrate a CFB-CaL system for WtE and Bio-CHP power plants in a 1.7 MW_{th} CFB-CaL pilot. As indicated in D3.1, initial experimental campaigns were carried out in the pilot plant after a long period of inactivity by using biomass pellets as a fuel in the calciner (coal was the only fuel in all tests carried out in la Pereda before CaLby2030). These tests were aimed to evaluate the operability of the pilot under typical process conditions and to ensure smooth work of the existing fuel feeding system using biomass wood pellets. Some of these initial tests were carried out with the calciner operated in a closed mode, with the external circulation valve closed and the internal circulation valve opened.

As indicated in the previous section, the calciner operates in a quasi-adiabatic mode as there are no bayonet tubes installed to extract heat in said reactor. Therefore, high flows of limestone were used in order to fulfil the energy balance in the calciner while burning the fuel under expected conditions (gas velocities, temperatures,…). The use of high limestone flows in these calcination tests have provided useful experimental information for the parallel developments in the Biomass & WtE, cement (WP1), steel sectors (WP2) within the Calby2030 where it will be common to operate oxy-fired calciners with flow of solid materials entering the calciner one or two order of magnitude larger that what would be standard in a postcombustion CFB-CaL system attempting to minimise make up flows of limestone. As example of these test, Figure 2 shows an oxy-calcination test period of 6 hours duration. During this test, a flow of limestone of 700 kg/h was fed into the calciner. To sustain the calciner temperatures needed for fast $CaCO_3$ decomposition in the calciner atmospheres (T slightly above 900ºC), an average biomass flow of 285 kg/h was burned, with an inlet oxygen concentration of 30 $\%_v$ in the O_2/CO_2 oxidant mix. The flue gas leaving the calciner had an average composition of $5\%_v$ and 74 $\%_v$ of O_2 and CO_2, respectively.

The calciner was operated with average inventory of solids of around 500 kg/m^2. This inventory and the strong circulation of solids allow to achieve a homogeneous temperature profile in the calciner, with differences of temperature between the dense bed and the exit below 50ºC, while there is an average temperature of 915 ºC. The graph at the bottom of Figure 2 shows the main flows of CO_2 in the calciner. A total CO_2 flow of 41 kmol/h leaves the calciner, being the CO_2 fed with the oxidant the main contributor (around 65%). On the other hand, the CO_2 produced by calcination and biomass combustion are 6.6 and 6.7 kmol/h, respectively. An average calcination efficiency of 0.966 has been calculated from the solid samples taken periodically during the tests (red dots on the bottom graph of Figure 2).

From the flow of biomass and the fuel heating value, a thermal input into the calciner of 1520 kW (Q_{Comb}) can be calculated. During this test, the oxidant was fed into the calciner at ambient temperature ($Q_{oxidant}$=0). The average flue gas flow leaving the calciner was 2590 kg/h. As results the heat leaving the reactor with this stream was 800 kW ($Q_{CO2\ flue\ gas}$). The power needed to heat up the solids fed into the reactor at ambient temperature is 250 kW (Q_{Solids}). The calcination heat calculated from the flow of limestone fed into the reactor is 315 kWth (Q_{Calc}). Using these values, the heat balance of Equation 14 can be closed by assuming heat losses of 155 kW (Q_{loss} CC). This value agrees with the total heat losses estimated for the calciner taking into account the external wall temperatures.

As indicated above, two of the most important variables on the reactor performance are the calcination temperature and the inventory of solids (Martínez et al. 2013). The calciner has to be operated in a relatively narrow range of calcination temperatures. On one hand, the temperature should be above that given by CO_2-CaO equilibrium to ensure calcination of the $CaCO_3$ in the reactor. Operating the calciner close to the equilibrium conditions could promote additional carbonation and calcination cycles in the reactor, thus reducing the sorbent activity (Diego, 2017). Typically, temperatures above 20-30ºC over the equilibrium are sufficient to avoid this effect and also to ensure high calcination rates. On the other hand, high calcination temperatures (above 950 ºC) should be avoided to minimize the sintering of the CaO and other potential ash-related issues that would lead to a higher make-up flow consumption in the CaL system. Regarding the inventory of solids in the calciner, it has an important effect on the residence time of solids in the reactor and therefore on the calcination efficiency.

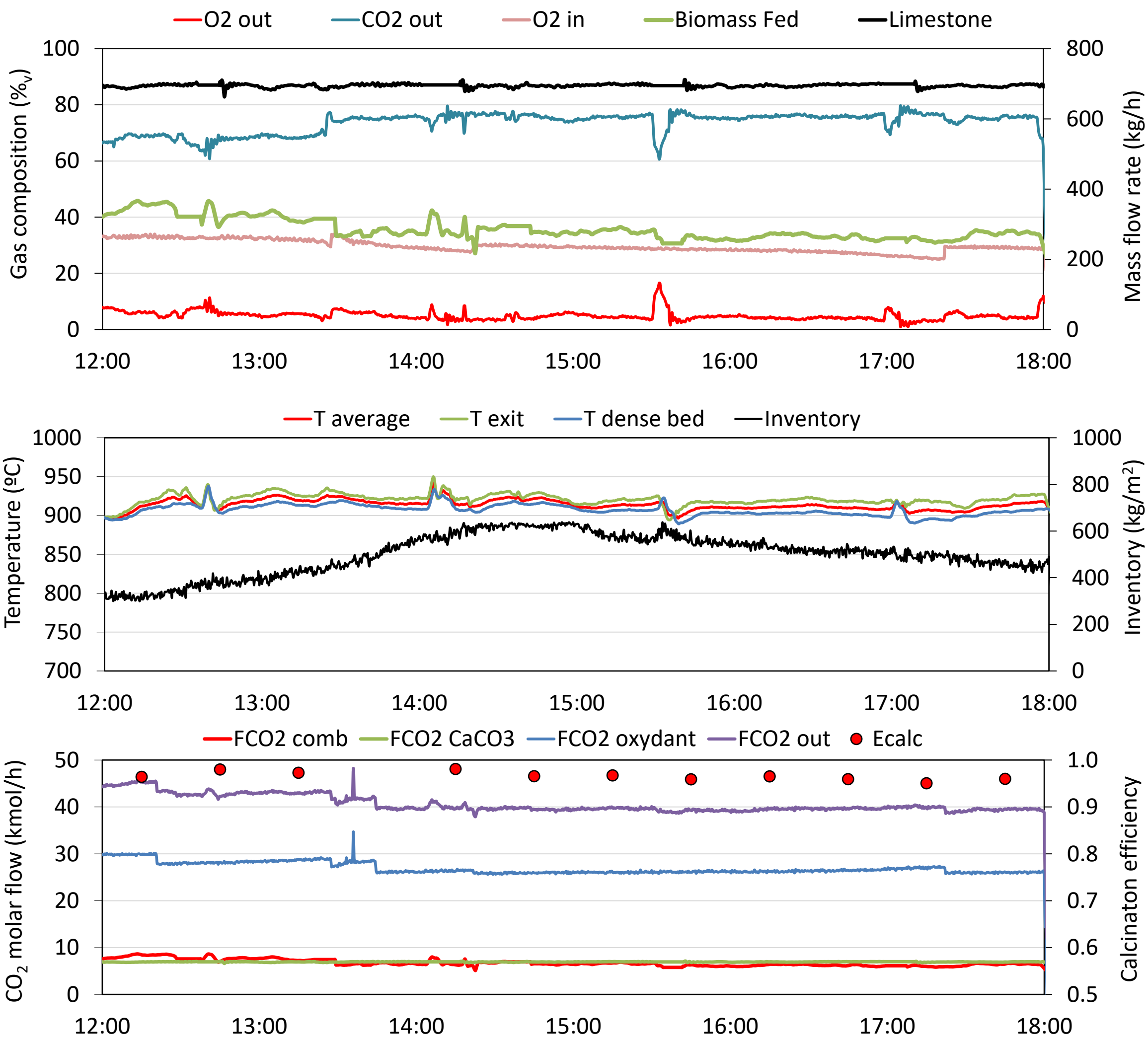
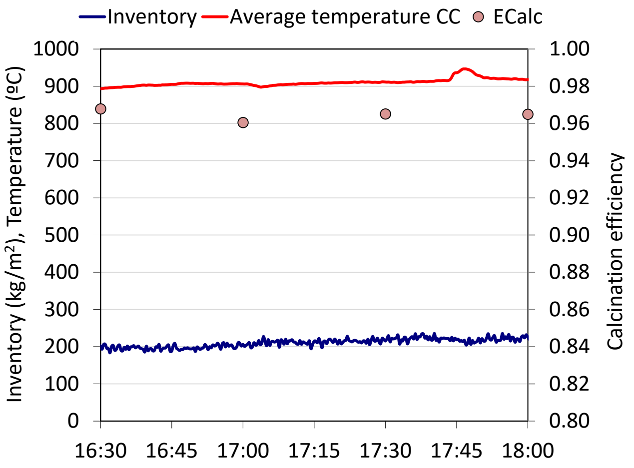


Figure 2. Example of oxy-calcination test operating the calciner in a closed mode.

To illustrate the effect of the calcination conditions, Figure 3 shows two experimental calcination periods. A limestone flow of 700 kg/h has been used in both cases. Also, the calciner has been operated with a similar average temperature of 910 ºC and similar CO_2 concentration at the outlet around 80%$_v$. The main difference between both periods is the inventory of solids in the riser which are 200 kg/m^2 (Figure 3 left) and 400 kg/m^2 (Figure 3 right). As can be seen in this figure, the higher inventories allow to increase the calcination efficiency from 0.965 to 0.980 due to the higher residence time of the solids in the reactor.



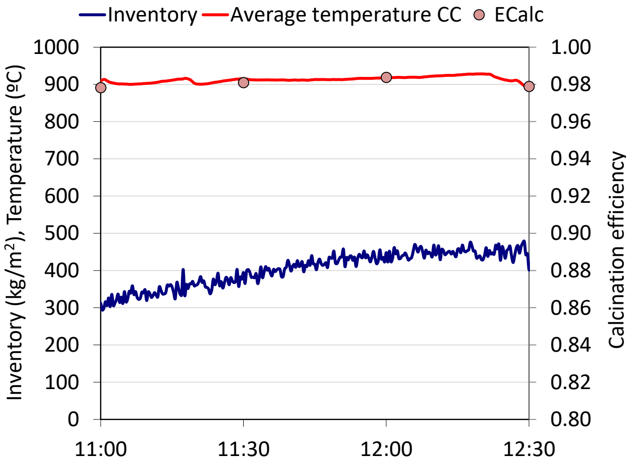


Figure 3. Comparison of two calcination periods showing the effect of the inventory of solids: left) 200 kg/m^2, right) 400 kg/m^2. (average values: 700 kg/h of limestone, 30 % O_2 at the calciner inlet, 5 %O_2 and 80% CO_2 at the calciner outlet).

Part of the activities included in the DoA of WP3 was to explore the possibility of operating the calciner with very low oxygen concentrations, which could facilitate the downstream process stages needed to purify CO_2 produced in the Calcium Looping process. For this purpose, a few tests were carried out in la Pereda pilot plant operating the calciner under such close-to-stoichiometric conditions. Figure 4 shows an experimental period of more than 5 hours, aimed to study the emissions when there is low oxygen excess in the calciner. As can be seen in this graph, it is not easy to maintain a constant excess of oxygen at the outlet of the calciner. This can be attributed to small fluctuations in the biomass flow rate that modify the excess oxygen and the combustion conditions, specially when operating close to the stoichiometric conditions. In commercial systems, the buffer effect of the larger capacity of the oxy-fired calciner could help to maintain more stable conditions at the outlet of the reactor. However, the results obtained during these tests allow to obtain some trends.

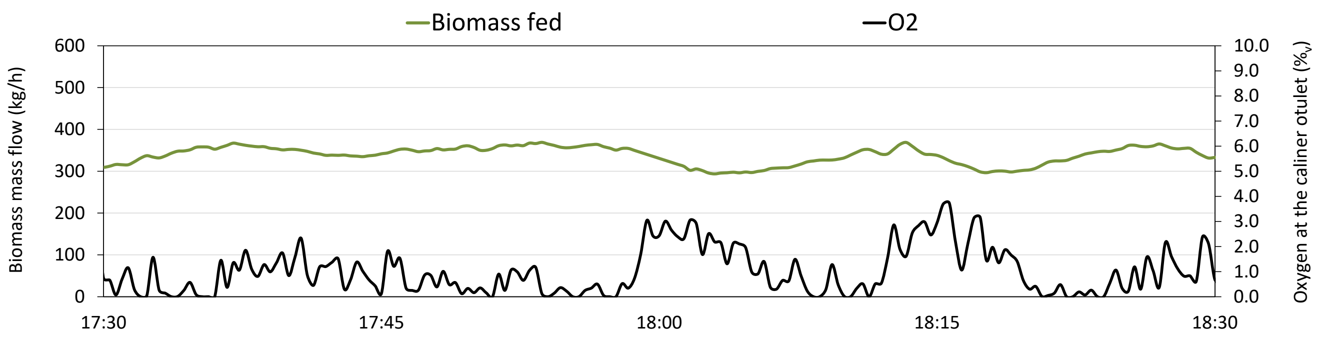


Figure 4. Operation of the calciner under low excess of oxygen.

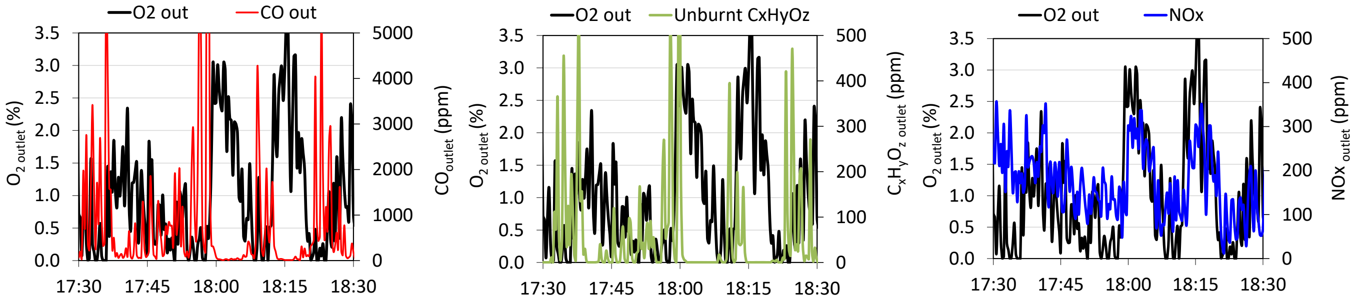


Figure 5. CO, unburnt ($C_xH_yO_z$) and NOx emissions operating the oxy-calciner under low excess of oxygen.

Figure 5 shown the CO (left), unburnt carbon ($C_xH_yO_z$) (center) and NO_x (right) emissions during the period shown in Figure 4. The unburnt emissions ($C_xH_yO_z$) correspond to the sum of the emissions of CH_4, C_2H_6, C_2H_4, C_3H_8, C_6H_{14} and CHOH that have been measured using the FTIR analyser. Within the period shown in these graphs, there are four periods with an excess of oxygen below 0.5% around 17:35, 17:55, 18:10 and 18:25. Regarding CO emissions (Figure 5-left), peaks above 1500 ppm can be observed when operating the calciner below 0.5%v O_2. However, for oxygen concentration at the exit of the calciner above 1.0%$_v$, the CO emissions drops drastically well below 100 ppm and even close to zero for excess above 2%$_v$ O_2 (around 18:05 and 18:15). The emissions of unburnt carbon ($C_xH_yO_z$) present some peaks above 200 ppm during the periods of low excess of oxygen (>0.5%$_v$). But similarly to CO, the emissions are reduced to close to zero for excess of oxygen above 1.0 %. Finally, the excess of oxygen has an effect on NOx emissions. Figure 5-right shows peaks of NOx emissions around 300 ppm at 18:05 and 18:15 when the excess of oxygen is around 2%v. However, the other periods operating with lower excess of oxygen allows to reduce the NOx emissions at values below 200 ppm.

The oxy-calcination tests carried out in la Pereda pilot plant have confirmed the capability of the pilot to reach intense oxy-calcination conditions when using biomass pellets as a fuel in the CFB-calciner. These have also demonstrated the possibility of operating the calciner under low excess of oxygen with moderate emissions of CO and unburnt carbon.

First CO_2 capture tests in the carbonator with oxy-combustion of biomass in the calciner

As indicated in Deliverable 3.1, the long period of inactivity of the main power plant of la Pereda has required to develop a new operational strategy to allow CO_2 capture testing in la Pereda CFB-CaL pilot. This involves the use of a synthetic flue gas in the carbonator, by mixing air with CO_2 from the cryogenic tank to simulate that produced in the power plant. In addition, HUNOSA had to operate the induced draft, ID fan of the main power plant (when such plant was off) to cause a negative pressure as needed in the return point of the gases from the pilot plant to the main power plant. To avoid any flue gas leakage in other parts of the main plant and to ensure a proper pressure balance when the pilot was operated in this mode, both the force draft and ID fans of the power plant were used. More information about the small retrofits and power plant configuration to maintain the pressure balance is available in Section 3 of D3.1.

After some initial successful tests (reported in the D3.1 and 1st technical report RP1), some malfunctions were detected in the circulation of solids between reactors. These resulted into an unstable solid flow between reactors and frequent accumulation of solids in the calciner stand pipe. After several failed tests to check for possible causes of such malfunctions (blockages, unwanted combustion in stand-pipes or loop seals, ash-softening issues), it was detected that this problem was linked to a blockage of some of the fluidization nozzles of the calciner loop seal, undetectable from pressure drops measurements, as discussed below. Figure 6 shows an example of such random unstable operation of the pilot. Between 11:00 and 12:00, there was a stable operation that resulted into a rather constant inventory of solids and average temperatures in the carbonator and calciner. Between 12:00 and 12:30, a sharp decrease on the inventory of solids in the carbonator can be observed and a fluctuation of the temperature in both reactors. An accumulation of solids in the stand pipe was detected, that stopped the flow of solids entering the carbonator. This kind of blockages (rare in normal conditions) can be solved in this facility by injecting compressed air at different heights of the calciner stand-pipe, thus facilitating the movement and fluidization of the accumulated solids. During the period shown in the figure, this action had to be done three times between 12:15 and 12:30, but the injection of air only restored temporarily the circulation of solids (see the increase of the inventory and temperature).

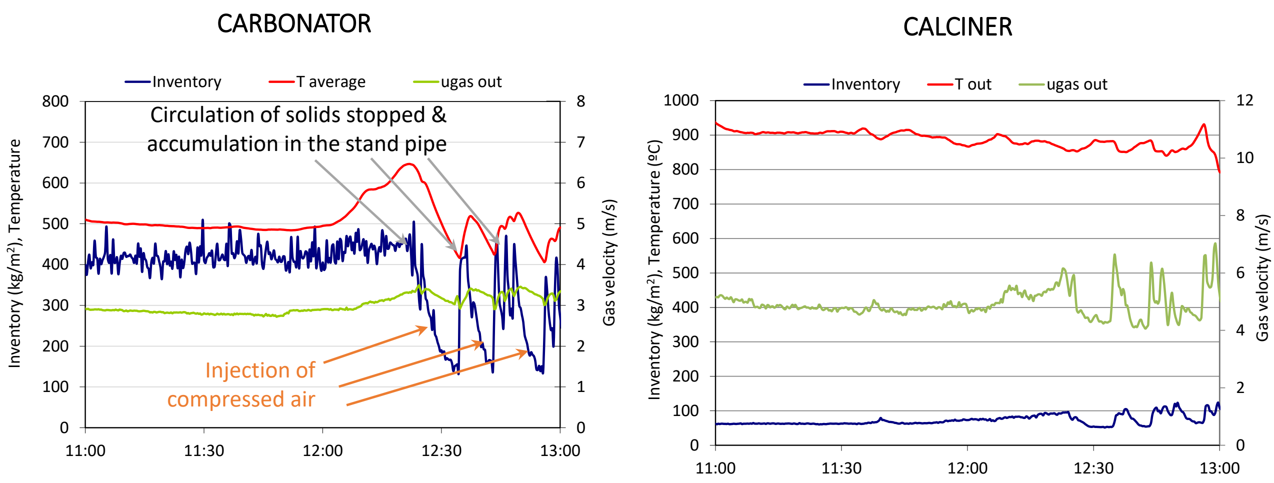


Figure 6. Example of unstable of operation of the pilot plant due to the blockage of some fluidization nozzles in the calciner loop seal.

After testing several other potential causes of these problems, the loop seal was opened for inspection at ambient temperature. The feeding of fluidisation air to the loop seal was in principle trouble free, because normal pressure drops in such gas lines were measured. However, while injecting fluidising air to the opened loop seal, it was visually evident that some of the nozzles were blocked, mainly in the zone that receives the solids coming from the calciner. Figure 7 shows some schematics of the calciner loop seal and the fluidization system. The gas fed into the loop seal is split and introduced through five fluidization zones.

As result of the blockage of nozzles, this zone was partially defluidized, facilitating the accumulation of solids in the loop seal and making difficult to achieve stable operation. An additional problem was related with the splitting of the gas into the different plenum zones (i.e. the five empty spaces below the nozzles, that divide the loop seal in five sections as shown in Fig 7). Two of these plenum zones, the one receiving the solids from the calciner (zone 1 in Figure 7) and the adjacent zone (zone 2 in Figure 7) were not air tight, they were connected due to a failure in a welding of the flat sheet of metal separating the plenum zones. This defect could not be noticed during normal operation (when there are no nozzles blocked) as the main fraction of the gas fed into each zone enters into the loop seal directly through the nozzles. However, as the nozzles were blocked, the air fed into plenum zone 1 leaked to plenum zone 2. This made difficult to detect malfunction of the nozzles. To solve this problem, the windbox of zone 1 was modified to feed compressed air to each individual nozzle (see Figure 8). After this modification, it was possible to achieve stable pilot plant operation and completing part of the experimental activities.

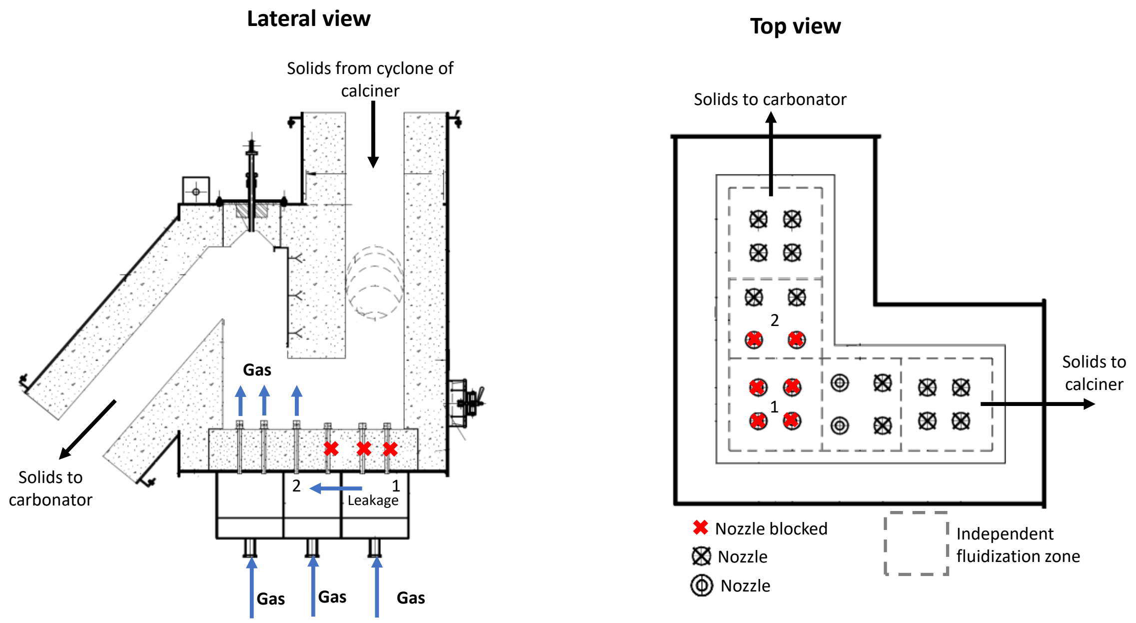


Figure 7. Schematics of the calciner loop seal and fluidization system.

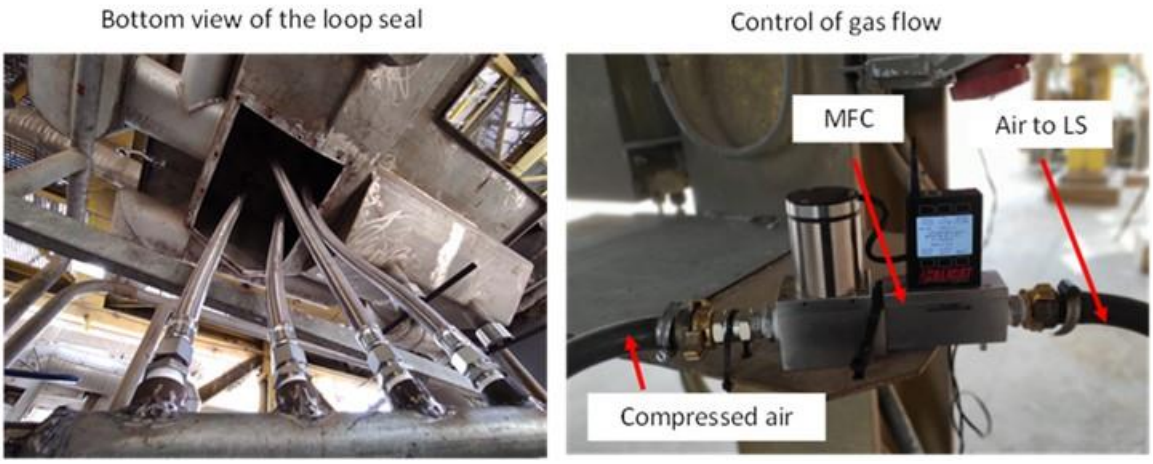


Figure 8. Modification of the fluidization of the calciner loop seal.

The pellets of biomass used in the CFB-CaL test with CO_2 capture and oxy-combustion of biomass in the calciner, have a composition of 50.7 $\%C_{wt}$, 6.0 $\%H_{wt}$, 34.6 $\%O_{wt}$, 8.4 $\%H_2O_{wt}$ and a lower heating value (LHV) of 19.1 MJ/kg. They have typical dimensions of 6-8 mm diameter and a maximum length of 45 mm as the existing fuel feeding system can handle this kind of fuel after tuning some of the operational parameters. As example of pilot plant stability, Figure 9 shows a typical experiment and the main variables. After an initial period to preheat the pilot, and to achieve temperatures above 800 ºC in the calciner (not shown in the graph for simplicity), the combustion conditions in the reactor are switched from air to oxy-fuel with an average oxygen concentration of $37\%_v$ in the oxidant (at 7:40). As a result, there is a sharp increase in the CO_2 concentration at the outlet of the calciner (see Figure 9 top). Regarding the carbonator, the gas fed into the reactor is changed from air to a flue gas with a CO_2 concentration of 11.0 %v at 8:00 (Figure 9 middle). After a short period, the average temperature in the calciner and the carbonator is stabilized and maintained at values around 935 ºC and 615 ºC, respectively. This is achieved by burning an average biomass flow rate of 365 kg/h (resulting into a thermal input of 1.94 MW_{th}) with an excess of oxygen at the outlet of the calciner below 5%v. From this point, the gas velocities in the reactors are maintained constant at 3.3 and 3.8 m/s in the carbonator and calciner, respectively. Under these conditions the circulation of solids between reactors is 1.4 kg/s, with solid inventories of 570 and 195 kg/m^2 in the carbonator and calciner, measured from the pressure drop readings.

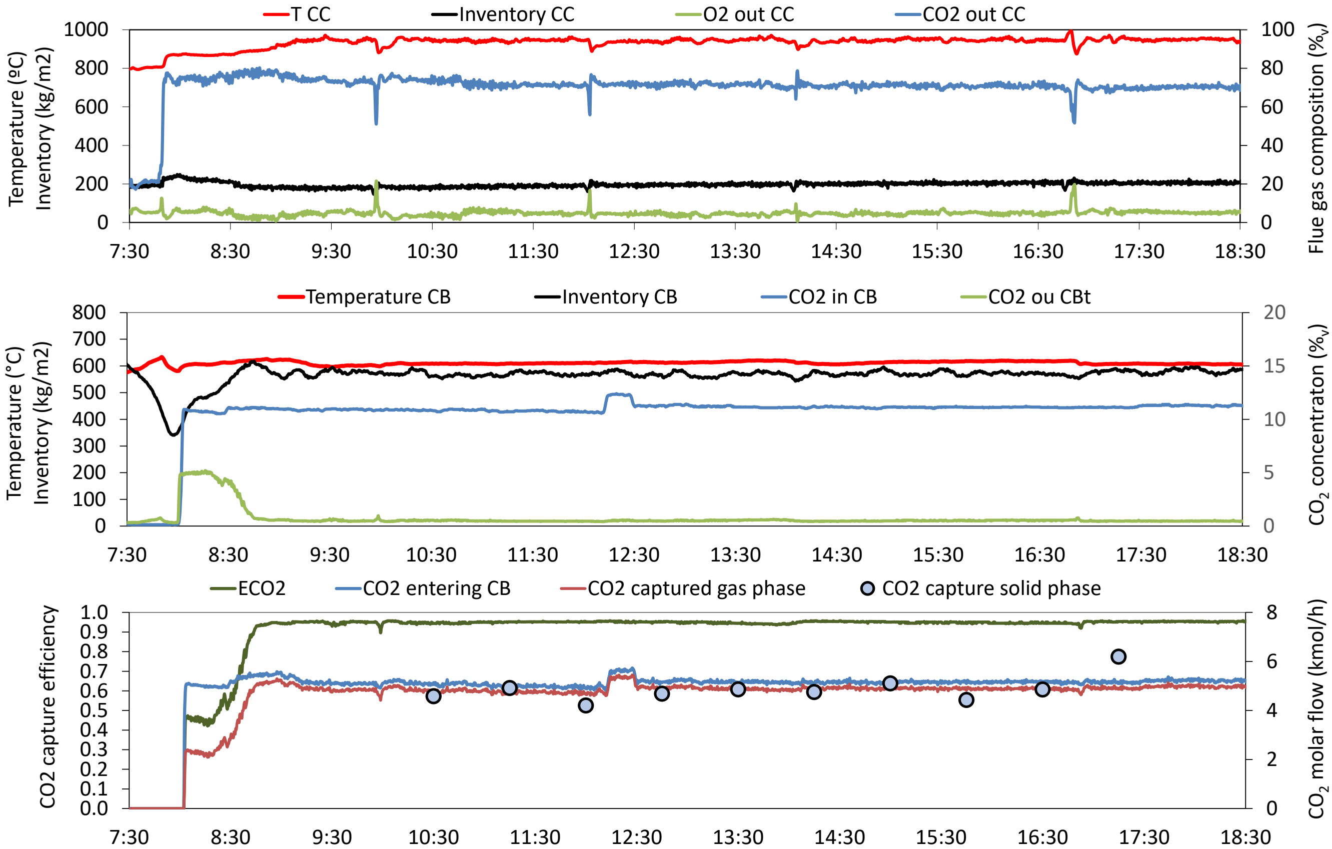


Figure 9. Example of an experimental CO_2 capture test with oxy-fuel combustion of biomass in the calciner.

Figure 9 bottom shows the flow of CO_2 captured in the carbonator. As indicated above two values are shown in this graph: one corresponds to that calculated from the gas phase (solid green line in Figure 9 bottom), and the other from the mass balance in the circulating solids (blue dots in Figure 9 bottom). As can be seen, there is a good agreement between both methods, yielding a flow of CO_2 captured of about 4.6 kmol/h. This results into an average CO_2 capture efficiency of 0.96 during this period.

4 DYNAMIC TESTS IN SUPPORT OF WP2

One of the objectives marked in WP3 is to generate a database of experimental information useful for modelling/scaling up purposes in WP4, including dynamic operation data for WP2. To this end, in support of the design and construction of this new pilot, it was planned to carry out some preliminary dynamic experiments in la Pereda pilot plant to produce experimental information useful for designing activities in WP2 and modelling activities in WP4 linked to steel-sector CFB-CaL applications. Thus, some tests dedicated to dynamic experiments by modulating changes in the CO_2 concentration and gas velocities to the carbonator were carried out in la Pereda pilot plant. These experiments were coordinated between SFW, CSIC and HUNOSA.

Figure 10 shows an example of a dynamic period aimed to test the buffer effect of the active inventory of solids on the CO_2 capture efficiency. This graph shows the main CO_2 molar flows in the carbonator. For simplicity, the operation conditions in the calciner are not shown. These were maintained constant during the period shown in Figure 10 with an average thermal input of 2.0 MW_{th}, supplied by burning a flow of 370 kg/h of biomass pellets under oxy-fuel conditions.

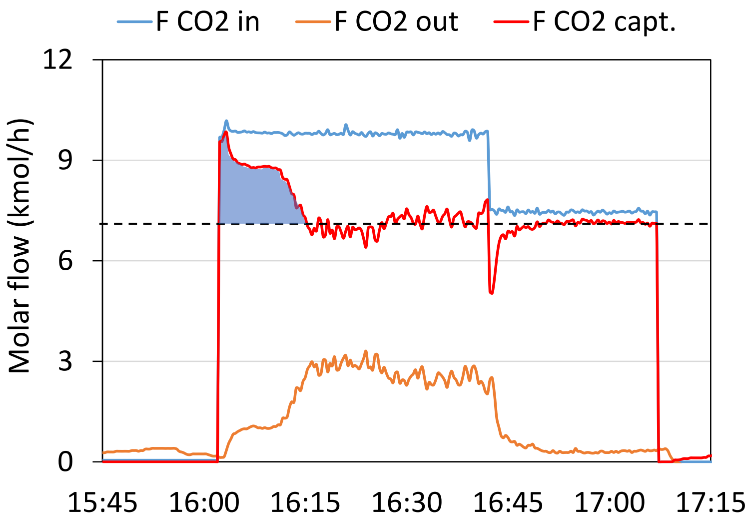


Figure 10. Example of a dynamic CO_2 capture period aimed to test the buffer capacity of the inventory of solids against CO_2 molar flow loads into the carbonator.

Until 16:00, the system's solids inventory was mainly composed of calcined solids. To facilitate this process, the carbonator was fluidized using air (i.e. no carbonation). From that point, the carbonator was switched to CO_2 capture mode by feeding a flue gas with an inlet CO_2 molar flow of 9.8 kmol/h. At the beginning (16:00), the molar flow CO_2 captured almost matches the inlet value and it decreases progressively until stabilizes into a value around 7.1 kmol/h. At 16:45, the CO_2 molar flow inlet into the carbonator is reduced up to 7.5 kmol/h by changing the CO_2 concentration of the flue gas. After this change, the CO_2 captured molar flow remained almost constant and the CO_2 at the outlet was reduced from 2.7 up to 0.4 kmol/h. The constant flow of the CO_2 captured between both periods (from 16:15 until 17:10) indicates that the capture efficiency is limited by the operation conditions in the calciner into a value of around 7.1 kmol/h.

The extra amount of CO_2 captured between 16:00 and 16:15 (marked in Figure 10 in blue) can be attributed to the amount of free CaO produced during the calcination period (before 16:00). By integrating the area, a CO_2 captured of 0.34 kmol can be estimated. During the calcination period, the $CaCO_3$ molar content of the solids was 3.3%molar and during the CO_2 capture period remained rather stable into a value of 9.4 %molar. This allows to calculate an amount of CaO in the carbonator of around 360 kg which agrees reasonably well with the amount of solids in the riser and the loop seal of the carbonator estimated from pressure measurement readings.

Figures 11 and 12 show other examples of experimental periods with several changes in the carbonator and calciner, respectively. The methodology followed to carry out these tests was to start from a reference point, then make a step change in one variable for one hour and then back again to the reference point before introducing a new step change. The graphs on Figure 11 show the gas composition at the inlet and outlet of the carbonator, the gas velocity, the molar flow of CO_2, the inventory of solids in the reactors and the average temperature in the carbonator. Three step changes are shown in this graph. In this case, there was an increase of CO_2 at the inlet of the carbonator, a decrease of CO_2 at the inlet of the carbonator and an increase in the flue gas load.

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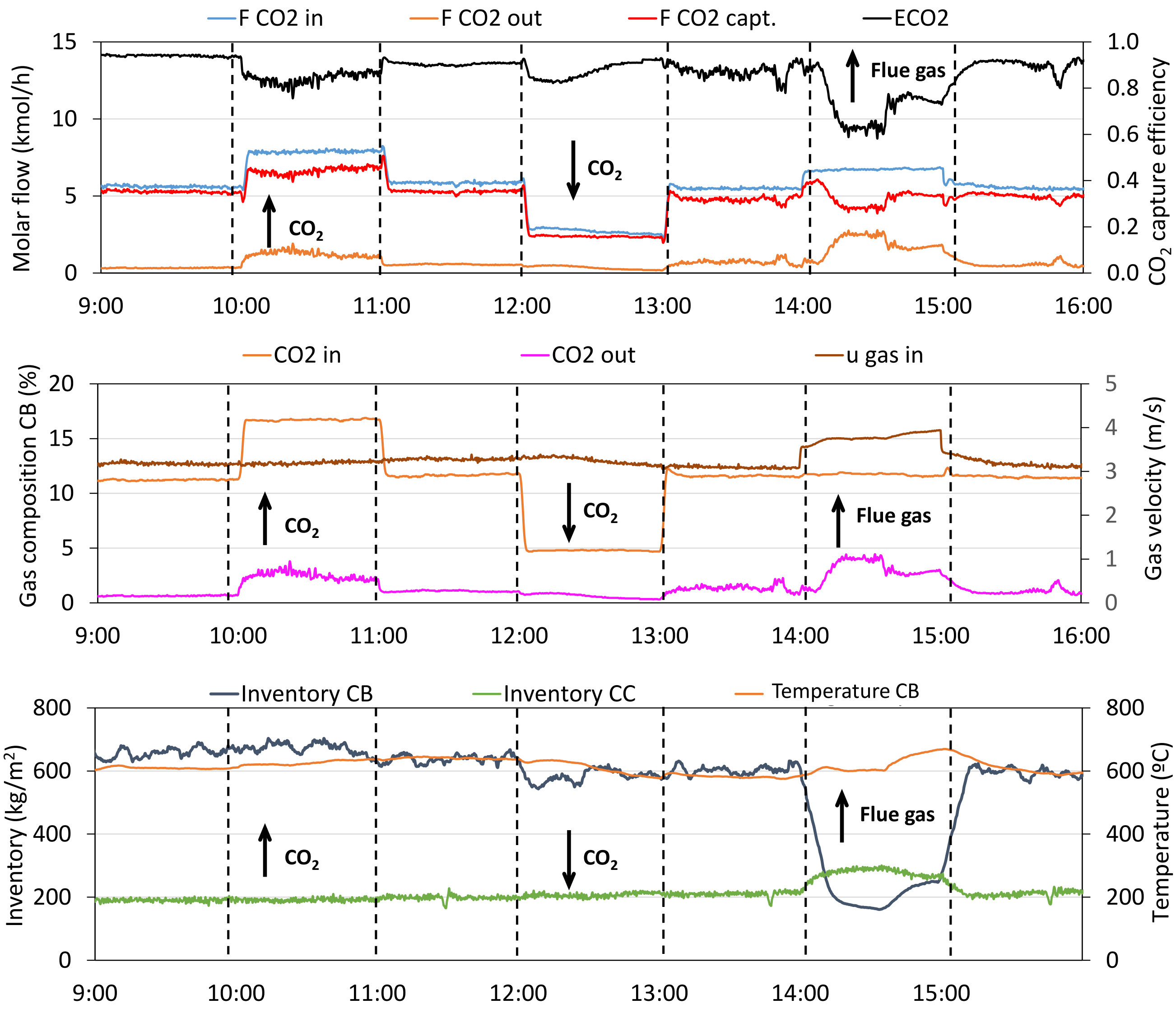


Figure 11. Dynamic tests with changes in the flue gas fed into the carbonator.

During the initial reference period (between 9:00 to 10:00), the CO_2 concentration at the inlet of the carbonator was 11.2%$_v$ and a CO_2 capture efficiency of 0.93 was achieved. At 10:00, the CO_2 concentration was increased up to 16.7%$_v$ (around 50% higher respect to the reference). This results into an increase of the CO_2 at the outlet of the carbonator and a drop in the capture efficiency up to 0.83. The second step change started at 12:00 and the CO_2 concentration at the inlet of the carbonator was reduced from 11.5%$_v$ up to 4.8 %$_v$ (a reduction of 60% respect to the reference). This has a limited effect on the system. There is a small drop in the temperature due to the reduction of the carbonation heat released in the reactor. There is also a small decrease in the CO_2 capture efficiency.

At 14:00, there is an increase in the flue gas flow from 1330 kg/h up to 1585 kg/h (an increase of 20%) while maintaining a constant CO_2 concentration. This step change has an important effect on the operation conditions. The increase of the gas velocity in the carbonator has an important effect on the distribution of the inventory of solids in the reactors. Thus, the inventory of solids in the carbonator decreases from 600 to 200 kg/m^2. This results into a decrease on the CO_2 capture efficiency in the carbonator up to 0.7. This step change also increased the temperature in the carbonator due to an increase in the solid circulation between reactors. Then at 15:00, the flue gas load was reduced again to the reference point and the operation conditions in the pilot were recovered.

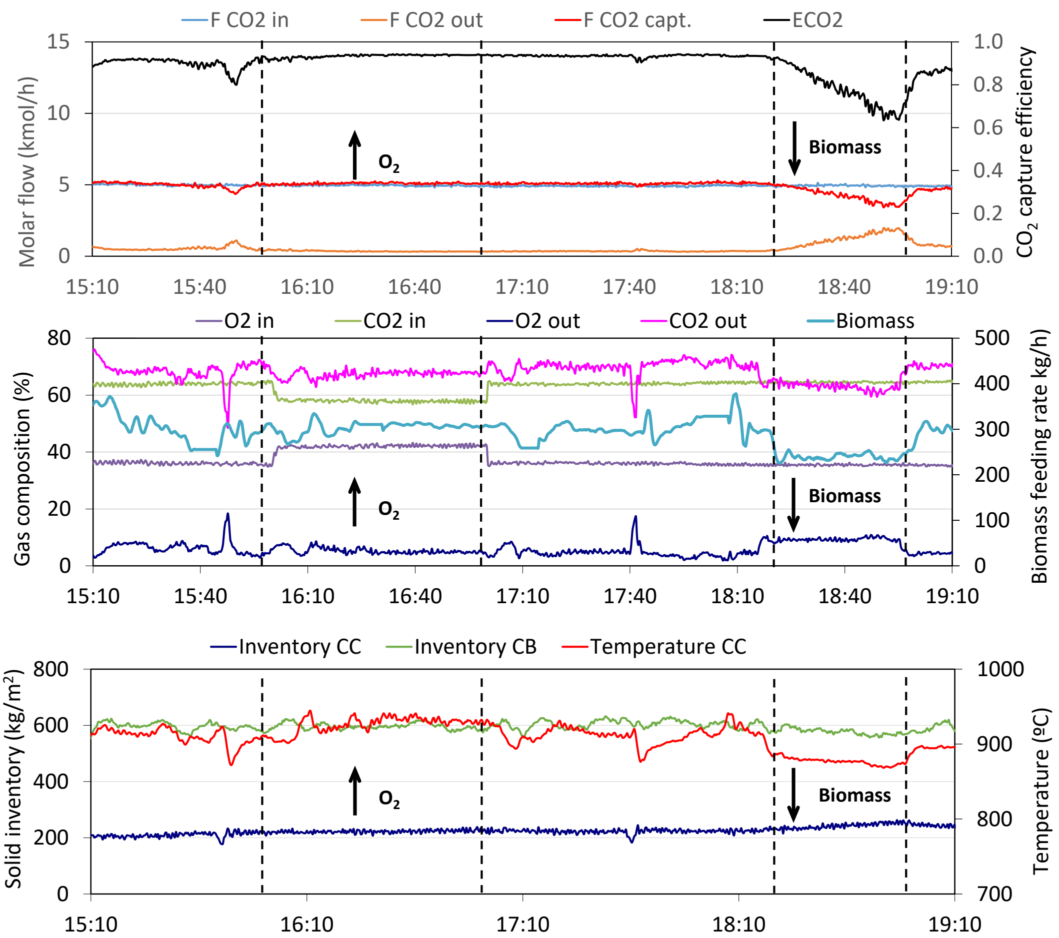


Figure 12. Dynamic tests with changes in the oxy-calciner.

Figure 12 shows two step changes on the calciner operation conditions. The first one corresponds to an increase in the oxygen concentration from 35 to 41% (maintaining the total oxygen flow fed into the calciner and reducing the CO2 flow) (between 16:00 to 17:00). This resulted in a reduction of the gas velocity at the inlet of the calciner of around 10%. As can be seen in the figure, this has a little impact on the rest of the operation conditions in the calciner and carbonator. The second step change was introduced at 18:20 and consisted of a reduction in the biomass flow rate from 295 kg/h to 240 kg/h, thus reducing the thermal input by 20%. This resulted in a decrease in the reactor temperature and the power available for calcination. This has an impact on the operation of the carbonator and there is a reduction in the CO_2 capture efficiency.

5 OPERATING THE CARBONATOR WITH CO_2 CAPTURE RATES >99%

One key objective of WP3 is to demonstrate CO_2 capture rates over 99% using $Ca(OH)_2$ as an additional sorbent, including co-capture of acid gases. To this aim, the results presented in this section have been obtained during several experimental campaigns carried out in La Pereda 1.7 MW_{th} pilot plant aimed to advance in the demonstration of the high-CO_2 capture efficiency carbonator configuration. A basic scheme of this reactor configuration is shown in Figure 13. This involves a carbonator with enhanced cooling capabilities to operate with a cooler region of enhanced carbonation at the top of the reactor as represented in Figure 13-left (for simplicity, other heat transfer equipment in the CaL system is not included). The purpose of the additional heat exchange in the upper part is to reduce the temperatures in that region to well below 600ºC, so that the CO_2-CaO equilibrium allows deeper decarbonisation of the flue-gases. For example, as represented in Figure 13-right, for a typical flue gas inlet of 12%v CO_2, thermodynamics allows 99% capture efficiency when the carbonator is designed to operate at 550 ºC.

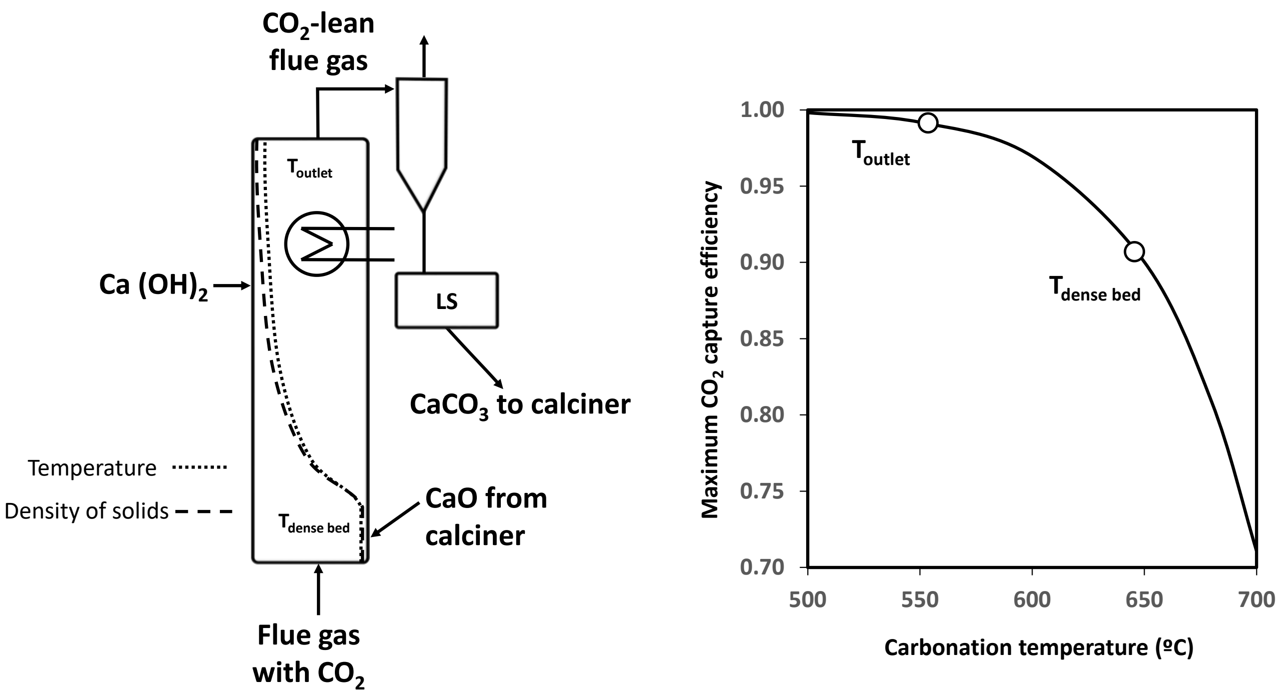


Figure 13. Left) Basic scheme of the carbonator configuration targeted to achieve high CO_2 capture efficiencies. Right) Maximum CO_2 capture efficiency in the carbonator of a CaL system as a function of temperature (for an inlet gas with $12\%_v$ CO_2, using the equation of Baker, 1962).

In an initial experimental phase, before implementing the retrofit to allow feeding of $Ca(OH)_2$ solids into the carbonator, experiments have been carried out to demonstrate the viability of enhanced carbonation by adjusting the temperature profile as shown in Figure 13. Part of the results described in this section have been published in a peer reviewed publication (Arias et al. 2024). As shown below, such experiments have already demonstrated the capability of the CFB-CaL system to reach CO_2 capture efficiencies over 99% in the carbonator while operating the calciner under oxy-combustion of biomass. In a second phase, it is expected to install the retrofit to inject $Ca(OH)_2$

into the carbonator as discussed at the end of this section. For this initial phase, the pilot has been operated in the range of operation conditions summarized in **¡Error! No se encuentra el origen de la referencia.**

Table 1. Range of operating conditions and main variables during the tests devoted to achieve high CO_2 capture efficiencies in the carbonator.

Average temperature in the carbonator, T_{CB}	ºC	530-660
Superficial velocity at the carbonator	m/s	2.5-4.0
Inventory of solids in the carbonator	kg/m^2	350-650
Inlet CO_2 volume fraction at the carbonator inlet		0.03-0.14
Maximum CO_2 carrying capacity of the solids, X_{ave}		0.10-0.40
Average temperature in the calciner, T_{CC}	ºC	840-945
Superficial velocity at the calciner	m/s	3.0-5.5
Inventory of solids in the calciner	kg/m^2	50-250
O_2 volume fraction in the oxidant		0.30-0.40
Biomass mass flow rate	kg/h	250-450
CO_2 capture efficiency, E_{Carb}		0.60-0.995

Most of these tests were carried out with a high make up flow of $CaCO_3$ fed into the calciner to operate the system with a sorbent with high CO_2 carrying capacities (X_{ave}) ensuring a sufficient flow of active CaO material in the upper zone of the carbonator.

Figure 14 shows an example of an experimental period aimed to achieve high CO_2 capture efficiencies. For this specific test, the low temperatures in the carbonator were obtained by feeding a flue gas with a low CO_2 concentration (5.8%$_v$) to reduce the heat generated by the carbonation and also, by maximizing the heat extraction with the four water-cooled bayonet tube heat exchangers fully inserted into the carbonator. In addition, the conditions were adjusted to operate with a high excess of active sorbent ($F_{Ca}X_{ave}$) respect to the molar CO_2 flow (F_{CO2}) fed into the carbonator ($F_{Ca}X_{ave}/F_{CO2}$ of 1.8). The inventory of solids in the carbonator during this test was 495 kg/m^2, which presented a typical distribution in CFB reactors, with the presence of a dense zone in the bottom of the reactor and a lean zone in the upper part (see Figure 14b). As shown in Figure 14a, from 12:30 to 13:20, the temperature in the carbonator was maintained constant. The temperature profile along the reactor during this period is shown in Figure 14c (white dots). As can be seen, there is homogeneous temperature of around 570 ºC in the bottom dense zone. From this point, there is a sharp drop in the temperature profile with an average value of 475 ºC in the upper lean. During this initial period, a CO_2 capture efficiency of 0.995 was achieved in the carbonator as shown in Figure 14a. Then, the bayonet tubes in the carbonator were partially removed to reduce the heat extraction at 13:20. As a result the temperature in the reactor increased, especially in the upper lean zone (from 475 up to 525 ºC) resulting in a decrease in the CO_2 capture efficiency as can be seen in Figure 13a.

Using the temperature profiles along the carbonator, two different average zones with their respective average temperatures were defined to facilitate the data interpretation that follows. One corresponds to the average temperature in the bottom dense zone of the carbonator, T_{DZ} (from 0 to 3 meters above the grid) and the other to the temperature in the upper lean zone, T_{LZ} (from 8 to 15 meters above the grid). These two temperatures, represented in Figure 14a, were used to calculate the maximum capture efficiency that can be achieved considering CO_2 partial pressure given by the equilibrium ($E_{Carb\ eq\text{-}TLZ}$ and $E_{Carb,\ eq\text{-}TDZ}$, respectively in Figure 14a). As can be seen, the experimental capture efficiency matches the maximum efficiency given by the equilibrium considering the temperature in the upper lean zone, while it clearly exceeds that limited by the temperature in the dense bed. This can be seen clearly during the second period operating at higher temperature. In this case, the experimental CO_2 capture efficiency was 0.985 while the temperature in the dense bed only allows for a maximum capture of 0.915.

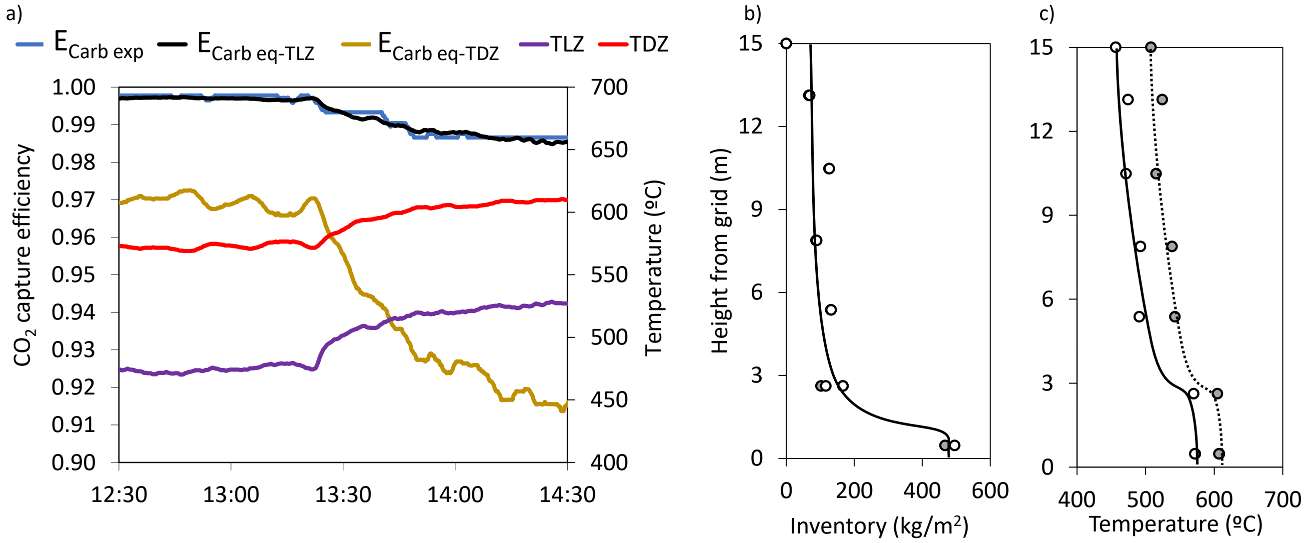


Figure 14. a) Example of the effect of carbonator temperature on the carbonation efficiency, b) and c) inventory of solids and temperature profile along the carbonator (grey dots: from 12:30 to 13:20; white dots: from 14:00 to 14:30).

To interpret the observations presented above in a more quantitative manner, the basic 0D reactor model presented above in Section 2 has been used. This model assumes that the solid phase behaves as a perfect mix reactor while the gas phase can be considered as a plug flow. It also assumes the reaction rate of the particles is constant until the maximum carbonate conversion (X_{ave}) is achieved, being zero after that point. According to the temperature and solid profiles, as shown in Figure 14, the carbonator is assumed to be composed of two zones, one dense zone located at the bottom part and one lean zone in the upper part, operating at two different temperatures, T_{DZ} and T_{LZ}. It can be argued that the mixing of solids between these two zones is sufficiently intense to assume that the whole inventory of solids in the carbonator is perfectly mixed respect to the solid composition, but sufficiently limited to allow the observed difference in temperatures between the two zones when the cooling capacity in the upper part is sufficiently intense. On the other hand, the gas phase is considered as two plug flow reactors connected in series. With these simplifying assumptions, the following CO_2 mass balance closure can be solved for each zone (see also Figure 15a):

$$F_{CO2in,i}\,E_{carb,i}=n_{Ca,i}f_a\left(\frac{dX}{dt}\right)_{reactor,i}=n_{Ca,i}f_{a,i}k_s\varphi X_{ave}\left(\overline{v_{CO2}-v_{CO2,eq}}\right)_i \qquad \text{Equation 15}$$

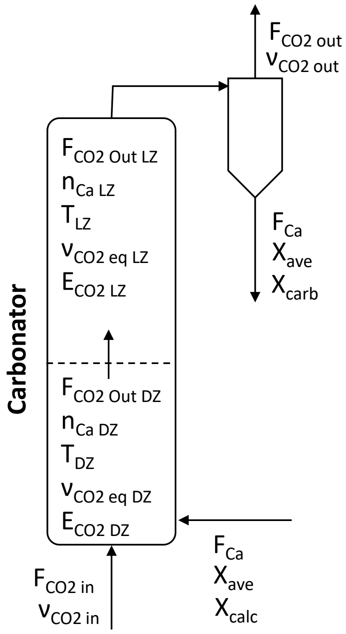
where $F_{CO2in,i}$ is the molar flow of CO_2 entering each zone, $E_{carb,i}$ is the CO_2 capture efficiency, $n_{Ca,i}$ is the inventory of solids, $k_s\varphi$ is an apparent constant reaction rate which has a value of $0.36 s^{-1}$ for the limestone used in these tests, the average CO_2 concentration and $f_{a,i}$ is the fraction of active solids which is calculated as follow, from the residence time distribution curve of a well-mixed reactor:

$$f_{a,i} = \left(1 - e^{\frac{-t_i^*}{n_{Ca}/F_{Ca}}}\right)$$ Equation 16

being n_{Ca} the total inventory of solids, F_{Ca} the molar flow rate entering the carbonator and t_i^* the time needed to achieve the maximum CO_2 carrying capacity under the reaction conditions in each zone:

$$t_i^* = (X_{ave} - X_{calc}) / (k_s \varphi(\nu_{CO2} - \nu_{CO2eq}))$$ Equation 17

Figure 15b presents the results obtained when operating the carbonator at different temperatures, being the inlet CO_2 concentration into the carbonator of 14.2 $\%_v$ with a molar flow of 5.7 kmol/h. The total inventory of solids in the carbonator was 675 kg/m^2. The dots in this figure present the CO_2 capture achieved for different temperatures in the lean zone (T_{LZ} values in ºC are shown in the figure as labels). As can be seen, reducing the temperature by 85ºC in the lean zone increases the CO_2 capture efficiency from 0.91 up to 0.99. This graph also includes two lines that have been calculated using the methodology described above for two cases that consider the same temperature in the dense bed (T_{DZ}=650ºC) and two temperatures in the lean zone (T_{LZ}=550 ºC and 650 ºC). As can be seen, the experimental values fall reasonably inside the region between these two cases. The results shown in this graph indicate that the improvement in the CO_2 capture efficiency is only noticeable when there is an excess of active sorbent flow entering the carbonator (i.e., $F_{Ca}X_{ave}/F_{CO2}$>1.5).



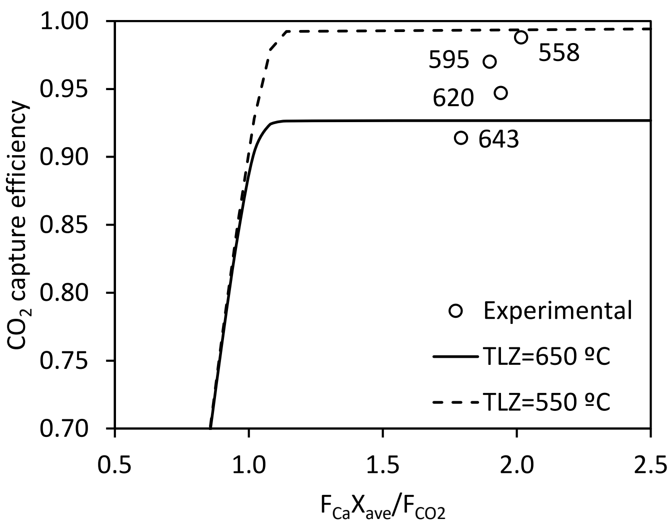


Figure 15. a) Scheme of the CFB carbonator with the main variables involved. b) Effect of the active sorbent/CO_2 ratio on the CO_2 capture efficiency for two different temperatures in the lean zone (lines) and experimentally obtained (dots).

Finally, Figure 16 compares the experimental CO_2 capture efficiency and the values calculated with the model including a wider range of operation conditions (e.g., inventory of solids, temperature, CO_2 inlet concentrations, etc.). The data shown in this figure corresponds to experimental periods in which there was sufficient flow of active sorbent entering the carbonator ($F_{Ca}X_{ave}/F_{CO2}$>1.3). A reasonable agreement can be observed between both values.

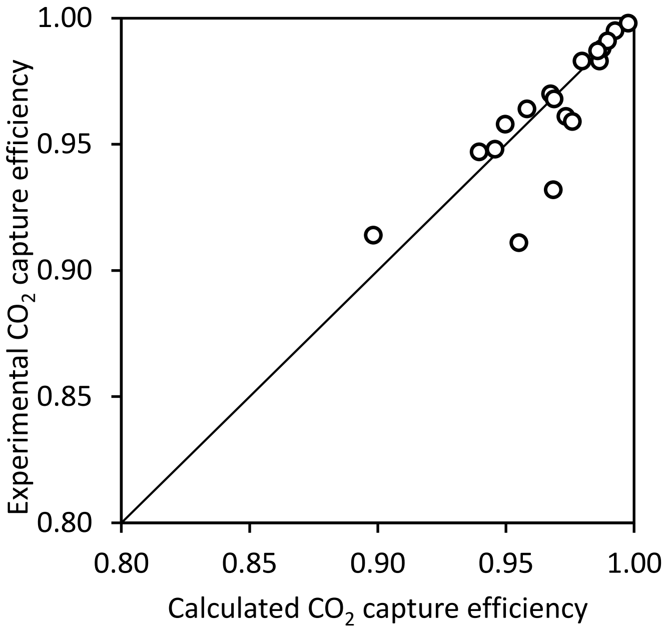
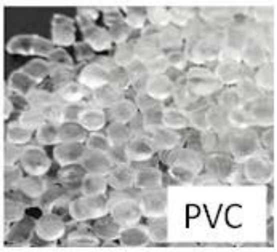


Figure 16. Comparison of the experimental CO_2 capture efficiency and the calculated values.

The results obtained during these tests highlight the need to fulfil two simultaneous conditions to achieve deep decarbonisation in the carbonator of a CFB-CaL system: a temperature around 550ºC (or below) in the upper part of the reactor to overcome thermodynamic limitations, and a sufficient flowrate of active sorbent in the upper region of the carbonator. As indicated above, this second requirement has been achieved during these initial tests by using large make up flows of limestone in order to ensure the presence at the top of the carbonator of an excess of active CaO a sorbent with a high CO_2 carrying capacity (X_{ave}). For most post-combustion applications (except in cement or lime plants where the CaO-rich purge is a co-product and high make up flows will be used), this approach could be too demanding (in terms of high operating costs). Therefore, as discussed in Figure 13, retrofits in La Pereda pilot plant will be carried out to inject a $Ca(OH)_2$ polishing flow, allowing it to reach such high CO_2 capture rates with moderate values of make-up flow of limestone.

6 TESTS INCLUDING ACID GASES (HCl AND HF) IN THE CALCINER.

Following the DoA under Task 3.2, tests in la Pereda pilot have been carried out to generate relevant results for the design of CFB-CaL systems in Waste to Energy plants, WtE. These experiments are devoted to investigate the fate of the acid gases (HCl, HF in addition to the standard measurements of NO_x, SO_2, CO, etc) in CFB-CaL systems. The CaL system represents an opportunity to reduce the cost of downstream gas purification equipment in WtE plants if the emission of these gases is reduced by reacting with the CaO present in the bed. On the other hand, an increased level of accumulation of these trace compounds in the solids will likely affect the CO_2 carrying capacity of the sorbent and the circularity aspects regarding the use of calcium-rich purges (Task 3.3). Therefore, the experimental campaigns in la Pereda pilot include extensive sampling of solids in the pilot and detailed chemical analysis of the solid samples. As discussed in D3.1, the direct injection of acid gases (HCl and HF) into the gas entering the carbonator and/or calciner of La Pereda pilot was ruled out due to strict regulatory and legal issues that prevent any deliberate release of these compounds in gas form to the environment. Therefore, to fulfil the objectives related to the WtE application in Task 3.2, it was decided to study the retention of these acid gases at the calciner conditions by feeding chlorine and fluorine in solid form into the calciner. This was done by feeding pellets of PVC (polyvinyl chloride, -C_2H_3Cl-) and polytetrafluoroethylene (PTFE, -C_2F_4-) as sources of chlorine and fluorine. Figure 17 shows a picture of the pellets used. This figure also shows two small screw feeders that were installed in la Pereda pilot plant to dose these pellets. The screws were manufactured and calibrated to allow the feeding of up to 20 kg/h of solids to the pilot. Figure 17 also shows the composition of the commercial PVC and PTFE pellets used during these tests. Both have similar dimensions of a few millimetres to facilitate the dosing of the pellets. The pellets of PVC have a purity of 75.3%w (being the rests a plasticizer free of Cl) which results into a chlorine content of 42.7$\%_w$. On the other hand, the pellets of PTFE have a purity of 100% resulting into a fluorine content of 76.0$\%_w$.



	PVC pellets	PTFE pellets
Dimension (mm)	2×4	2×4
Purity (%w)	75.3	100
Cl content (%w)	42.7	0
F content (%w)	0	76.0

Figure 17. Picture of the PVC and PTFE feeder and the pellets used. Characteristics of the PVC and PTFE pellets.

To facilitate the injection of this plastic pellets into the calciner, the existing solid feeding system installed in the calciner can be used. Figure 18 shows a schematic of the solid feeding system for fuel and limestone. It is composed of two independent silos to dose independently the fuel and limestone. Then, these two streams are mixed in a screw mixer before being introduced into the calciner through a rotary valve to avoid overpressure in the reactor. In order to facilitate the injection of PVC and PTFE, the flow of pellets is introduced into the mixer of solids, so they are fed together with the fuel and limestone.

An initial test was carried out to study the fate of Cl and F in the calciner. In order to facilitate the interpretation of the data from this test the calciner was operated in air mode. In addition, there was no CO_2 capture during this test and the carbonator was fluidized with air. The calciner was operated at an average temperature around 830 ºC burning biomass as fuel in the calciner with an excess of oxygen around $5\%_v$.

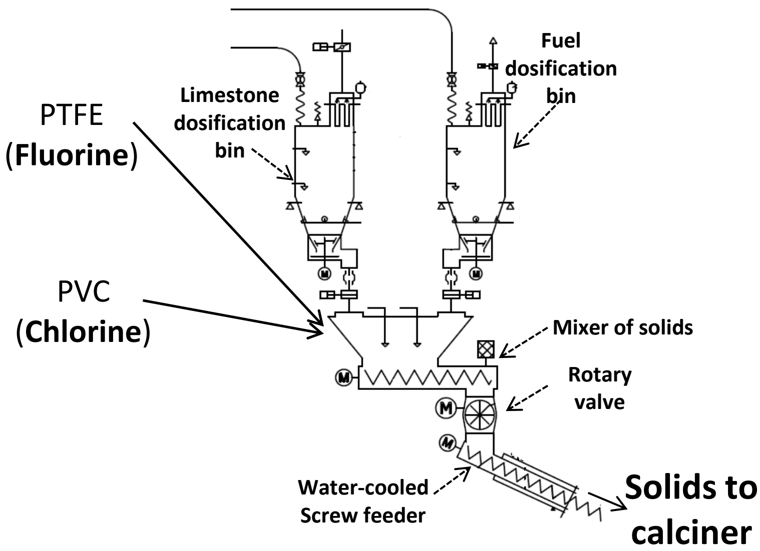


Figure 18. Schematics of the solid feeding system in la Pereda pilot plant.

Figure 19 presents some of the parameters measured during this test of 12 hours. In the graph at the top, it is shown the solids feeding rate into the calciner while the graph at the bottom shows the composition of the flue gas at the exit of the calciner (O_2, CO_2, HCl and HF).

There are two periods in which PVC and PTFE pellets were fed into the calciner. The first period, between 9:00 and 14:00, corresponds to the feeding of 3.5 kg/h of PVC pellets (1.5 kg/h of Cl). The expected HCl concentration at the outlet of the calciner during this period if there is no chlorine retention would be 570 ppm of HCl. However, as can be seen in the bottom graph of Figure 19, the concentration at the outlet of the calciner is negligible. The second period, between 14:30 and 19:30, corresponds to the feeding of 2.2 kg/h of PTFE pellets (1.7 kg/h of F). In this case of no HF retention, an emission of 1200 ppm would be expected. However, no HF was measured at the exit of the calciner. This initial result suggests that HCl and HF could be retained in the calciner when using SRF fuels as fuel.

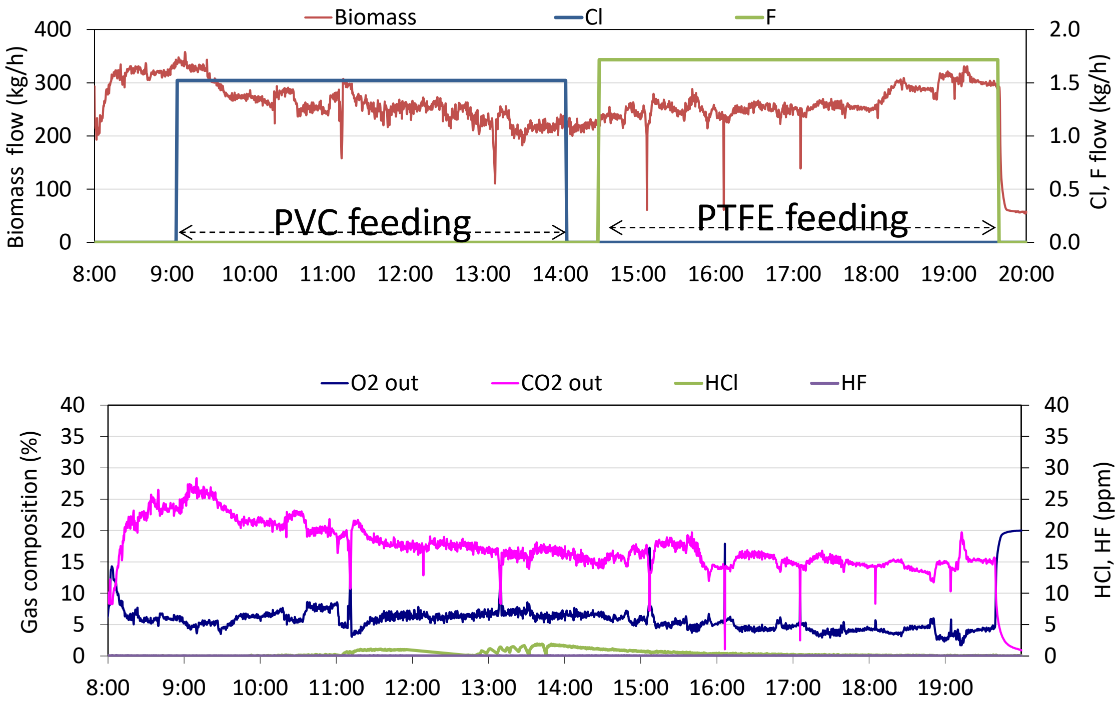


Figure 19. Initial test feeding PVC and PTE pellets into the calciner to study the fate of acid gases.

More experimental campaigns are planned to validate this result. In parallel, in view of the negligible detections of these gases in the gas outlet of the la Pereda pilot, more detailed and controlled experiments at laboratory scale (in a TG and/or low TRL reactors) will be carried out to facilitate the interpretation of the results obtained in La Pereda pilot plant and confirm such deep removal efficiencies of these acid gases in the CFB-CaL system. These will be reported in the future deliverable D3.3 (Results of the experimental campaigns in the 1.7 MWth pilot plant, II) and should also contribute to D3.4 (Use of CFB-CaL purges from biomass-fired and WtE power plants).

7 CONCLUSIONS

The main conclusions from the works reported in the previous sections 3-6 and associated Annex are as follows:

- The pilot plant of la Pereda is fully functional again and able to operate in steady state mode or dynamic mode when using biomass as a fuel in the oxy-fired calciner, with thermal power input over 2 MWth, fuel combustion efficiencies exceeding 99% in most conditions tested in the calciner (at T>900ºC and O_2 excess>1%vol), reaching calcination efficiencies between 96-99%, low content of NOx (<200 ppmv) when operating the calciner with a low oxygen-excess.
- Dynamic tests in support of WP2 activities were completed. WP4 beneficiaries will use these results to simulate SWERIM pilot optimum configurations for the steel sector to support the foreseen commissioning and experimental campaigns.
- A novel strategy to increase the CO_2 capture efficiency in the carbonator of a Calcium Looping system using CFB reactors has been successfully tested. This consists of the cooling of the upper part of the carbonator to create a low temperature zone (<550 ºC) and avoid the equilibrium limits on the minimum CO_2 concentration achievable. For this purpose, experiments have been carried out with high make up flows of limestone. The results confirm that it is possible to reach CO_2 capture efficiencies above 99%.
- Initial test with proxy-fuels of Waste to Energy plants (i.e. feeding to the calciner PVC and PTFE polymers mixed with the biomass to achieve representative Cl and F contents in the fuel) seems to indicate that the CFB-CaL system is an extremely efficient system to capture acid gases, as negligible concentrations have been so far registered of these gases at the exit of the calciner.

These conclusions should be completed and confirmed with new data from experiments planned on the la Pereda pilot, after the retrofits to allow $Ca(OH)_2$ powder injection to the carbonator and flue gas recycle to the calciner (see D3.1) are completed.

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8 LIST OF SYMBOLS

A_{carb}: section of the carbonator

c_{ps}: heat capacity of the solids

E_{Calc}: calcination efficiency in the calciner

$E_{Carb\ eq}$: the maximum capture efficiency limited by the equilibrium

E_{carb}: CO_2 capture efficiency in the carbonator

f_a: fraction of active solids in the carbonator

F_{Ca}: molar circulation rate between carbonator and calciner reactors

F_{CaCO3}: CO_2 fed with the make-up flow of limestone

$F_{CO2\ fuel}$: source of CO_2 generated during the combustion of fuel

$F_{CO2\ oxidant}$: CO_2 entering with the oxidant

$F_{CO2,\ in}$: molar flow of CO_2 entering the carbonator with the flue gas

G_s: total solid circulation rate of solids arriving to the carbonator

k_s: constant reaction rate that depends on the limestone used

$n_{Ca\ CC}$: inventory of solids in the calciner

n_{Ca}: the inventory of solids in the carbonator

Q_{calc}: calcination heat demand

Q_{carb}: heat released due to carbonation reaction

$Q_{CO2\ capt}$ is the heat leaving the carbonator with the CO_2 captured

$Q_{CO2\ flue\ gas}$: heat output with the concentrated CO_2 flue gas

Q_{comb}: heat released due to the combustion of coal

Q_{comb}: heat released due to the combustion of the small amount of coal arriving the carbonator

$Q_{flue\ gas}$: heat entering the carbonator with the flue gas fed

$Q_{heatloss}$: heat loss though carbonator walls

$Q_{leangas}$: heat leaving the carbonator with the flue gas

Q_{lossCC}: heat losses through the reactor walls

$Q_{oxidant}$: heat input with the oxidant

Q_{refrig}:heat removed with the bayonet tubes

Q_{solids}: heat input needed to heat up the stream of solids circulating between the reactors.

t*: time needed to increase the carbonate content from X_{calc} to X_{ave}

T_{calc}: average reactor temperature

T_{carb}: average carbonator reactor temperature

T_{DZ}: temperature in the bottom dense zone of the carbonator

T_{LZ}: temperature in the upper lean zone of the carbonator

X_{ave}: CO_2 carrying capacity

X_{calc}: carbonate content of the solids coming from the calciner

X_{Carb^*}: average $CaCO_3$ content of the solid entering the calciner considering the solids arriving from the carbonator and the make-up flow of limestone

X_{carb}: carbonate content of the solids leaving the carbonator

τ_{active}: active space time

ϕ: gas-solid contacting factor defined

9 LIST OF FIGURES AND TABLES

- Figure 14. a) Example of the effect of carbonator temperature on the carbonation efficiency, b) and c) inventory of solids and temperature profile along the carbonator (grey dots: from 12:30 to 13:20; white dots: from 14:00 to 14:30).
- Figure 15. a) Scheme of the CFB carbonator with the main variables involved. b) Effect of the active sorbent/CO_2 ratio on the CO_2 capture efficiency for two different temperatures in the lean zone (lines) and experimentally obtained (dots).
- Figure 16. Comparison of the experimental CO_2 capture efficiency and the calculated values.
- Figure 17. Picture of the PVC and PTFE feeder and the pellets used. Characteristics of the PVC and PTFE pellets.
- Figure 18. Schematics of the solid feeding system in la Pereda pilot plant.
- Figure 19. Initial test feeding PVC and PTE pellets into the calciner to study the fate of acid gases.
- Table 1. Range of operating conditions and main variables during the tests devoted to achieve high CO_2 capture efficiencies in the carbonator.

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11 ANNEX

This Annex contains a summary of the more relevant experiments carried out in CFB-CaL pilot of La Pereda. The experimental information included in this annex is provided through tables with the main operational variables and a brief description of the experiment is also included. The raw data in the form of datalogs and a detailed analysis of the results in form of excel files obtained from the experiments in excel has been shared with the partners involved in design and modelling activities in the project.

As indicated in the main body of this deliverable, these experiments were focussed on different aspects: oxy-combustion tests of biomass in the calciner (Bio-CHP), dynamic tests, operating the carbonator with CO2 capture rates (>99%) and some initial tests including acid gases in the calciner. Some of these different aspects have studied in parallel. So, the experimental information has been organized chronologically in different monthly experimental campaigns. For each experiment, a table with the main operation parameters is included. Also, several graphs are included displaying the evolution of this parameters with time.

There were several additional days of operation during January. However, it was not feasible to achieve stable operating conditions in the plant. As indicated in Section 3 of this deliverable, the unstable operation was due to the blockage of some nozzles in the calciner loop seal. However, several procedures to improve the start-up of the pilot were adjusted during these experiments (i.e. the use of enriched air to enhance the biomass combustion in the calciner and to reduce the gas velocity in the calciner and increases the inventory of solids, feeding of large pulses of biomass at low temperatures to speed up the heating and improve the biomass combustion). During a typical start-up, the pilot plant is heated up using two burners fired with propane installed in the carbonator and calciner at 3 meters above the grid. In order to heat up the stand pipes and loop seals, it is necessary to establish a certain circulation of solids between reactors that transfer the heat release during propane combustion. Once the bed of the calciner reaches enough temperature (around 300 ºC), biomass is fed to increase the thermal input to the system and finally reach the typical operation temperatures.

In order to illustrate the operational issues occurred during this period, a few days of unstable operation are reported. This technical issue was then solved by the end of January, and it was possible to run the subsequent successful experimental campaigns. The last test included in this section corresponds to a test with stable operation.

Experiment 16/01/2024

This experiment shows a typical start-up of the pilot. There is an initial period when the pilot is heated using by firing propane using the start-up burner located in the carbonator and calciner (from 7:50 to 10:00). Once a temperature around 300 ºC is achieved in the bottom bed of the calciner, the biomass is fed into the reactor in batches of 50 kg. In order to enhance the combustibility of the biomass, the calciner is operated under enriched air (Figure A.6). Moreover, a batch of bottom ash from the power plant was introduced in the calciner an attempt to create a dense bed zone of the reactor and increase the residence time of the pellets. Several peaks of temperature can be observed in Figure A.7 between 10:00 and 12:00. These correspond to the combustion/ignition of accumulated biomass. The feeding of biomass at relatively low temperatures (<300 ºC) during the start-up of the pilot is necessary to increase thermal input. However, the low temperatures result into an accumulation of biomass char in the inventory of solids which can ignite as the temperature increases. These peaks are typically observed between 400-500 ºC. From this point, biomass feed rate can be increased to increase progressively the temperature. During this experiment, it was possible to feed continuously biomass from 10:30 to 16:00. However from this point, there was unstable operation due to accumulation of solids in the calciner stand pipe and the experiment was stopped. This resulted into large variations on the temperature of the reactors and inventory of solids as can be observed in Figures A.7. and A.10.

Table A.2. Average values of experimental key variables between 07:10 h and 19:30 h

Calciner data	
$T_{901\ dense\ bed}$ (°C)	363.1
$T_{out\ 906}$ (°C)	560.2
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	2.3
$O_{2\ in}$ (%)	26.0
$O_{2\ out}$ (%)	15.8
Limestone flow (kg/h)	57.2
Biomass flow (kg/h)	121.4
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	363.4
$T_{806\ out}$ (°C)	417.1
X_{ave}	-
$u_{gas\ in\ grid\ +\ LS}$	2.6
$CO_{2\ in}$ (%)	0.0
$CO_{2\ out}$ (%)	2.8

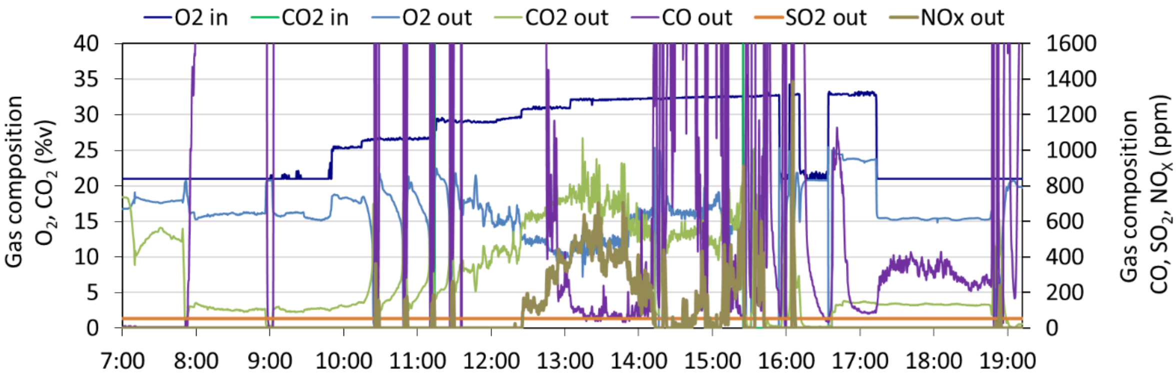

Figure A.6. Inlet and outlet gas concentration in the calciner reactor (Experiment 16/02/24).

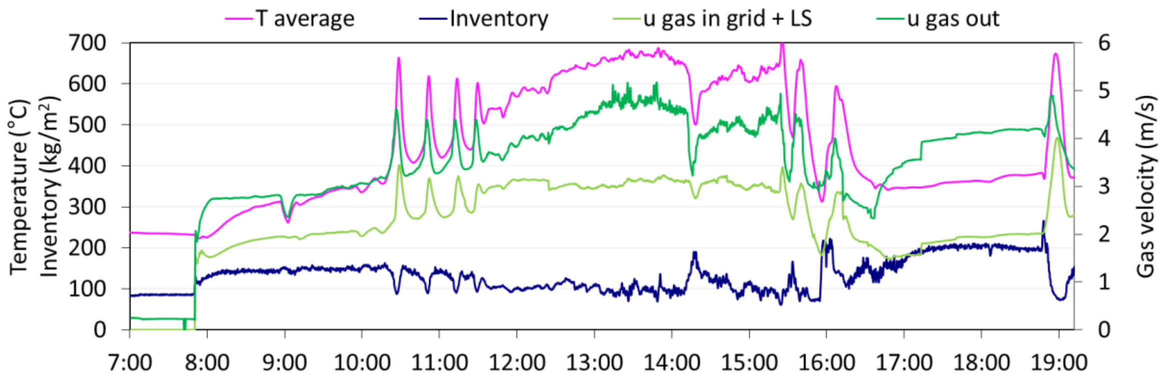

Figure A.7. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 16/02/24).

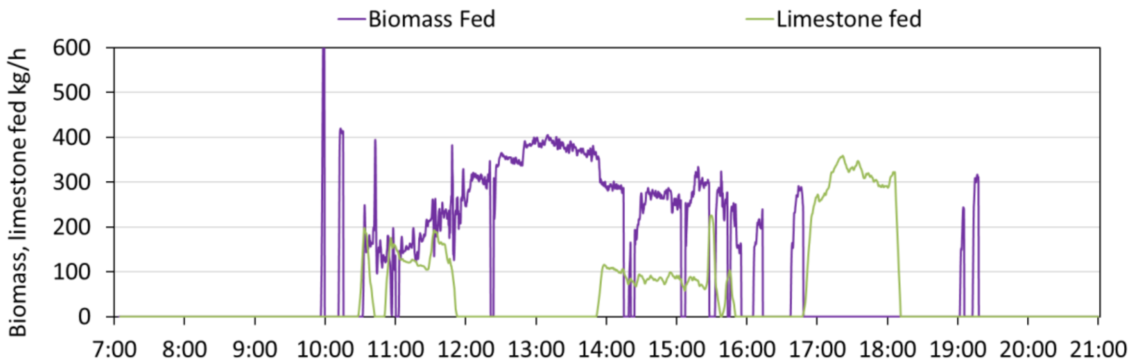

Figure A.8. Biomass and limestone feeding rates (Experiment 16/02/24).

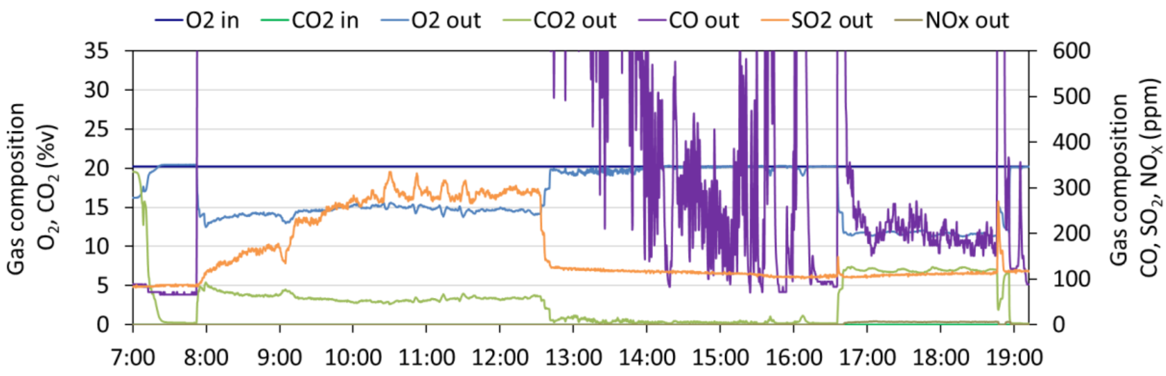

Figure A.9. Inlet and outlet gas concentration in the carbonator reactor (Experiment 16/02/24).

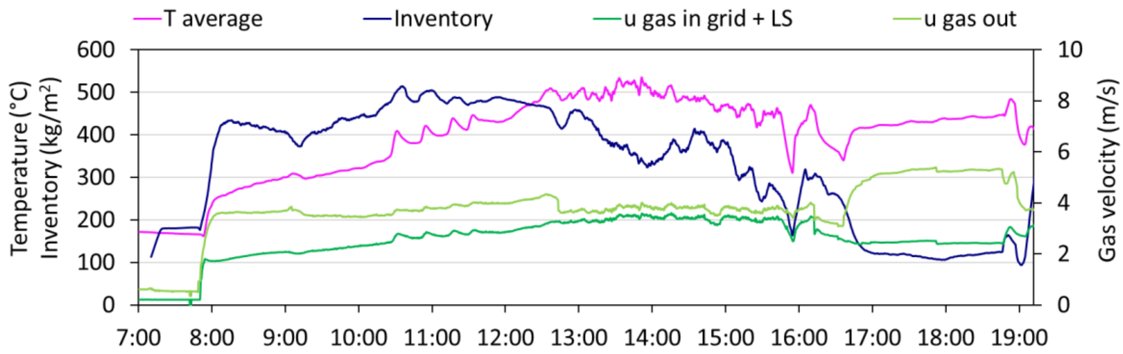

Figure A.10. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 16/02/24).

Experiment 31/01/2024

This experiment corresponds to a CO_2 capture test carried out in enriched air conditions in the calciner after solving the problem with the fluidization of the calciner loop seal. The burners are switched on at the beginning of the test (around 7:10). During around 2 hours, the pilot is preheated using only propane as fuel and the temperature of the reactors is increased progressively. When there is a temperature around 300 ºC in the calciner, several batched of biomass are fed. Around 50 kg of biomass is fed with each batch at a mass flow rate of around 400 kg/h. This allows a faster increase of the temperature in the reactors. After an initial attempt to carry out a CO2 capture test (between 14:40 to 15:30), the fluidization gas in the carbonator was changed from air to a synthetic flue gas with a CO2 concentration of 11%v at 17:00. These conditions were maintained during three hours. During these period, samples were extracted from the reactors to close the mass balances an analyse the experimental information.

Table A.4. Average values of experimental key variables between 14:45 h and 19:35 h

Calciner data	
$T_{901\ dense\ bed}$ (°C)	486.6
$T_{out\ 906}$ (°C)	795.4
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	2.6
$O_{2\ in}$ (%)	27.2
$O_{2\ out}$ (%)	9.6
Limestone flow (kg/h)	184.7
Biomass flow (kg/h)	291.5
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	523.4
$T_{806\ out}$ (°C)	472.4
X_{ave}	0.277
$u_{gas\ in\ grid\ +\ LS}$	2.7
$CO_{2\ in}$ (%)	8.7
$CO_{2\ out}$ (%)	4.6

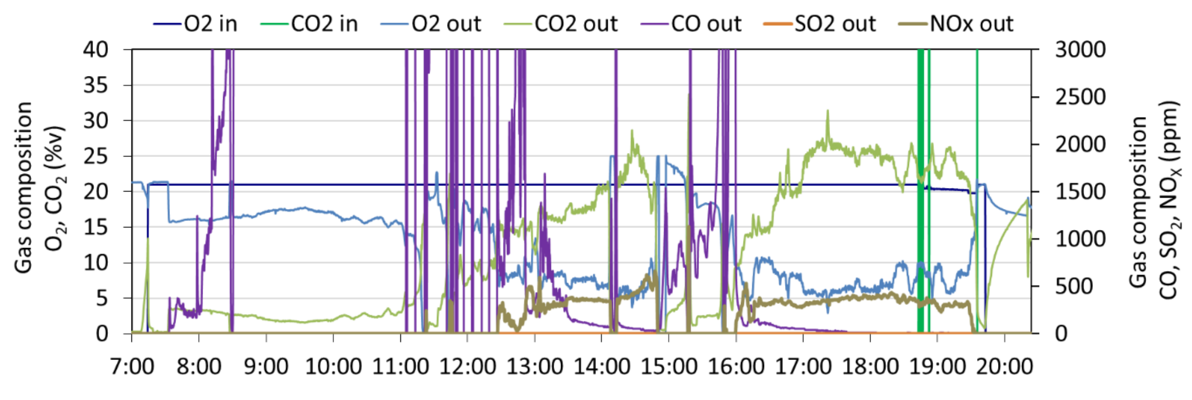

Figure A.16. Inlet and outlet gas concentration in the calciner reactor (Experiment 31/01/24).

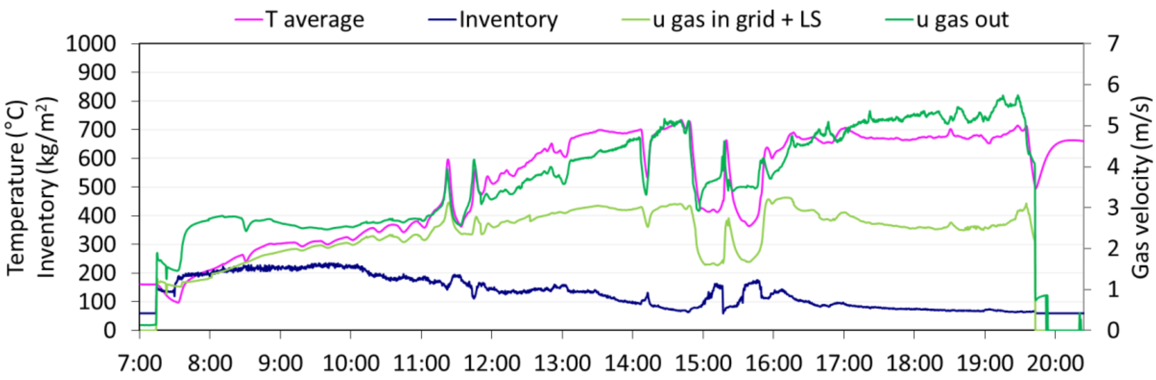

Figure A.17. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 31/01/24).

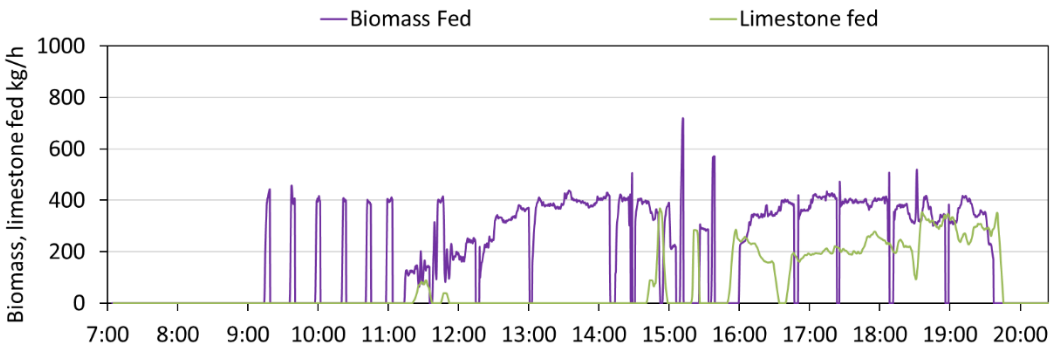

Figure A.18. Biomass and limestone feeding rates (Experiment 21/01/24).

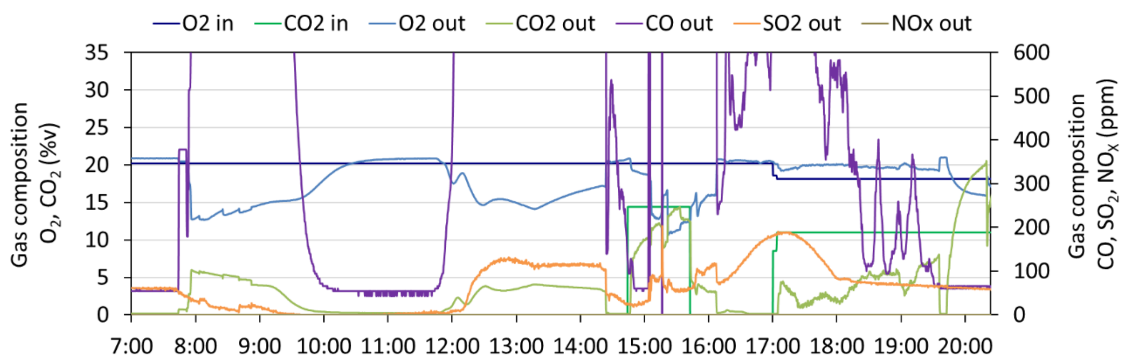

Figure A.19. Inlet and outlet gas concentration in the carbonator reactor (Experiment 31/01/24).

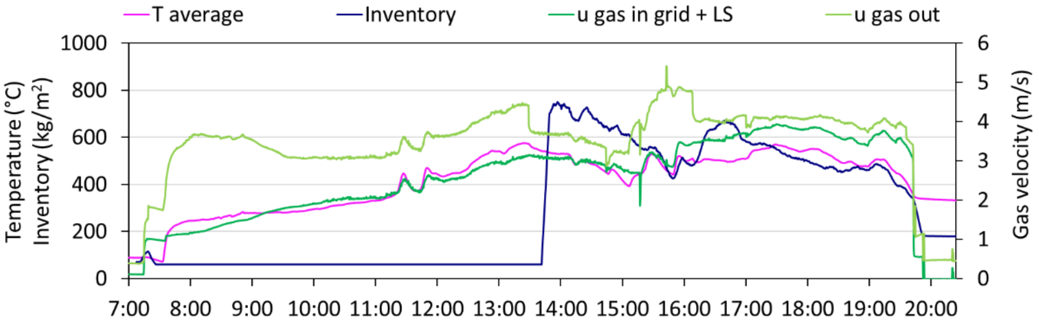

Figure A.20. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 31/01/24).

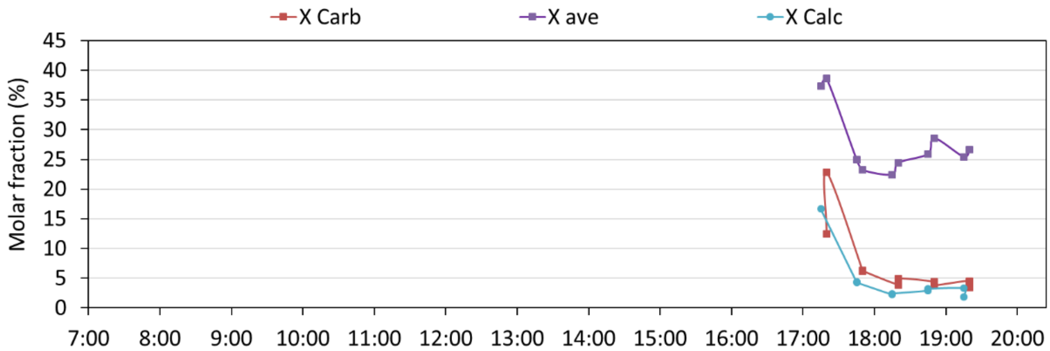

Figure A.21. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids (X_{ave}) (Experiment 31/01/24).

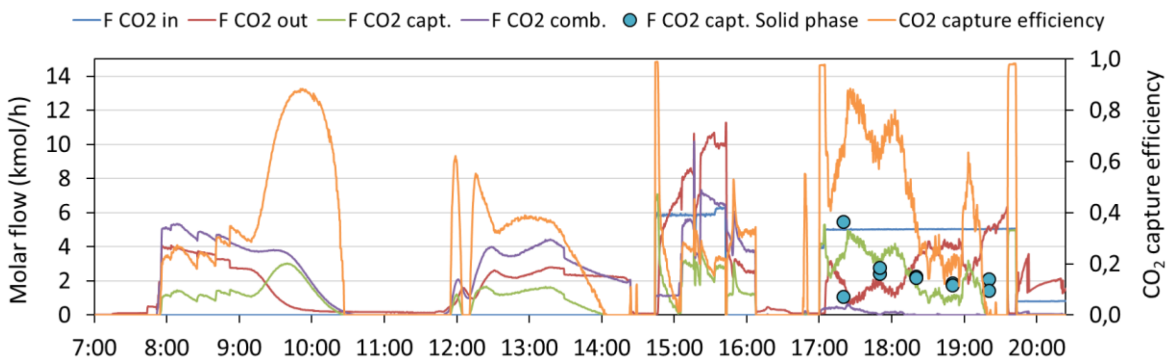

Figure A.22. CO_2 balance closure and CO_2 capture efficiency (Experiment 31/01/24).

Experiment: 06/02/2024

The purpose of this experiment was to conduct a carbon capture test under stable operation conditions trying to achieve high capture efficiencies (above 99%). In addition, this experiment includes a dynamic test (from 19:45). As shown in Figure A.28, the calciner, was operated under enriched-air conditions. The average temperature, inventory and gas velocities in the calciner are presented in Figure A.29. Since the calciner is operated with relatively low CO_2 concentrations at the outlet, the average temperature the reactor was 840 °C. The average inlet gas velocity was 3.4 m/s while the outlet gas velocity was 5.5 m/s. Regarding biomass and limestone flows, depicted in Figure A.30, from 08:00 h to 20:30 h, biomass was continuously fed to the calciner, being the average value 350.4 kg/h. The peaks observed in the biomass feeding rate correspond to the refilling of the dosification silo. Limestone feeding rate was kept at high value during the experiment in order to maintain reasonable circulation rates. The average limestone flow rate during the experiment was 500 kg/h.

Table A.6. Average values of experimental key variables 14:00 h and 20:30 h (Experiment 06/02/24)

Calciner data	
$T_{901\ dense\ bed}$ (°C)	614.2
$T_{out\ 906}$ (°C)	843.7
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.4
$O_{2\ in}$ (%)	27.35
$O_{2\ out}$ (%)	6.7
Limestone flow (kg/h)	499.0
Biomass flow (kg/h)	350.4
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	642.1
$T_{806\ out}$ (°C)	543.2
X_{ave}	0.370
$u_{gas\ in\ grid\ +\ LS}$	3.3
$CO_{2\ in}$ (%)	13.1
$CO_{2\ out}$ (%)	1.1

Concerning the carbonator, as illustrated in Figure A.31, from 14:00 h to 19:45 h, a synthetic flue gas with 11.8 % CO_2 was introduced. From 19:45 h to 20:10 h, the synthetic flue gas stream contained 20.61 % CO_2. Finally, between 20:10 h till the end of the test at 20:30 h, the CO_2 concentration was changed to 17.7 %. The average inlet gas velocity in the carbonator was 3.3 m/s while the average outlet gas velocity was 3.4 m/s. The evolution of the $CaCO_3$ molar composition of the solids is presented in Figure A.33. In addition, the average maximum carrying capacity of the solids was 0.370. This high value is due to the high flow of fresh limestone fed continuously to the calciner reactor. Moreover, in Figure A.34, it is possible to follow the progression of carbon capture efficiency during the test and the CO_2 balance closure. There is not a good agreement in the CO_2 balance closure for this test. Nevertheless, efficiencies close to 99 % were achieved, between 14:00 h to 19:43 h.

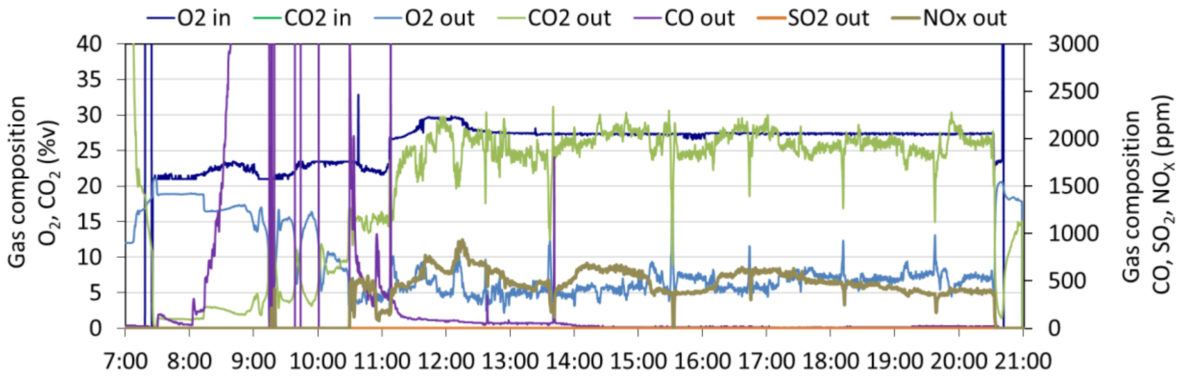

Figure A.28. Inlet and outlet gas concentration in the calciner reactor (Experiment 06/02/24).

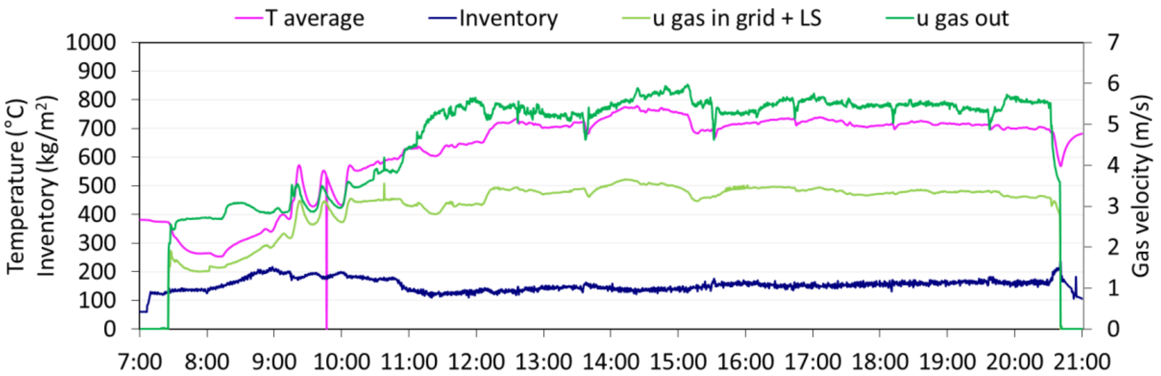

Figure A.29. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 06/02/24).

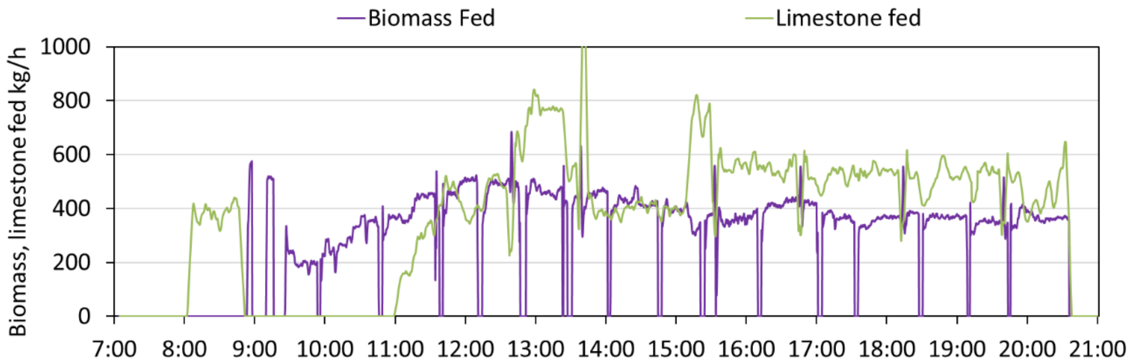

Figure A.30. Biomass and limestone feeding rates (Experiment 06/02/24).

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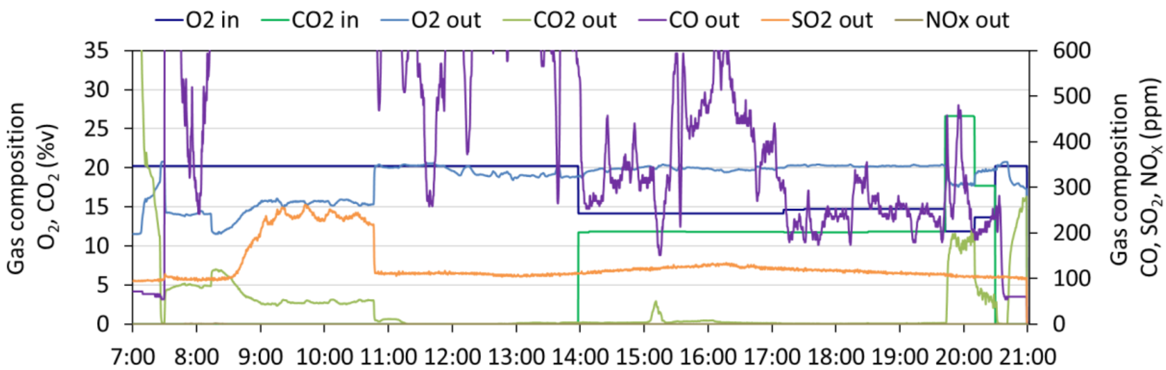

Figure A.31. Inlet and outlet gas concentration in the carbonator reactor (Experiment 06/02/24).

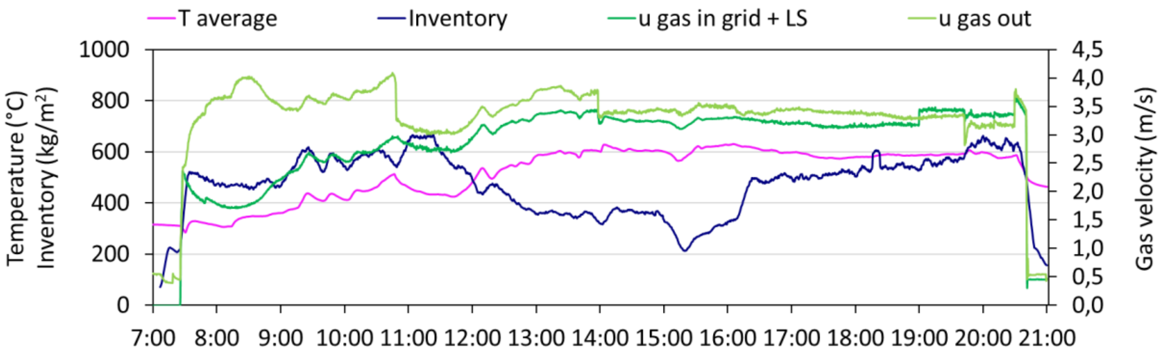

Figure A.32. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 06/02/24).

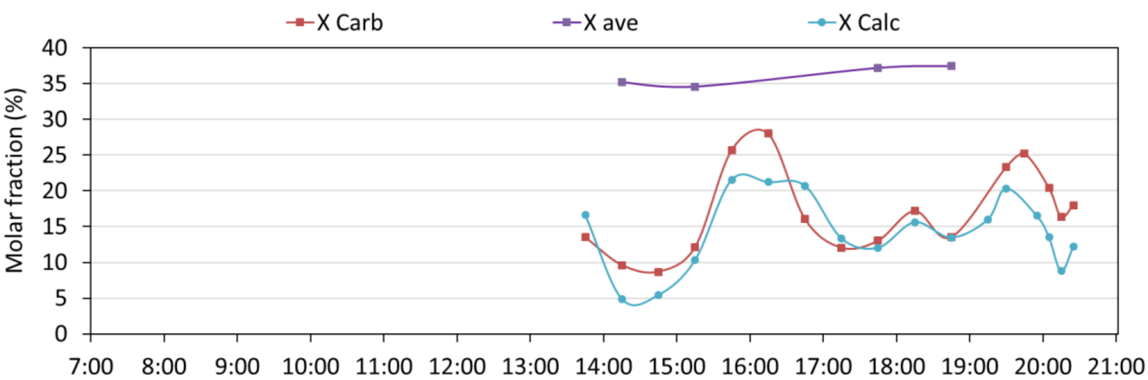

Figure A.33. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids in the carbonator reactor (X_{ave}) (Experiment 06/02/24).

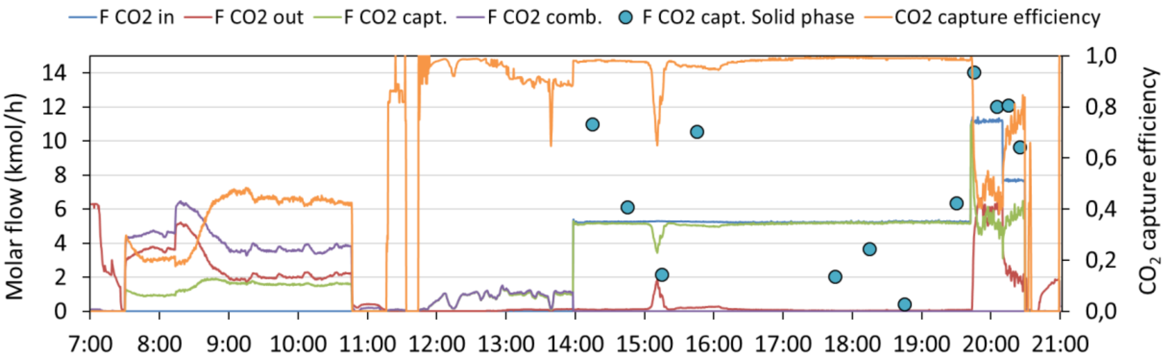

Figure A.34. CO_2 balance closure and carbon capture efficiency (Experiment 06/02/24).

Experiment: 07/02/2024

This experiment corresponds to a standard CO_2 capture test and also a dynamic test. During the high CO2 capture period, a synthetic flue gas stream with 13.1% CO_2, from 11:00 h to 15:20 h. Then, from 15:20 h to the end of the experiment, a dynamic test varying the CO_2 flue gas concentration was carried out. During this experiment, the calciner was operated under oxy-combustion conditions, as shown in Figure A.35. Gas velocities are depicted in Figure A.36, the average inlet gas velocity in the calciner was 2.4 m/s and the average outlet gas velocity 4.0 m/s. The average temperature in the upper section was 900 °C while in the dense bed 767 °C. High limestone flow rates were used during the experiment. In Figure A.37 is also presented the biomass flow rates during the experiment. From 09:30 h to 17:10 h, biomass was continuously fed to the calciner with an average rate of 380 kg/h, aiming to maintain the oxygen concentration in the outlet stream around 4%. Regarding the carbonator inlet flow, in Figure A.38, it can be noticed the different CO_2 concentrations tested during the experiment. After the initial period of the test, from 15:20 h to 16:05 h no CO_2 was fed to the reactor. Next, between 16:05 h and 16:45 h, CO_2 was incremented to 21.4 %. From that point in time to 17:10 h, CO_2 concentration in the synthetic flue gas was decreased to 16.0 %. The composition of the solids is presented in Figure A.40, for this test the average CO_2 carrying capacity was 0.291. Besides, in Figure A.41 It is possible to take a closer look to the carbon capture efficiencies. Carbon capture efficiencies above 80 % were reached during the first period of the experiment.

Table A.7. Average values of experimental key variables 10: 57 h and 17:08 h (Experiment 07/02/24).

Calciner data	
T $_{901\ dense\ bed}$ (°C)	767.0
T $_{out\ 906}$ (°C)	900.0
u $_{gas\ in\ grid\ +\ LS}$ (m/s)	2.4
$O_{2\ in}$ (%)	34.08
$O_{2\ out}$ (%)	4.4
Limestone flow (kg/h)	442.3
Biomass flow (kg/h)	377.4
Carbonator data	
T $_{801\ dense\ bed}$ (°C)	649.2
T $_{806\ out}$ (°C)	568.3
X_{ave}	0.291
u $_{gas\ in\ grid\ +\ LS}$	3.3
$CO_{2\ in}$ (%)	12.8
$CO_{2\ out}$ (%)	1.8

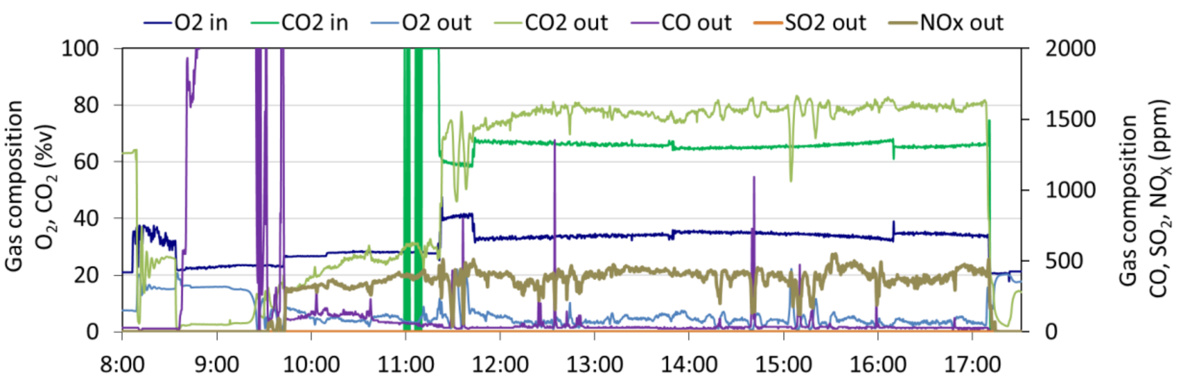

Figure A.35. Inlet and outlet gas concentration in the calciner reactor (Experiment 07/02/24).

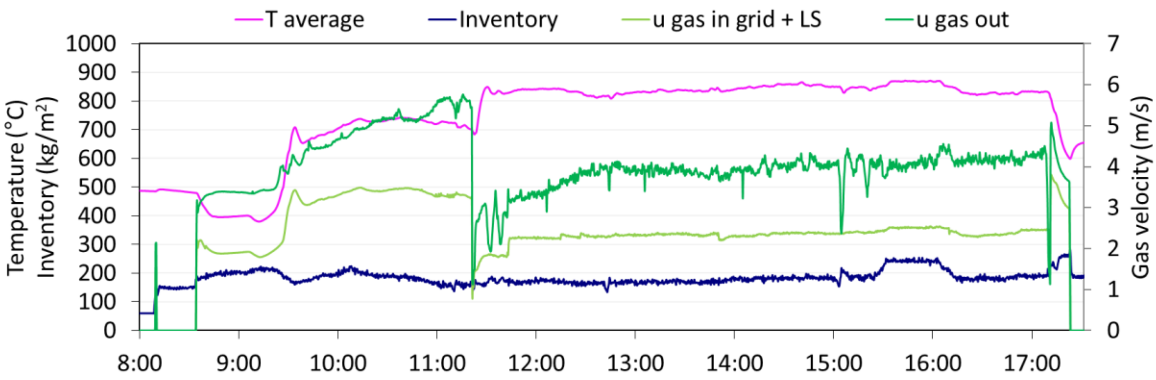

Figure A.36. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 07/02/24).

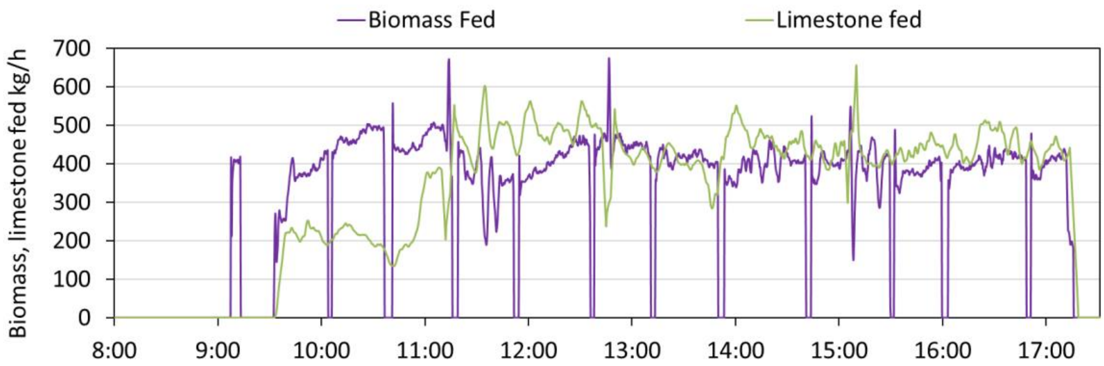

Figure A.37. Biomass and limestone feeding rates (Experiment 07/02/24).

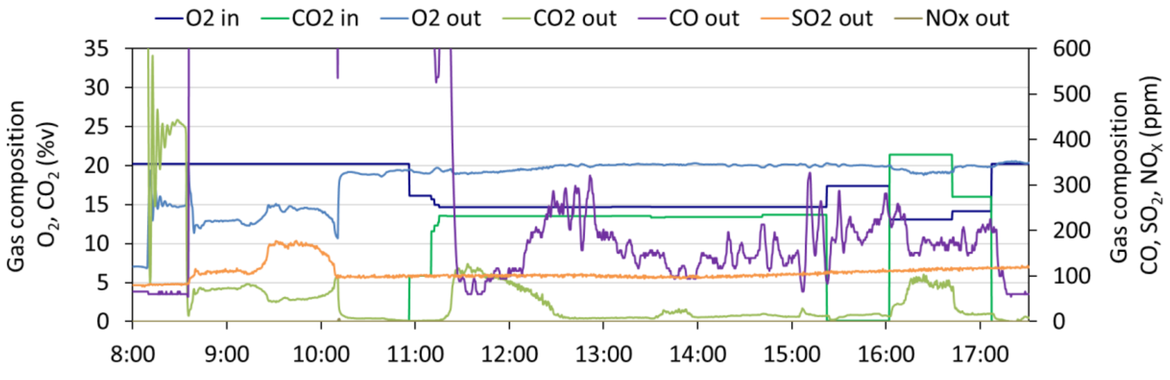

Figure A.38. Inlet and outlet gas concentration in the carbonator reactor (Experiment 07/02/24).

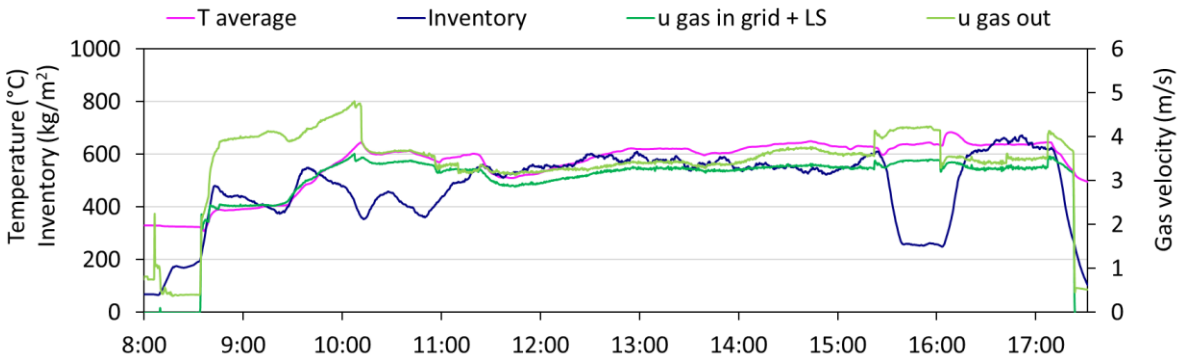

Figure A.39. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 07/02/24).

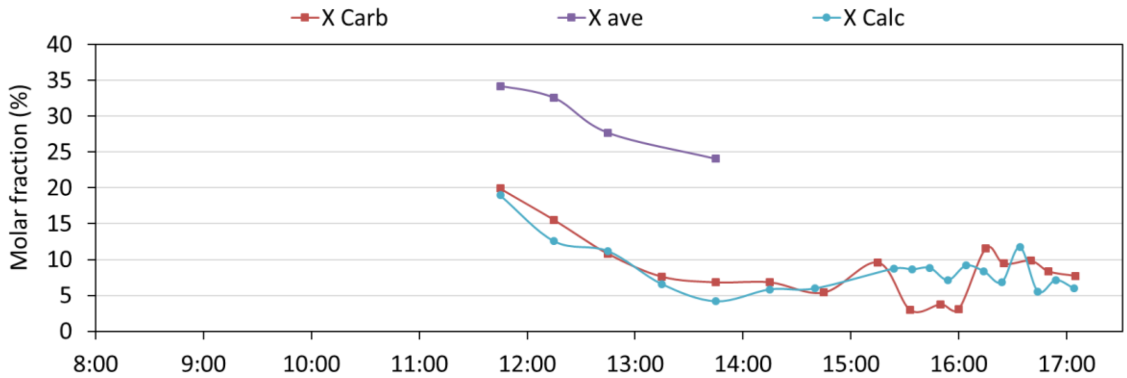

Figure A.40. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids (X_{ave}) in the carbonator reactor (Experiment 07/02/24).

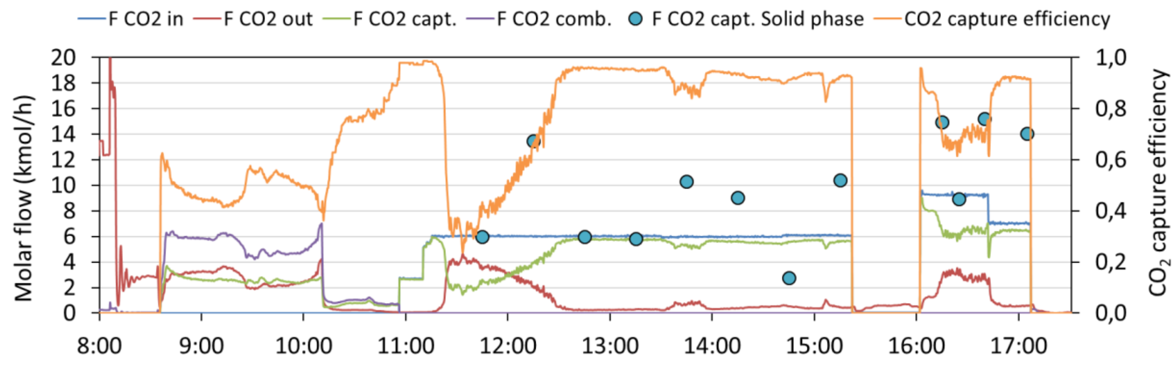

Figure A.41. CO_2 balance closure and carbon capture efficiency (07/02/24).

Experiment: 08/02/2024

The purpose of the experiment was to carry out a carbon capture test by alternating periods when no CO_2 was fed to the carbonator. In Figure A.42 is presented the evolution of the gas concentration in the inlet and outlet streams of the calciner reactor. As seen, the calciner was operated under enriched- air conditions and O_2 in the outlet stream was maintained during the whole experiment around 4 %. Gas velocities are depicted in Figure A.43, the average inlet gas velocity was 3.7 m/s and the average outlet velocity of the gas stream was 5.3 m/s. Illustrated in Figure A.44, limestone and biomass were continuously fed since the beginning of the experiment at 08:00 h. First, it was considered to feed a relatively low flow of limestone to the reactor. However, low solids circulation between the reactors was observed during this period. Hence, it was decided to increase the limestone feeding rate.

Table A.8. Average values of experimental key variables (Experiment 08/02/24).

Calciner data	
$T_{901\ dense\ bed}$ (°C)	661.1
$T_{out\ 906}$ (°C)	847.1
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.7
$O_{2\ in}$ (%)	23.15
$O_{2\ out}$ (%)	3.9
Limestone flow (kg/h)	197.1
Biomass flow (kg/h)	328.6
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	650.2
$T_{806\ out}$ (°C)	580.5
X_{ave}	0.265
$u_{gas\ in\ grid\ +\ LS}$	3.3
$CO_{2\ in}$ (%)	7.5
$CO_{2\ out}$ (%)	2.3

Concerning the carbonator reactor, as seen in Figure A.45, it was fed with a synthetic flue gas stream from 09:35 h to 11:45 h with an average CO_2 concentration of 12.9 %. After that, between 11:45 h to 12:55 h, CO_2 was not fed to the reactor since it was necessary to properly calcine the inventory. At 12:55 h, CO_2 was again introduced to the reactor, the average CO_2 concentration was 11.1%. From, 13:45 h to 14:50 h, the synthetic flue gas inlet was again cut off. Finally, between 14:50 h and 16:00 h, flue gas with a CO_2 concentration of 6.9 % was introduced. The evolution of the average temperature, gas velocities and inventory can be seen in Figure A.46. The average inlet gas velocity was 3.3 m/s while the average outlet gas velocity was 3.8 m/s. Concerning the solid samples taken during the experiment from both reactors, their $CaCO_3$ molar composition is presented in Figure A.47. Regarding the maximum CO_2 carrying capacity, the average value for the carbonator solids during the experiment was 0.297. It can be noticed in Figure A.48 that, for the experimental periods when CO_2 was fed to the reactor, carbon capture efficiencies above 80 % were reached.

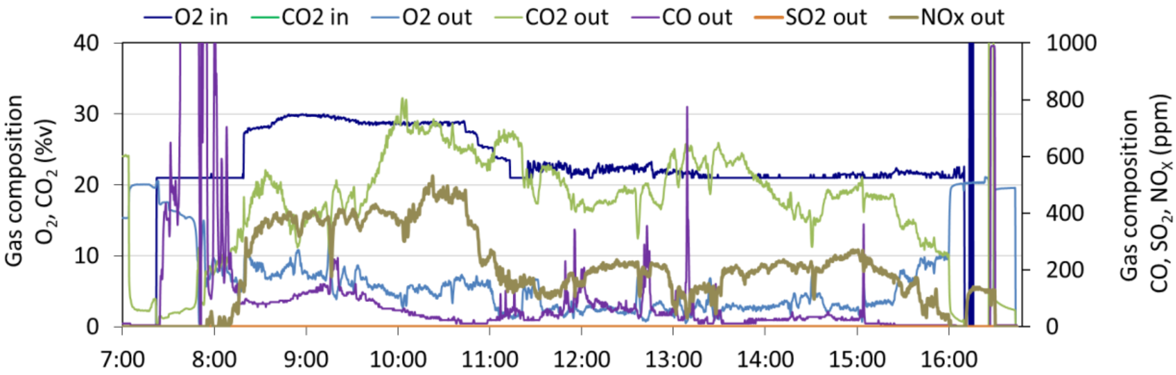

Figure A.42. Inlet and outlet gas concentration in the calciner reactor (Experiment 08/02/24).

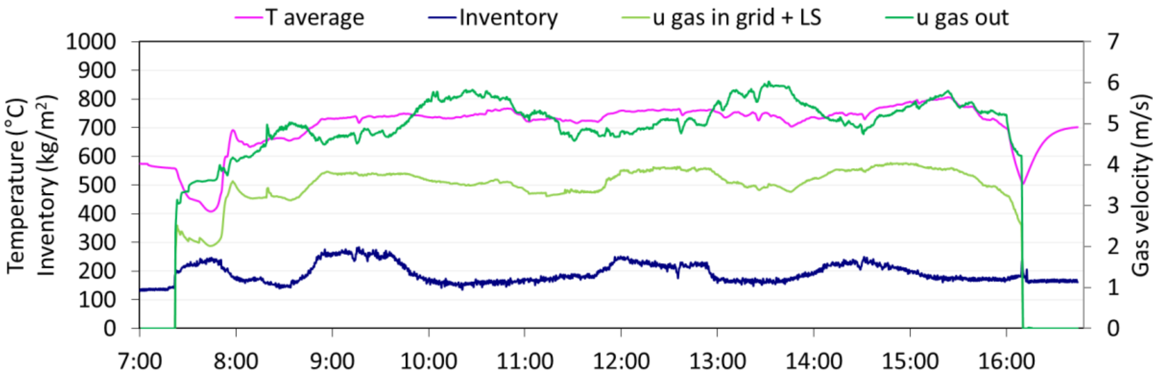

Figure A.43. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 08/02/24).

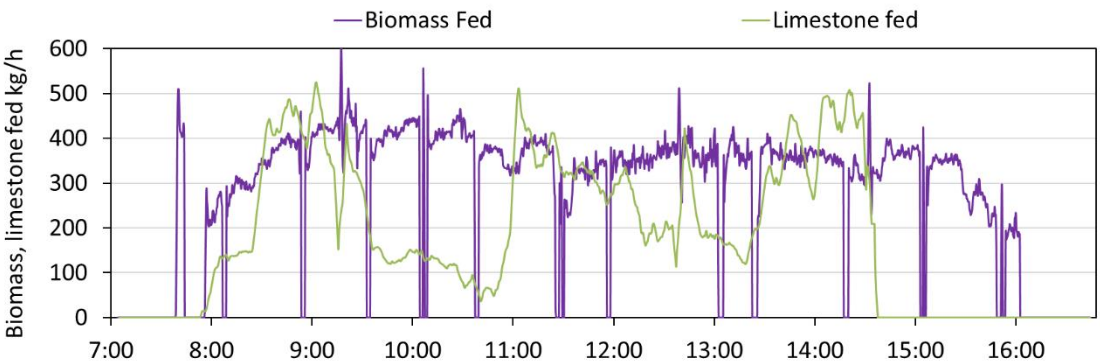

Figure A.44. Biomass and limestone feeding rates (Experiment 08/02/24).

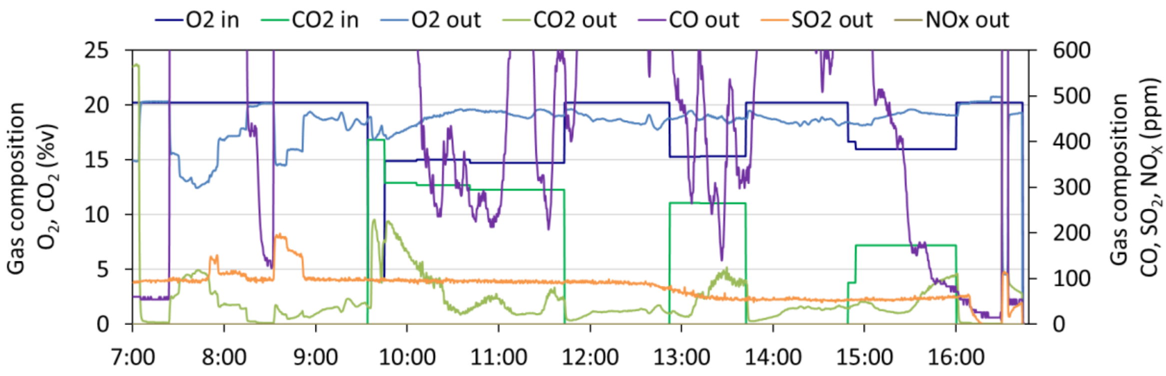

Figure A.45. Inlet and outlet gas concentration in the carbonator reactor (Experiment 08/02/24).

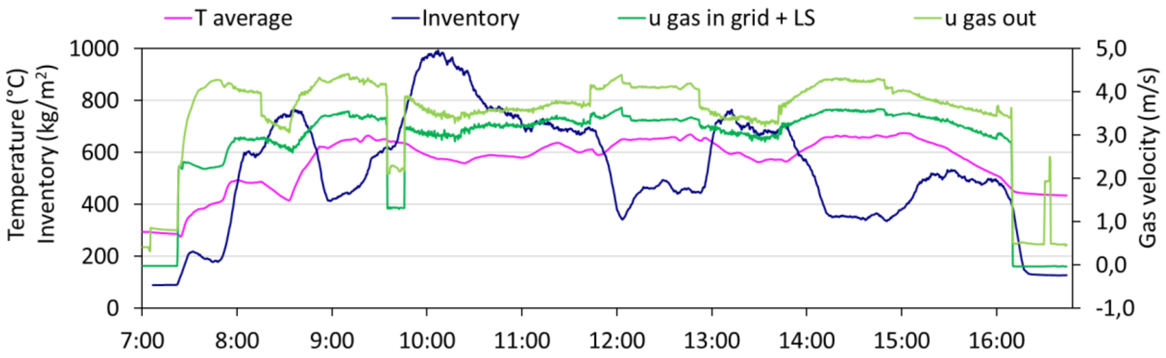

Figure A.46. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 08/02/24).

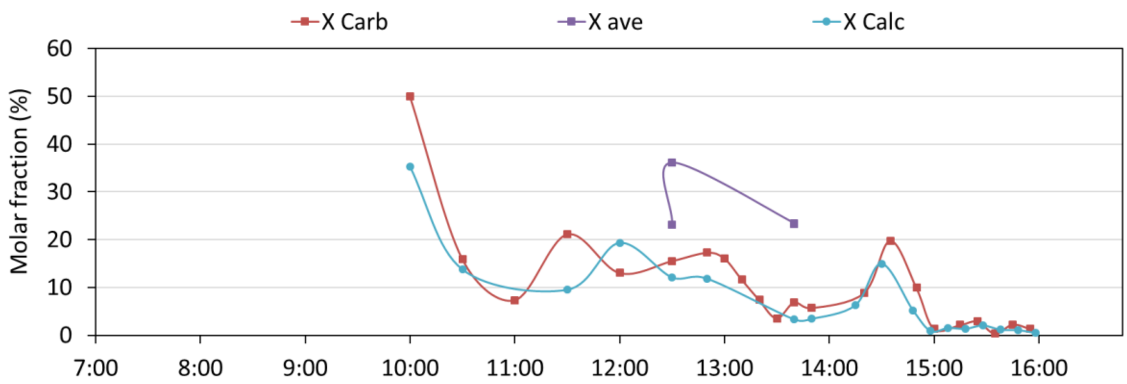

Figure A.47. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids (X_{ave}) in the carbonator reactor (Experiment 08/02/24).

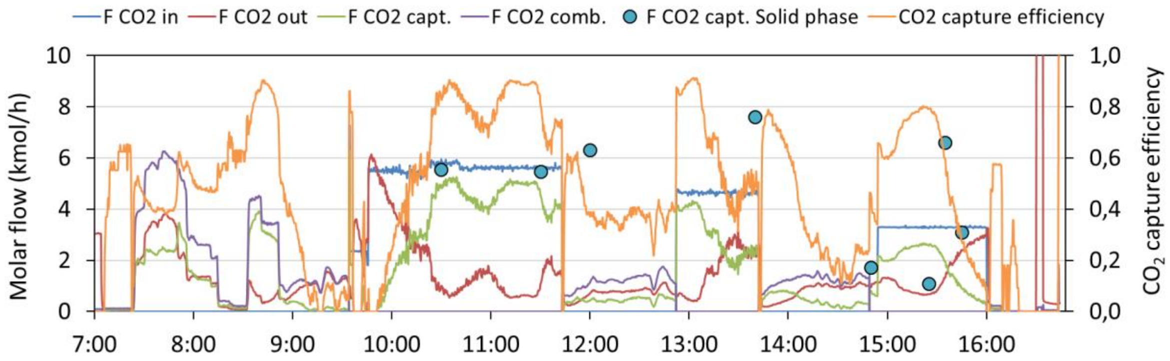

Figure A.48. CO_2 balance closure and carbon capture efficiency (Experiment 08/02/24).

Experiment: 14/02/2024

The purpose of this experiment was to conduct a carbon capture test close to the maximum allowed by the equilibrium. The calciner, as shown in Figure A.49, was operated from 14:50 h to 20:40 h, under oxy-fuel conditions. The average O_2 in the outlet stream of the calciner was 4.0 %. From 10:10 h to 20:40 h, a continuous operation period with fuel was conducted. In Figure A.50, it can be seen the evolution of the average temperature in the calciner, in the dense bed the average temperature was 790 °C and in the upper section 895 °C. The inlet gas velocity, 3.0 m/s while the average outlet gas velocity was 4.9 m/s. The evolution of the biomass and limestone fed during the experiment is illustrated in Figure A.51. The average biomass flow was 302.0 kg/h and the limestone fed was 245 kg/h.

Table A.9. Average values of experimental key variables 13:37 h and 20:38 h (Experiment 27/02/24)

Calciner data	
$T_{901\ dense\ bed}$ (°C)	789.4
$T_{out\ 906}$ (°C)	896.8
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.0
$O_{2\ in}$ (%)	34.90
$O_{2\ out}$ (%)	4.0
Limestone flow (kg/h)	245.4
Biomass flow (kg/h)	302.0
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	622.8
$T_{806\ out}$ (°C)	540.9
X_{ave}	0.172
$u_{gas\ in\ grid\ +\ LS}$	3.0
$CO_{2\ in}$ (%)	11.9
$CO_{2\ out}$ (%)	1.4

Regarding the carbonator reactor, the system was at CO_2 capture conditions from 13:40 h to 20:40 h. The CO_2 flue gas concentration was fixed during the experiment. As presented in Figure A.52, the CO_2 content in the inlet stream was 11.9 %. It can be noticed in Figure A.53, that there is an initial decrease of the carbonator temperature. After this, temperature increases until it stabilizes into an average value around 600 °C. This change in the temperature can be associated to the change from air to oxy-combustion conditions. The evolution of the composition of the solid samples and the capture efficiency can be followed in Figure A.54 and Figure A.55, respectively. From 13:40 h to 16:00 h, once switched to CO_2 capture, there is an initial period in which capture efficiency increases progressively. During this period, the calciner is switched from air to oxy-fuel conditions. There is no evidence of the initial calcination of the batch of solids during this period. Estimation of solid circulation between reactors during this period is not reliable. From 16:00 h to 20:40 h, high capture efficiencies, higher than 96% were reached. In addition, there is a good CO_2 closure between gas and solid phases, and the average CO_2 carrying capacity was 0.172.

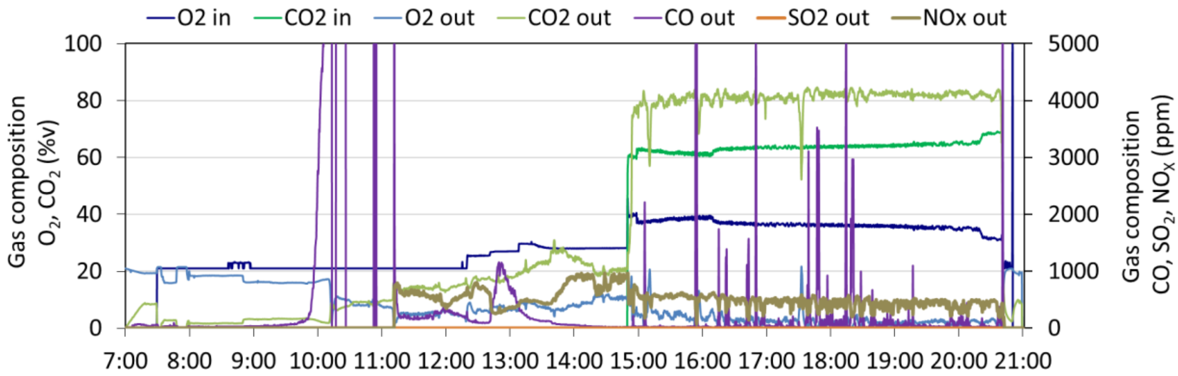

Figure A.49. Inlet and outlet gas concentration in the calciner reactor (Experiment 14/02/24).

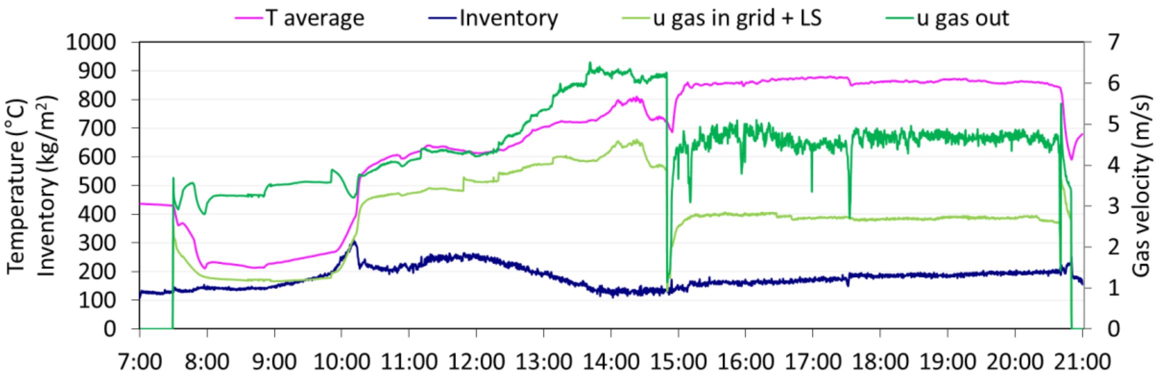

Figure A.50. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 14/02/24).

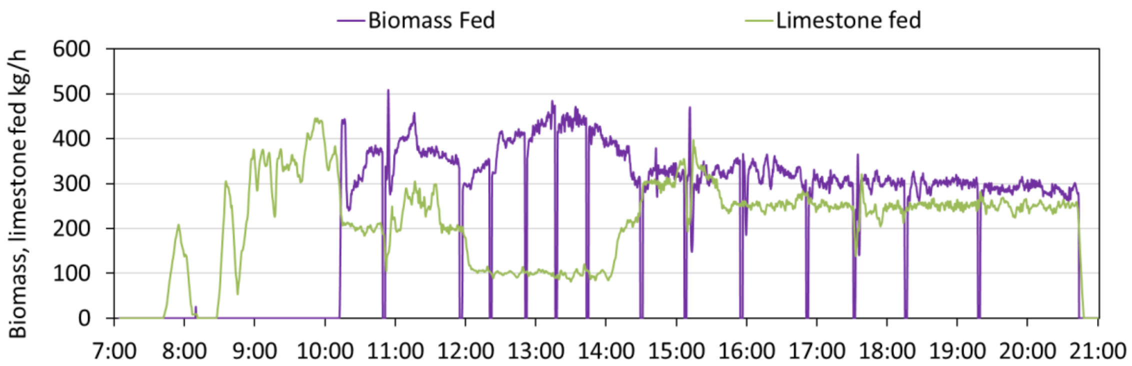

Figure A.51. Biomass and limestone feeding rates (Experiment 14/02/24).

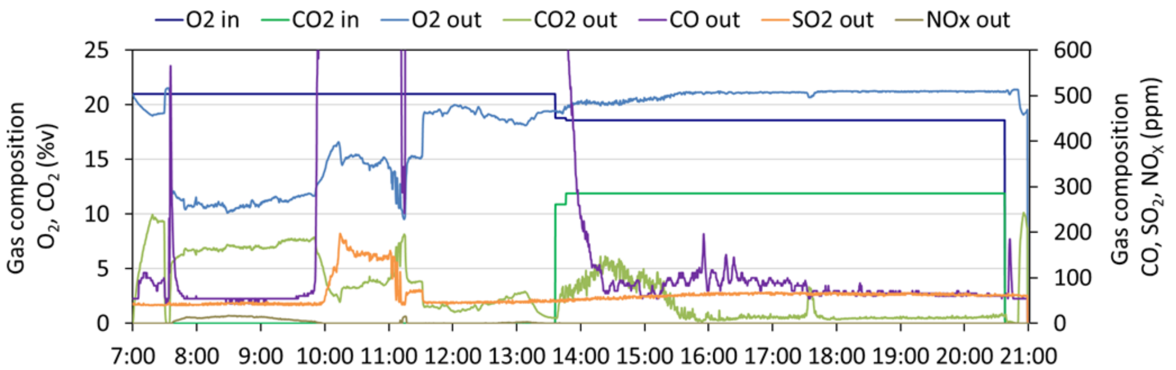

Figure A.52. Inlet and outlet gas concentration in the carbonator reactor (Experiment 14/02/24).

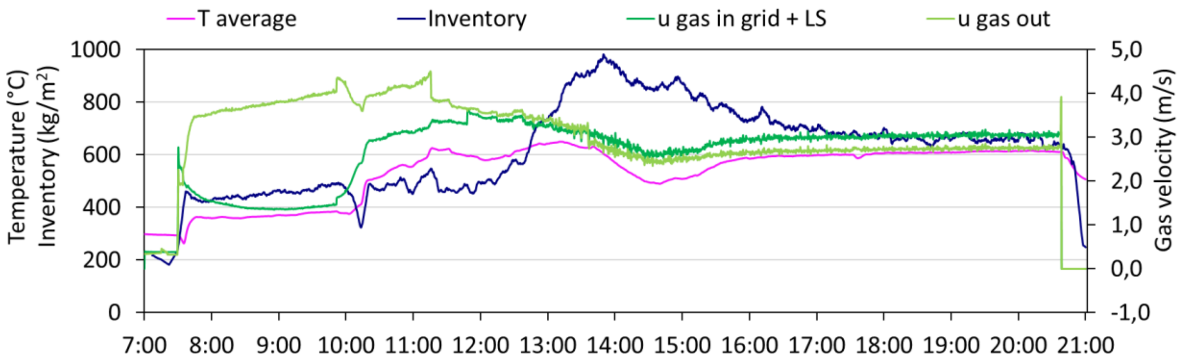

Figure A.53. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 14/02/24).

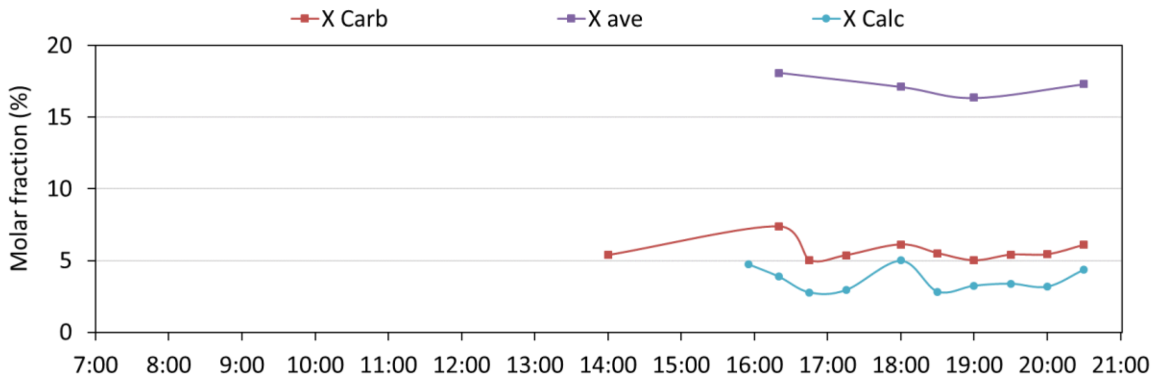

Figure A.54. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum carrying capacity of the solids in the carbonator reactor (X_{ave}) (Experiment 14/02/24).

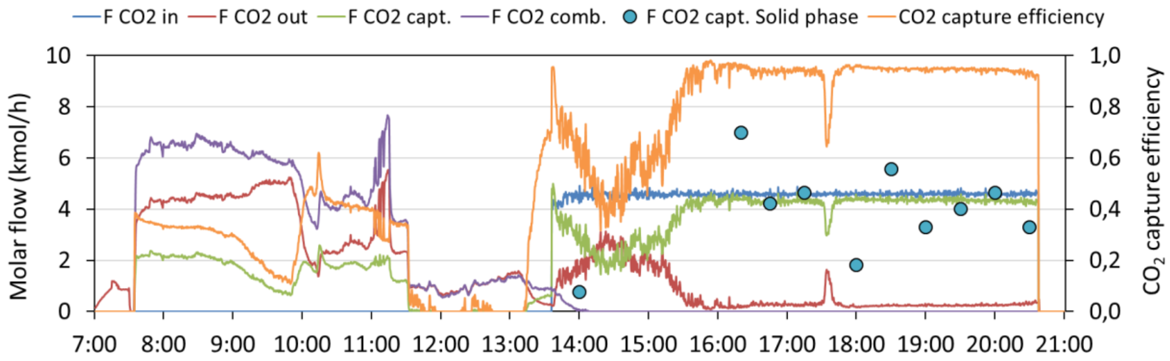

Figure A.55. CO_2 balance closure and carbon capture efficiency (Experiment 14/02/24).

Experiment: 15/02/2024

The objective of this experiment was to conduct a CO_2 capture test in oxy-fuel conditions while operating the calciner with low oxygen excess. Therefore, as presented in Figure A.56, the calciner was operated under oxy-fuel conditions from 13:30 h to 18:45 h. A decrease of NO_x emissions is observed as O_2 at the outlet decreases. In Figure A.57, it can be seen the evolution of the average temperature in the calciner reactor, once switched to oxy-fuel conditions at 13:30 h, the temperature in the reactor increased. The average inlet gas velocity was 3.3 m/s while the outlet was 4.8 m/s. In addition, as shown in Figure A.58, there was a period of continuous operation with fuel between 07:30 h to 18:45 h, with an average biomass flow of 335 kg/h. Regarding the limestone fed, the average flow was 300 kg/h.

Concerning the carbonator reactor, it can be noticed in Figure A.59 that a fixed CO_2 flue gas concentration of 12.2 %, was fed to the reactor. In Figure A.60, the temperature and gas velocities are depicted, being the average temperature in the dense bed 670 °C and in the upper section 595 °C, whereas the inlet gas velocity was 3.2 m/s and the average outlet gas velocity 3.0 m/s. A stop on the circulation of the solids can be observed at 11:30. Hence, it can be noticed a sharp decrease in the carbonator inventory. While solving this operating problem the CO_2 inlet to the carbonator was closed until the circulation was recovered. The evolution of the composition of solid samples and capture efficiency are presented in Figure A.61 and Figure A.62, respectively. The average CO_2 carrying capacity of the solids was 0.275. Moderate CO_2 capture efficiencies were reached, above 80%, from 15:00 h to 18:45 h.

Table A.10. Average values of experimental key variables between 09:02 h and 18:45 h (Experiment 15/02/24).

Calciner data	
$T_{901\ dense\ bed}$ (°C)	735.4
$T_{out\ 906}$ (°C)	847.9
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.3
$O_{2\ in}$ (%)	30.28
$O_{2\ out}$ (%)	4.6
Limestone flow (kg/h)	297.7
Biomass flow (kg/h)	335.1
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	668.6
$T_{806\ out}$ (°C)	591.9
X_{ave}	0.275
$u_{gas\ in\ grid\ +\ LS}$	3.2
$CO_{2\ in}$ (%)	12.2
$CO_{2\ out}$ (%)	4.1

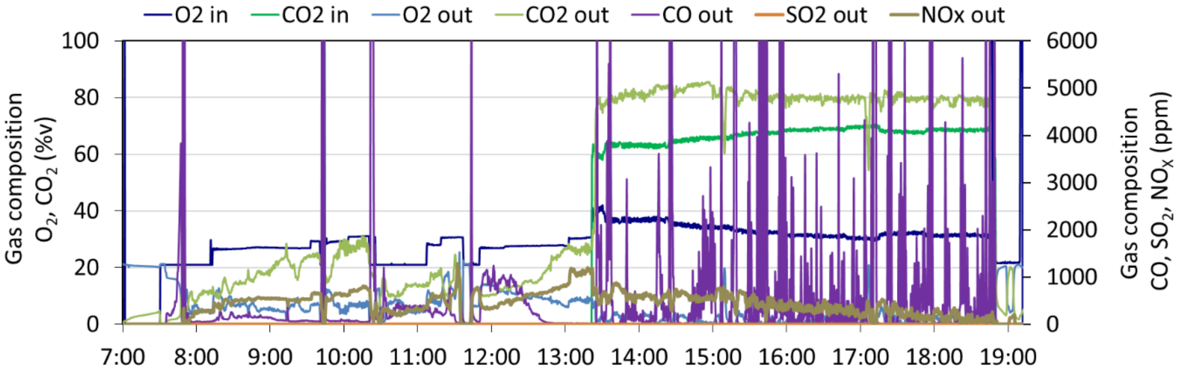

Figure A.56. Inlet and outlet gas concentration in the calciner reactor (Experiment 15/02/24).

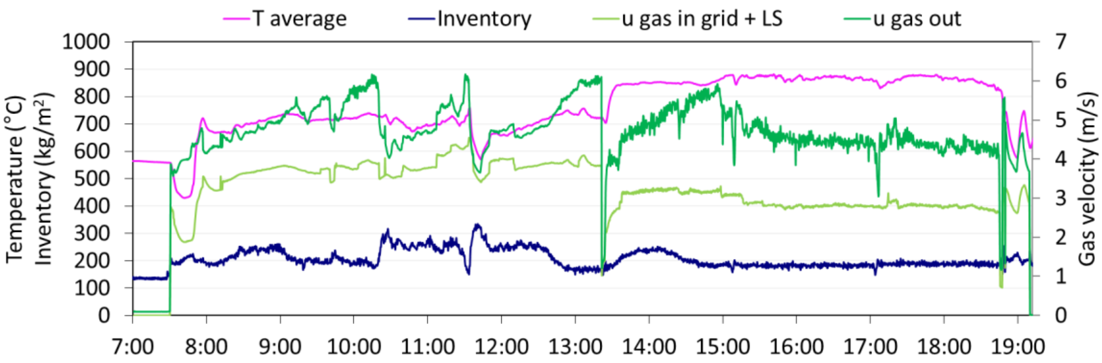

Figure A.57. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 15/02/24).

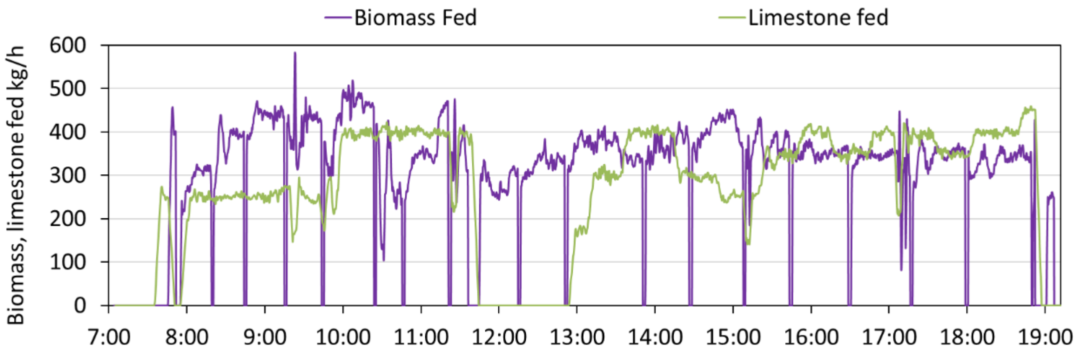

Figure A.58. Biomass and limestone feeding rates in the calciner reactor (Experiment 15/02/24).

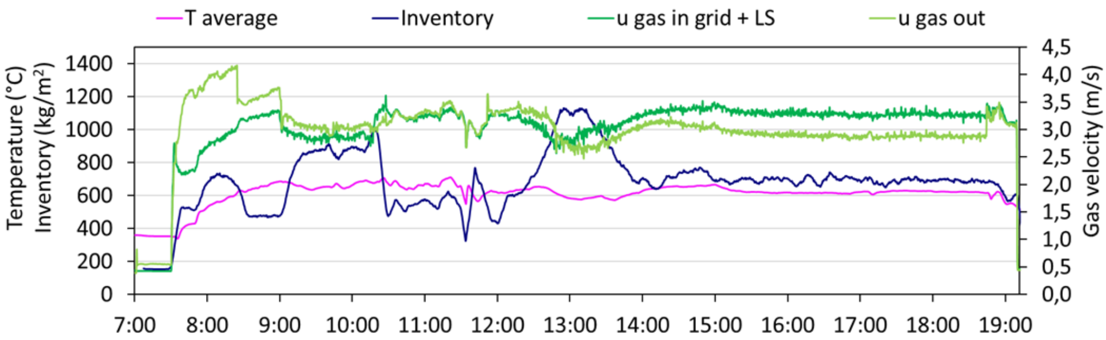

Figure A.59. Inlet and outlet gas concentration in the carbonator reactor (Experiment 15/02/24).

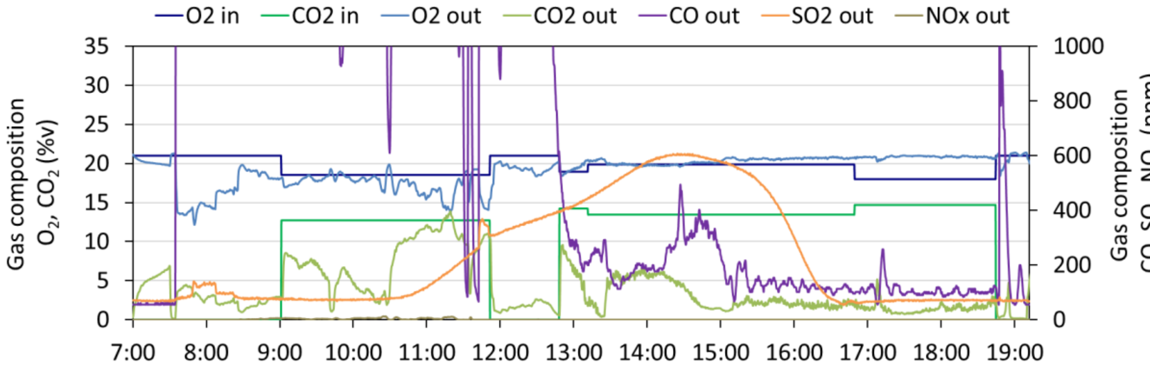

Figure A.60. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (15/02/24).

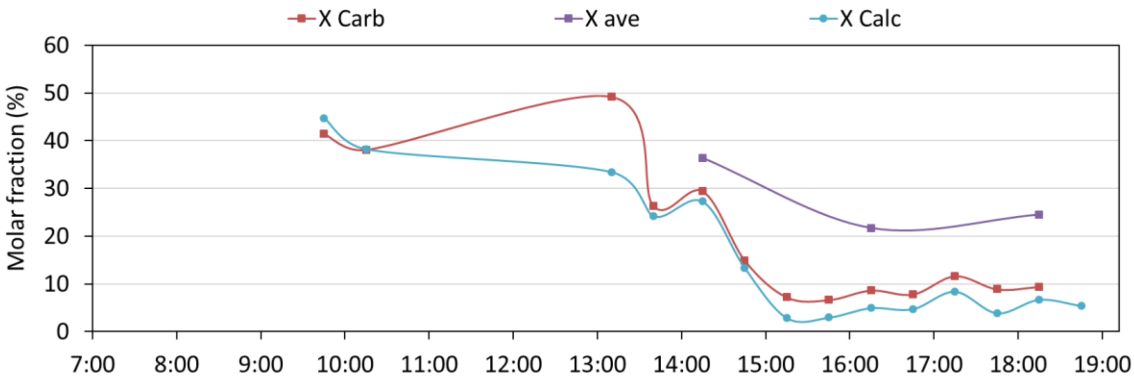

Figure A.61. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}), and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids in the carbonator reactor (X_{ave}) (Experiment 15/02/24).

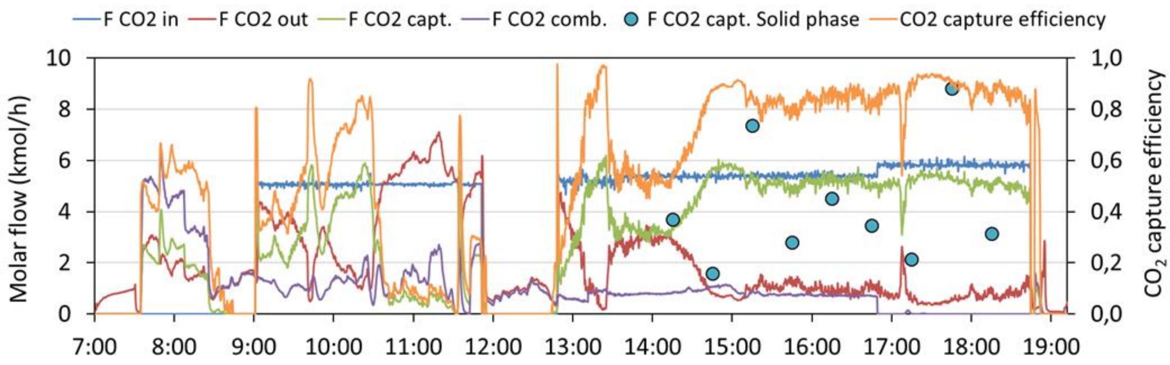

Figure A.62. CO_2 balance closure and carbon capture efficiency (Experiment 15/02/24).

Experiment: 16/02/2024

This experiment corresponds to a carbon capture test and as dynamic test. As shown in Figure A.63, the calciner was operated under enriched-air conditions. Regarding temperatures, the average temperature in the upper section of the calciner was 860 °C. Inventory and gas velocities are depicted in Figure A.64, the average inlet gas velocity was 3.3 m/s and the outlet gas velocity 5.5 m/s. As presented in Figure A.65, a fixed flow of limestone was introduced to the calciner, being the average 370kg/h.

Concerning the carbonator, dynamic tests were carried out. From 09:40 h to 14:45 h, a stream with 14.2 % CO_2 was introduced to the reactor as seen in Figure A.66. From 14:45 h to 15:10 h, CO_2 concentration was increased up to 18.1%. Then, from 15:10 h to 15:44 h, the stream contained 12.2 % CO_2. Then, from 14:44 h to 16:12 h, no CO_2 was fed to the reactor. Next, from 16:12 h to 16:52 h a stream with 21.7 % CO_2 was fed. Between 16:52 h to 17:21 h, the stream had a CO_2 content of 18.3 %. Finally, from 17:21 h to 18:06 h the stream fed had 21.3 % CO_2. Temperature, inventory and gas velocities are illustrated in Figure A.67. The inlet carbonator gas velocity was 2.8 m/s while the average carbonator outlet velocity was 2.7 m/s. In Figure A.68, it is possible to follow the evolution of the $CaCO_3$ composition and maximum carrying capacity of the solids, being the average 0.275. The CO_2 balance closure and capture efficiencies are presented in Figure A.69. From 10:00 h to 12:00 h, high capture efficiencies were achieved. However, during this period high temperatures can be noted in the carbonator. Between 12:00 h and 13:45 h, there was high CO_2 capture efficiency but unstable. In addition, from 13:45 h to 14:45 h, capture efficiency was almost close to 100 %.

Table A.11. Average values of the key variables of the experiment between 09:37 h and 18:06 h (Experiment 16/02/24).

Calciner data	
$T_{901\ dense\ bed}$ (°C)	621.1
$T_{out\ 906}$ (°C)	862.7
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.3
$O_{2\ in}$ (%)	27.48
$O_{2\ out}$ (%)	7.2
Limestone flow (kg/h)	366.8
Biomass flow (kg/h)	358.6
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	667.8
$T_{806\ out}$ (°C)	577.9
X_{ave}	0.257
$u_{gas\ in\ grid\ +\ LS}$	2.8
$CO_{2\ in}$ (%)	15.0
$CO_{2\ out}$ (%)	1.0

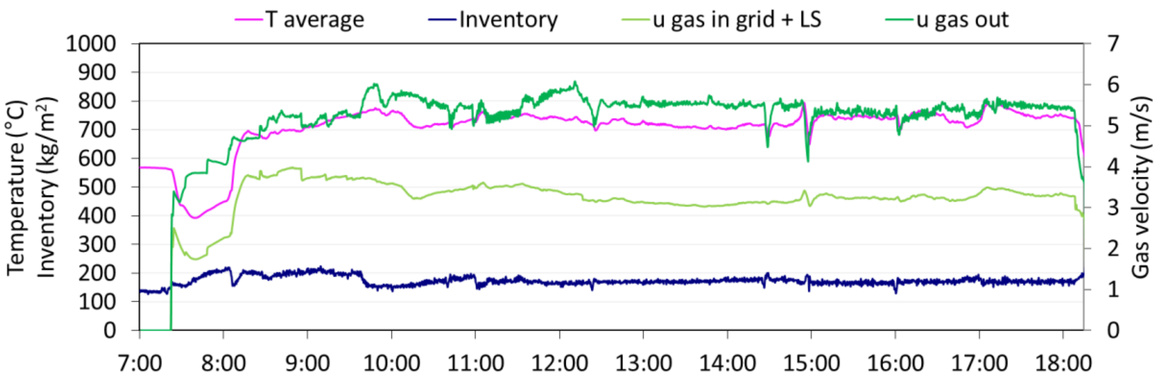

Figure A.63. Inlet and outlet gas concentration in the calciner reactor (Experiment 16/02/24).

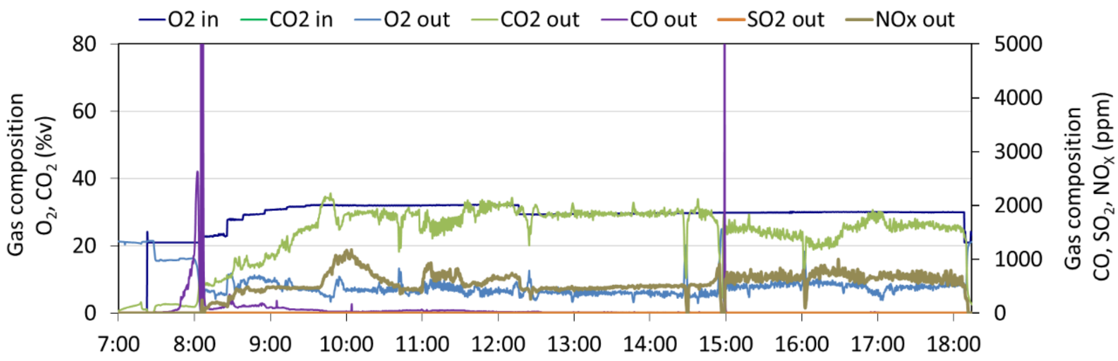

Figure A.64. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 16/02/24).

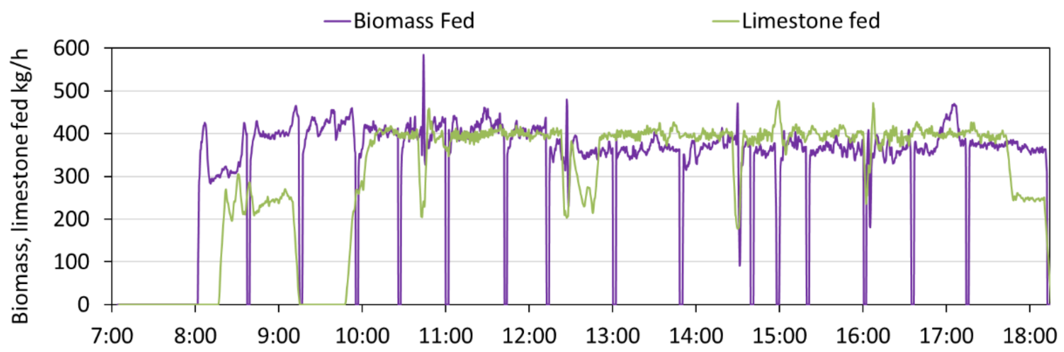

Figure A.65. Biomass and limestone feeding rates (Experiment 16/02/24).

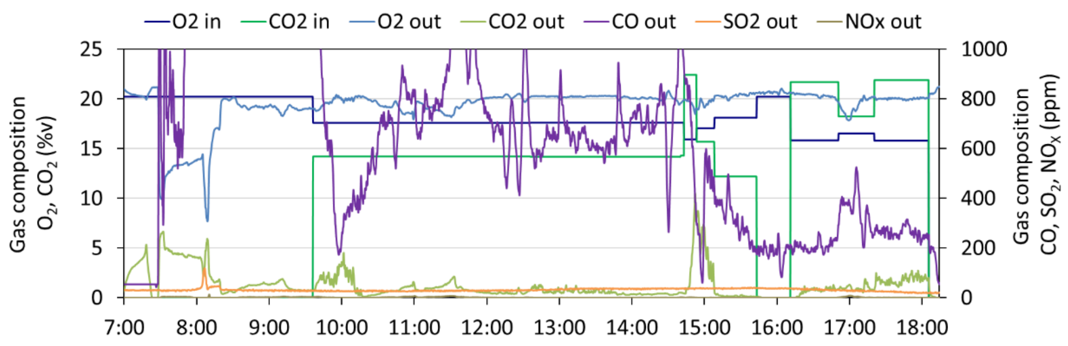

Figure A.66. Inlet and outlet gas concentration in the carbonator reactor (Experiment 16/02/24).

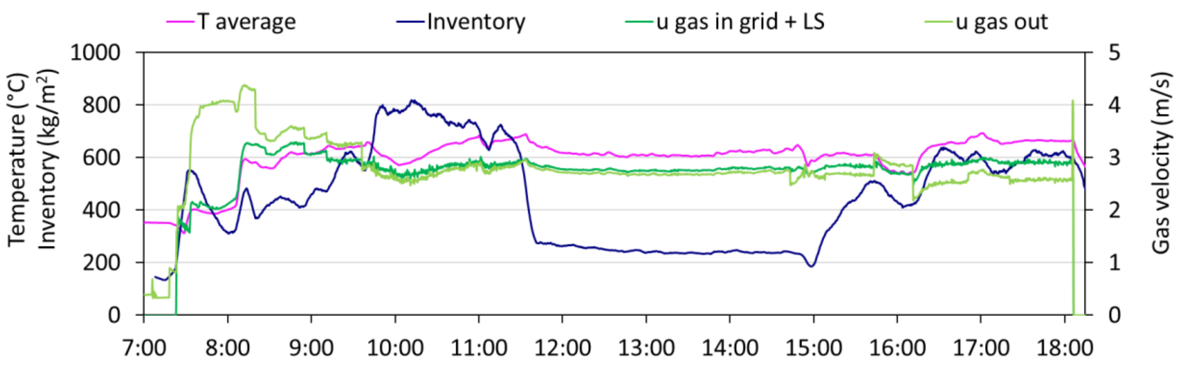

Figure A.67. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 16/02/24).

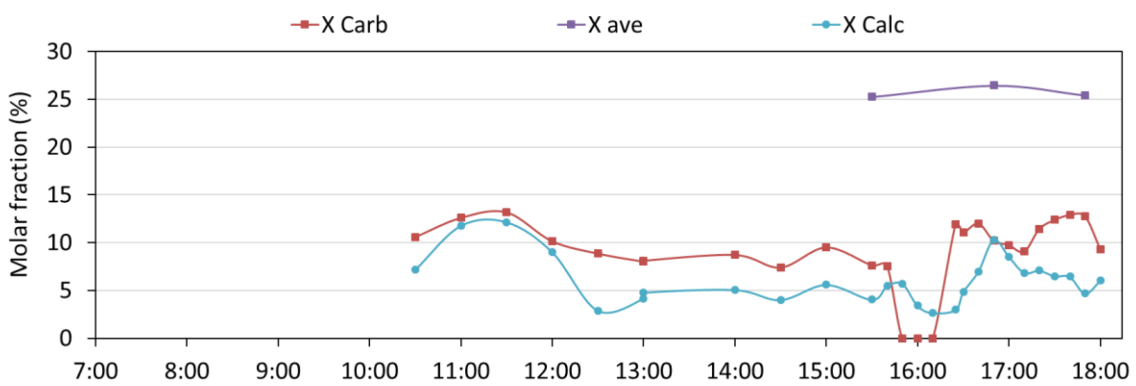

Figure A.68. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids (X_{ave}) in the carbonator reactor (Experiment 16/02/24).

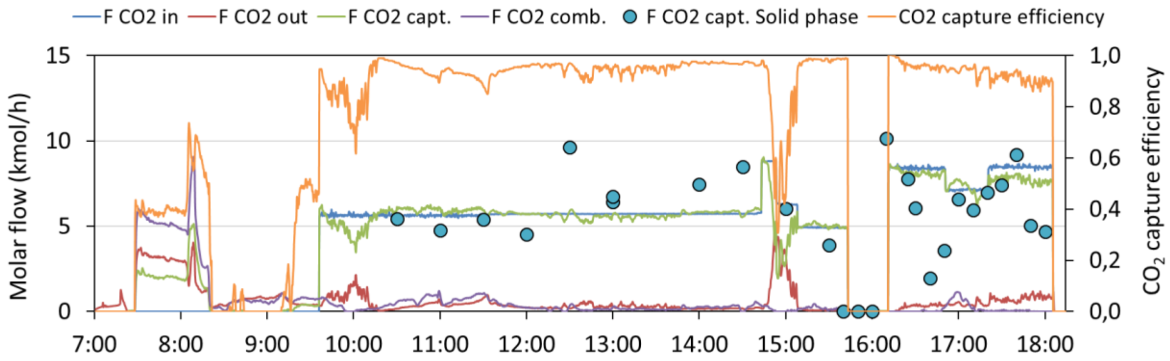

Figure A.69. CO_2 balance closure and carbon capture efficiency (Experiment 16/02/24).

Experiment: 27/02/2024

The aim of this experiment was to carry out a dynamic test, which consisted of varying three times the CO_2 concentration in the synthetic flue gas at the inlet of the carbonator reactor. It was conducted between 12:20 and 19:340. As can be seen in Figure A.70, the calciner was operated in enriched-air mode. The average O_2 concentration in the outlet stream of the calciner was 6.1 % and the average temperature in the upper section of the reactor was 840 °C. Regarding gas velocities, the average inlet gas velocity entering the calciner was 3.3 m/s while the outlet gas velocity was 5.4 m/s. An average biomass flow of 350 kg/h was fed to the calciner in order to heat up the reactor to the required operating temperature while maintaining the O_2 concentration in the outlet stream of the calciner at the desired value. Limestone fed to the reactor from 12:30. The average limestone flow fed to the calciner was 425 kg/h. High flows of limestone, enable to maintain an adequate circulation between the reactors. In addition, this renewal of the inventory allows to have a more active limestone, and consequently higher X_{ave}.

In regard to the carbonator, three CO_2 concentrations were tested:

- Between 12:20 h and 16:25 h, $CO_{2\ in\ CB}$ = 6.1
- Between 16:25 h and 18:00 h, $CO_{2\ in\ CB}$ = 2.6
- Between 18:00 h and 19:40 h, CO_2 i$_{n\ CB}$ =1 1.9

The average temperature of the reactor is presented in Figure A.74, the temperature in the dense bed was 600 °C while in the upper section 510 °C. The average inlet gas velocity in the carbonator was 3.4 m/s while the outlet was 3.04 m/s. Samples were taken between 12:45 h and 19:30 h, and the analysis results in terms of $CaCO_3$ molar composition and the maximum CO_2 carrying capacity are gathered in Figure A.75. Finally, Figure A.76 shows the CO_2 balance closure along with the CO_2 experimental carbon capture efficiency. It can be seen, that high capture efficiencies were reached since CO_2 was introduced to the reactor.

Table A.12. Average values of experimental key variables (Experiment 27/02/24)

Calciner data	
$T_{901\ dense\ bed}$ (°C)	594.6
$T_{out\ 906}$ (°C)	843.2
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.3
$O_{2\ in}$ (%)	25
$O_{2\ out}$ (%)	6.1
Limestone flow (kg/h)	423.0
Biomass flow (kg/h)	347.7
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	601.6
$T_{806\ out}$ (°C)	507.5
X_{ave}	0.256
$u_{gas\ in\ grid\ +\ LS}$	3.4
$CO_{2\ in}$ (%)	6.6
$CO_{2\ out}$ (%)	0.8

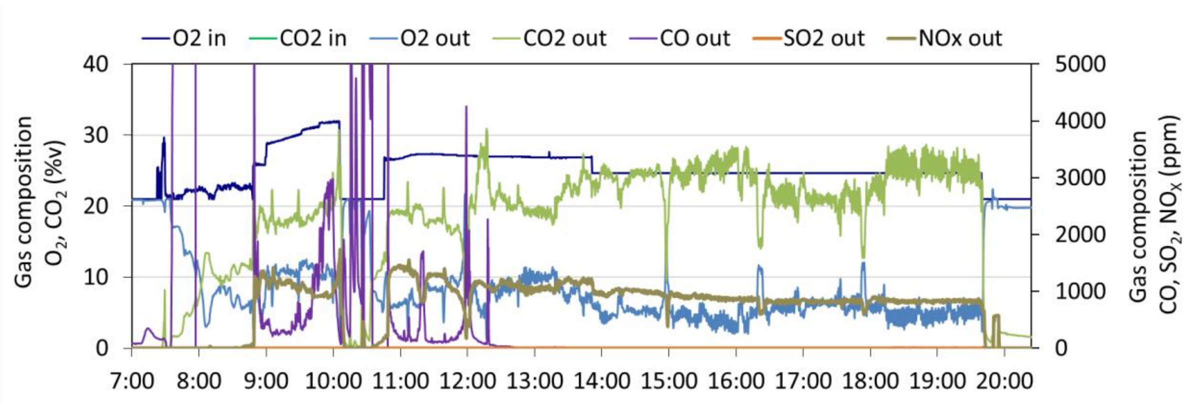

Figure A.70. Gas composition of the calciner reactor (Experiment 27/02/2024).

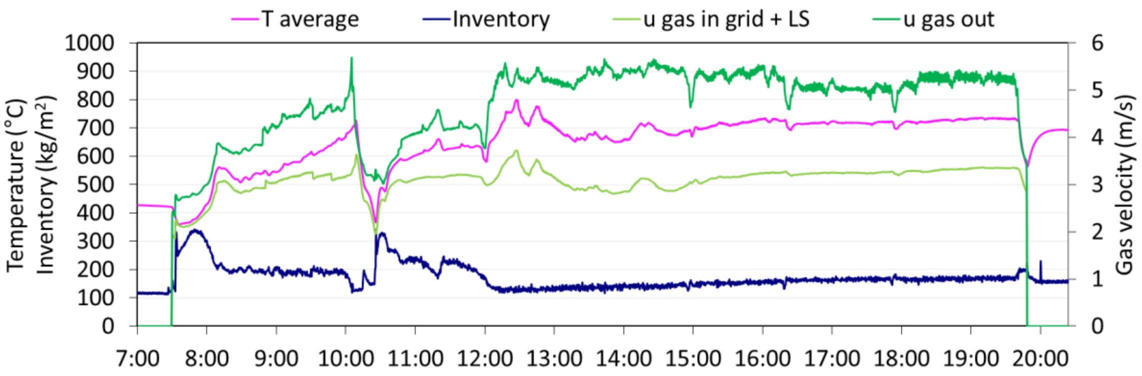

Figure A.71. Temperature, inventory, inlet and outlet gas velocities in the calciner (Experiment 27/02/2024).

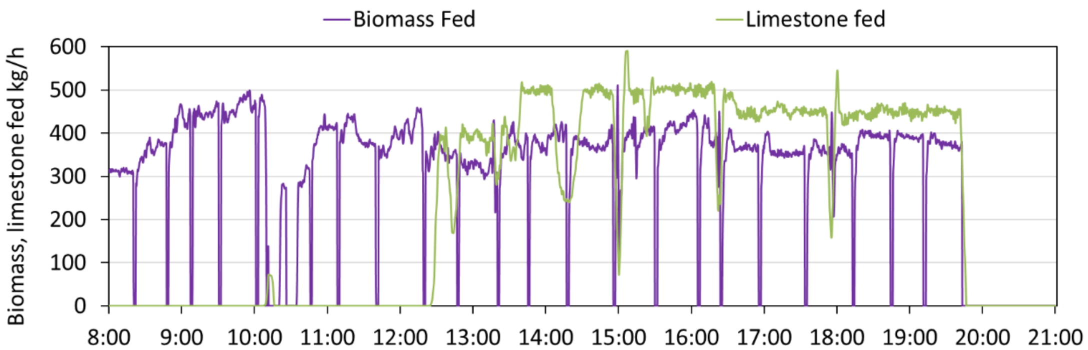

Figure A.72. Biomass and limestone feeding rates (Experiment 27/02/2024).

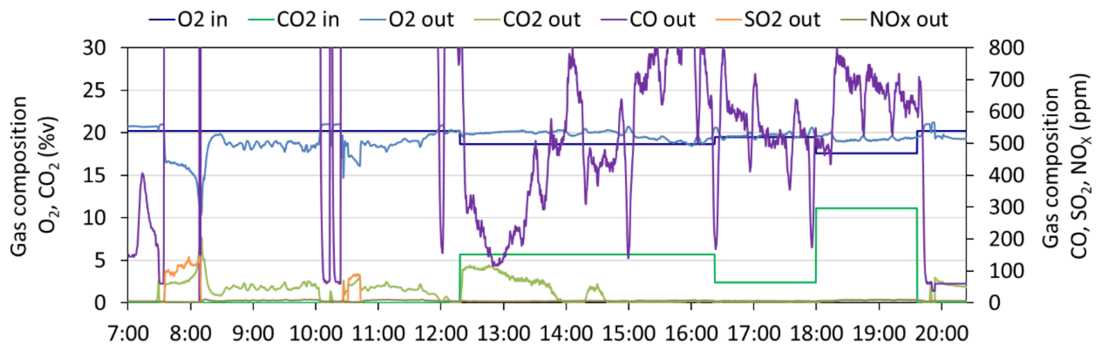

Figure A.73. Gas composition of the carbonator reactor (Experiment 27/02/24).

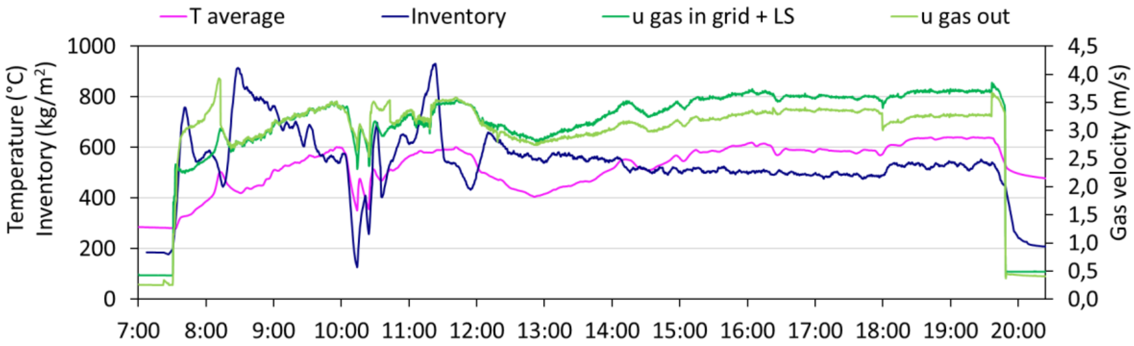

Figure A.74. Temperature, inventory, inlet and outlet gas velocity of the carbonator reactor (Experiment 27/02/24).

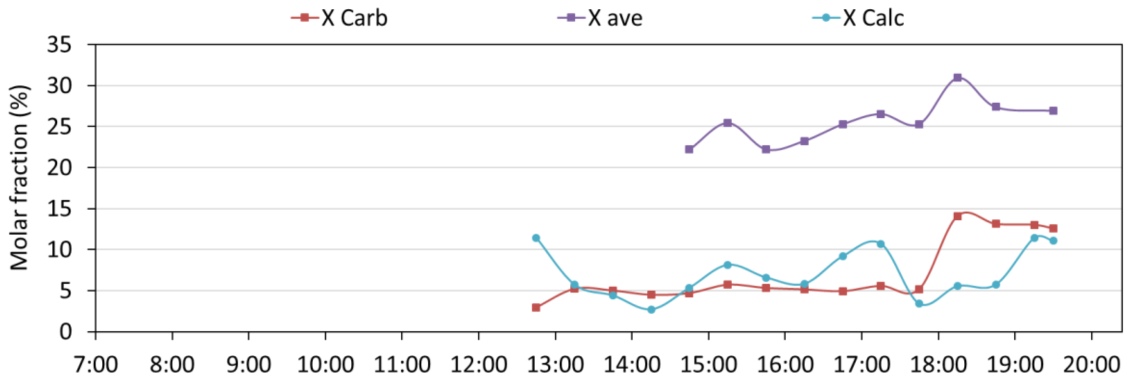

Figure A.75. $CaCO_3$ molar composition of the solids, in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids (X_{ave}) in the carbonator reactor (Experiment 27/02/24)

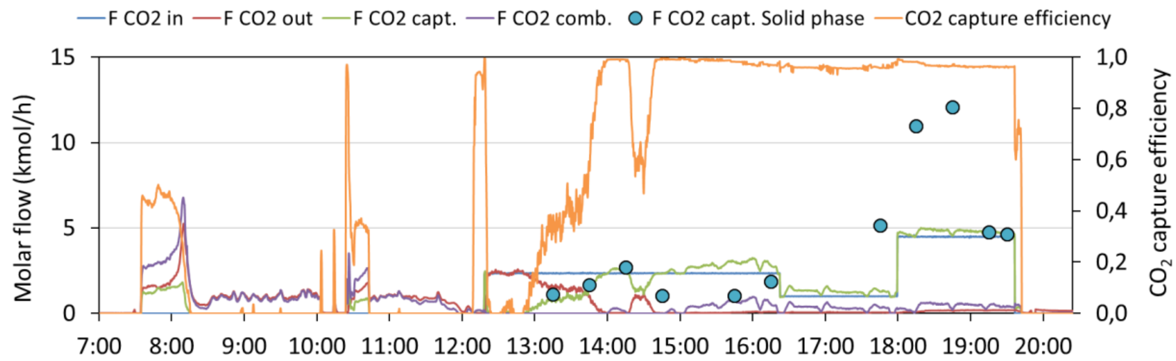

Figure A.76. CO_2 balance closure and capture efficiency (Experiment 27/02/24).

Experiment: 28/02/2024

The experiment consisted of a dynamic test. Between 09:05 h and 20:20 h, three different CO_2 concentrations were tested while operating the calciner in oxy-combustion mode. Table A.13 summarizes the key variables of the carbon capture experiment. As shown in Figure A.77, the experiment was carried out under oxy-combustion conditions. Regarding the temperatures in the calciner seen in Figure A.78, the average value in the dense bed was 820°C while in the upper section temperature reached 900°C. The average inlet gas velocity was 2.1 m/s while the average outlet gas velocity was 4.4 m/s. The biomass and limestone feeding flows are presented in Figure A.79. The average biomass flow fed to the calciner was 325 kg/h. In addition, 410 kg/h was the average limestone flow fed to the reactor.

Concerning the carbonator reactor, three different CO_2 concentrations were tested (Figure A.80).

- Between 09:06 h and 14:52, $CO_{2\ in\ CB}$ = 5.8%
- Between 14:52 and 19:24, $CO_{2\ in\ CB}$ = 13.0%
- Between 19:24 and 20:35, $CO_{2\ in\ CB}$ = 3.4%

The average temperature in the dense bed was 592.3°C and in the upper section 515.2°C. The inlet gas velocity for the experimental period was 3.4 m/s while the outlet was 3.1 m/s. The $CaCO_3$ analysis results of the collected samples are shown in Figure A.82. The average maximum CO_2 carrying capacity of the solids between 11:10 h and 20:15 h was 0.202. In relation to the balance closure, it can be seen in Figure A.83, that high capture efficiencies were achieved.

Table A.13. Average values of experimental key variables between 09:06 h and 20:21 h (Experiment 28/02/24).

Calciner data	
$T_{901\ dense\ bed}$ (°C)	821.8
$T_{out\ 906}$ (°C)	899.4
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	2.05
$O_{2\ in}$ (%)	34.8
$O_{2\ out}$ (%)	4.1
Limestone flow (kg/h)	409.1
Biomass flow (kg/h)	323.9
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	592.3
$T_{806\ out}$ (°C)	515.2
X_{ave}	0.202
$u_{gas\ in\ grid\ +\ LS}$	3.4
$CO_{2\ in}$ (%)	8.5
$CO_{2\ out}$ (%)	0.8

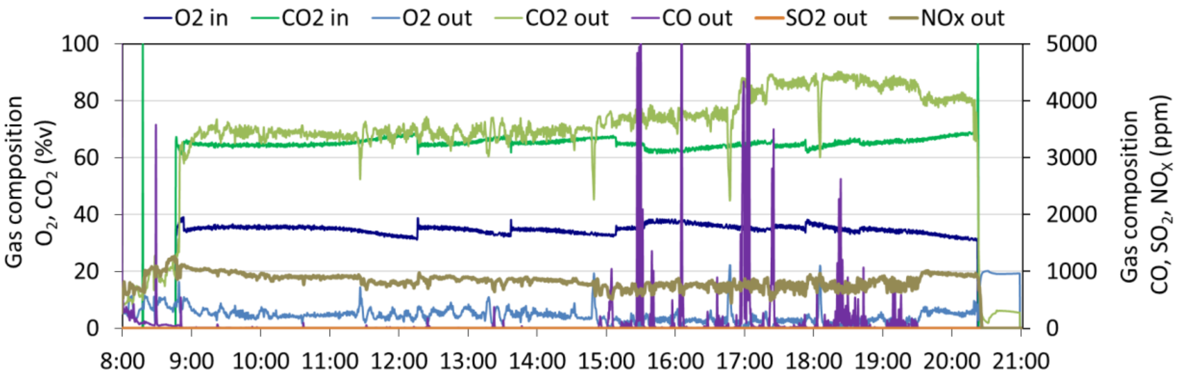

Figure A.77. Gas composition of the calciner reactor (Experiment 28/02/24).

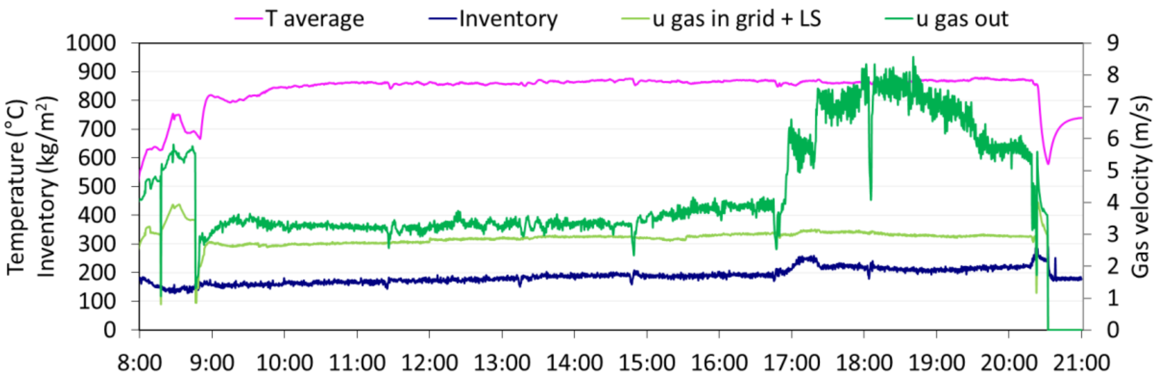

Figure A.78. Temperature, inventory, inlet and outlet gas velocities of the calciner reactor (Experiment 28/02/24).

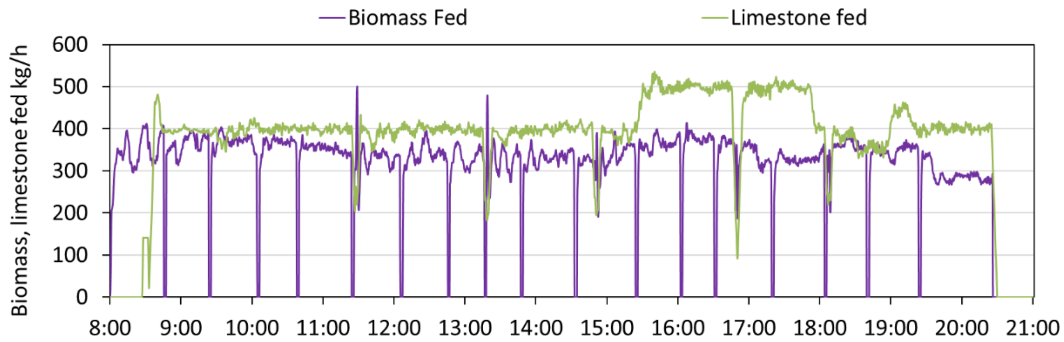

Figure A.79. Biomass and limestone feeding rates (Experiment 28/02/24).

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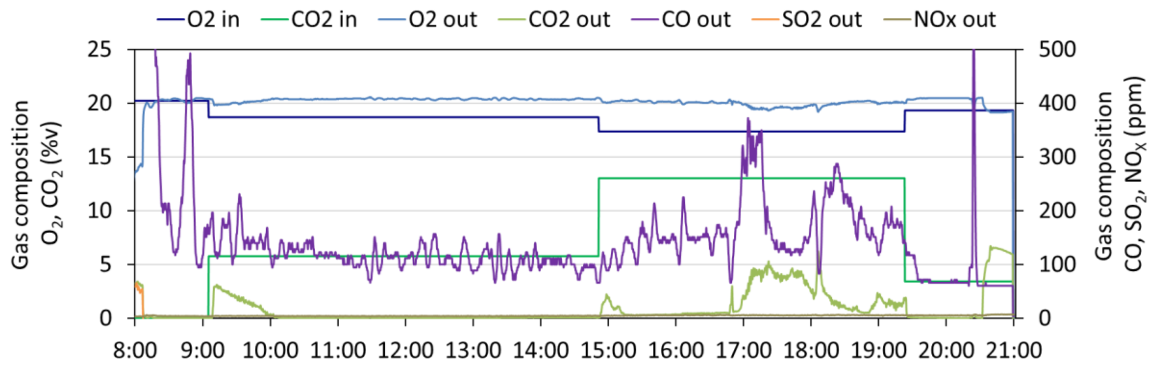

Figure A.80. Gas composition in the carbonator reactor (28/02/24).

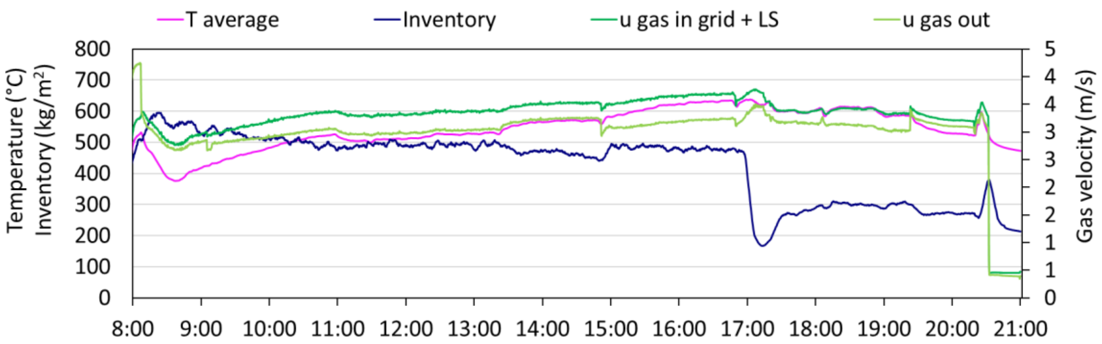

Figure A.81. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 28/02/24).

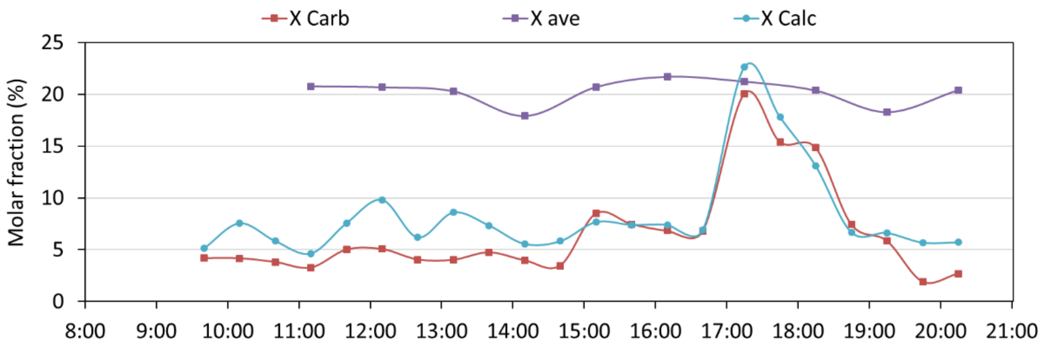

Figure A.82. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity (X_{ave}) (Experiment 28/02/24).

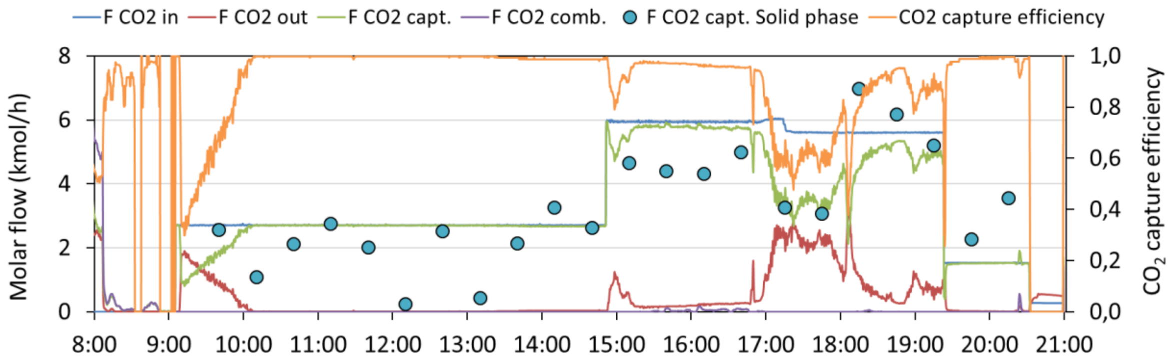

Figure A.83. CO_2 balance closure and CO_2 capture efficiency (Experiment 28/02/24).

Experiment: 29/02/2024

The experiment aims to study the influence of different limestone flow rates, by feeding the carbonator with a constant concentration of CO_2 and operating the calciner first in oxy-combustion conditions and then in air mode. This was conducted between 08:20 h and 13:15 h. In Figure A.84, the oxygen in the outlet stream of the calciner remained at the desired operating concentration, being the average 5.4% for that period. The temperature evolution in the calciner is shown in Figure A.85, for the referred period, the average temperature in the dense bed was 800.4°C while for the upper section 903.0°C, the necessary temperatures while operating the calciner in oxy-combustion conditions. The inlet gas velocity was 2.9 m/s and the outlet 3.6 m/s. The inventory remained stable during this period.

The aim of the test was to study the effect of operating the plant using different limestone flow rates. Therefore, the limestone flow rate fed to the calciner was altered during the experimental time as seen in Figure A.86. First, between 08:30 h and 11:45 h, 400 kg/h of limestone were fed to the reactor. Hereafter, till 12:05 h, the desired limestone flow was 325 kg/h. Next, between 12:05 h and 12:45 h the input feeding rate was 240 kg/h. Finally, between 12:45 h and 13:00 h limestone feeding rate was put back on the starting value, 400 kg/h. Meanwhile, the carbonator was fed with a synthetic flue gas stream with 11.1% CO_2, unaltered throughout the whole experiment. Illustrated in Figure A.88, the inlet carbonator gas velocity was 3.25 m/s and the outlet gas velocity 2.92 m/s. The temperature in the dense bed 580 °C while in the upper section 495 °C.

The second part of the experiment was developed between 13:15 h and 20:00 h, were the calciner was operated in air conditions, by introducing to the reactor an oxygen-enriched air stream. It is observed in Figure A.84, that the oxygen in the outlet stream was relatively higher than in the previous period, being the average 8.4 %. The temperature in the upper section 850 °C. The evolution in the gas velocities shown in Figure A.85, presents an increase in contrast to the previous period, the inlet gas velocity was 3.7 m/s and the outlet 5.4 m/s. Different limestone flow rates were also studied, as a consequence, Figure A.86, show different periods in the feeding of this material. Between, 13:25 h and 14:05 h the average limestone flow rate was 150 kg/h. Hereafter, the studied rate was 260 kg/h.

In regard to the carbonator, the average temperature in the dense bed was 515 °C and in the upper section 595 °C. Gas velocities were similar as the values of the previous part of the test, as a result, the inlet gas velocity was 3.4 m/s and the outlet 3.1 m/s.

Several samples were taken during both experimental periods, and the results in terms of $CaCO_3$ molar compositions are presented in Figure A.89, as well as the maximum CO_2 carrying capacity of the solids. In Figure A.90, is shown the CO_2 balance closure, and the evolution of the experimental carbon capture efficiency. It can be seen, that higher efficiencies close to 99% were reached during the oxy-combustion part of the experiment.

Table A.14. Average values of experimental key variables (Experiment 29/02/24).

Calciner data		
	Oxy - combustion	Air
$T_{dense\ bed}$ (°C)	800.4	666.9
T_{out} (°C)	903.0	852.2
$u_{gas\ in\ grid+\ LS}$ (m/s)	2.9	3.7
$O_{2\ in}$ (%)	36.7	27.2
$O_{2\ out}$ (%)	5.4	8.4
Limestone flow (kg/h)	356.9	243.9
Biomass flow (kg/h)	325.1	285.9
Carbonator data		
$T_{dense\ bed}$ (°C)	581.2	516.3
T_{out} (°C)	495.6	594.2
X_{ave}	0.199	0.206
$u_{gas\ in\ grid\ +\ LS}$	3.3	3.4
$CO_{2\ in}$ (%)	11.1	11.1
$CO_{2\ out}$ (%)	2.1	1.8

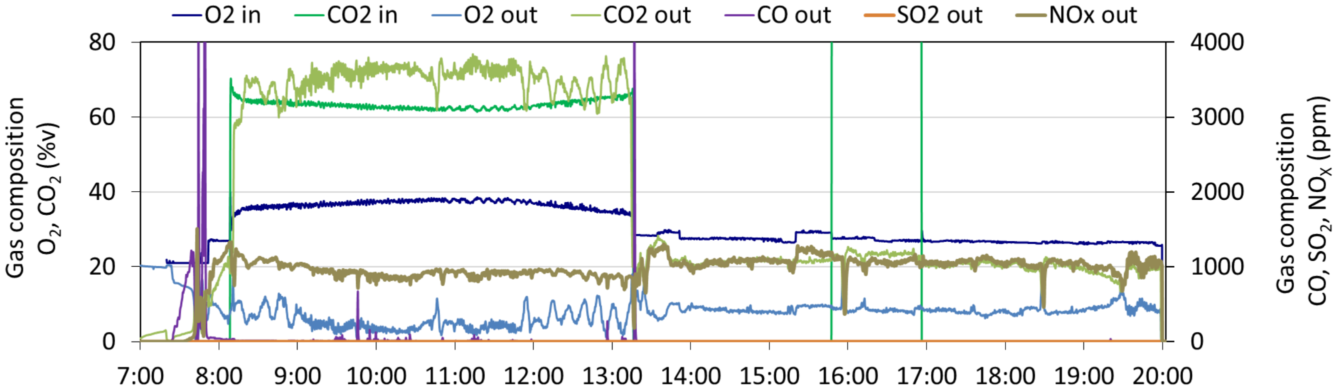

Figure A.84. Gas composition of the calciner reactor (Experiment 29/02/24).

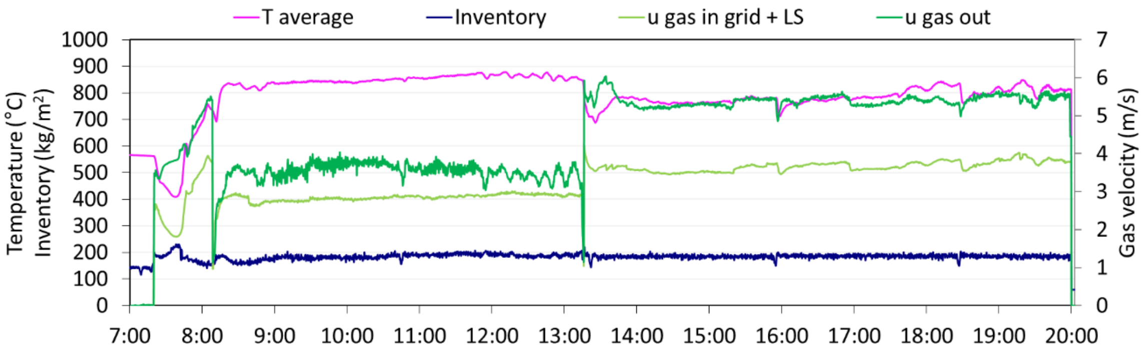

Figure A.85. Temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 29/02/24).

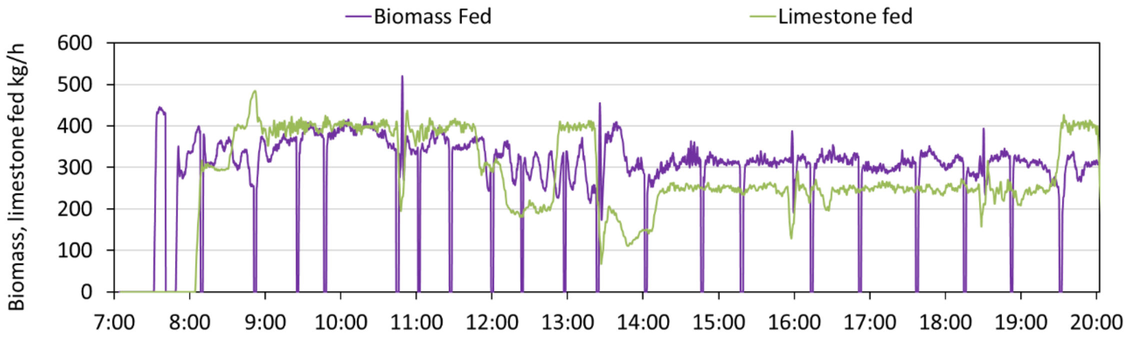

Figure A.86. Biomass and limestone feeding rates (Experiment 29/02/24).

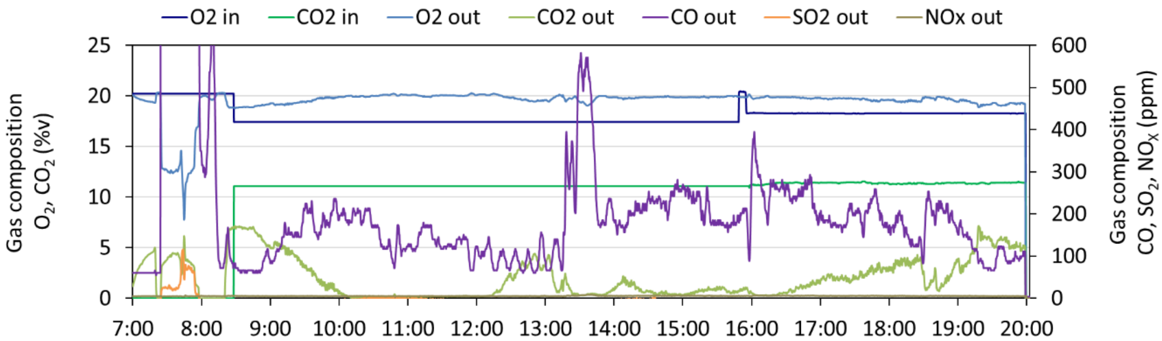

Figure A.87. Gas composition in the carbonator reactor (Experiment 29/02/24).

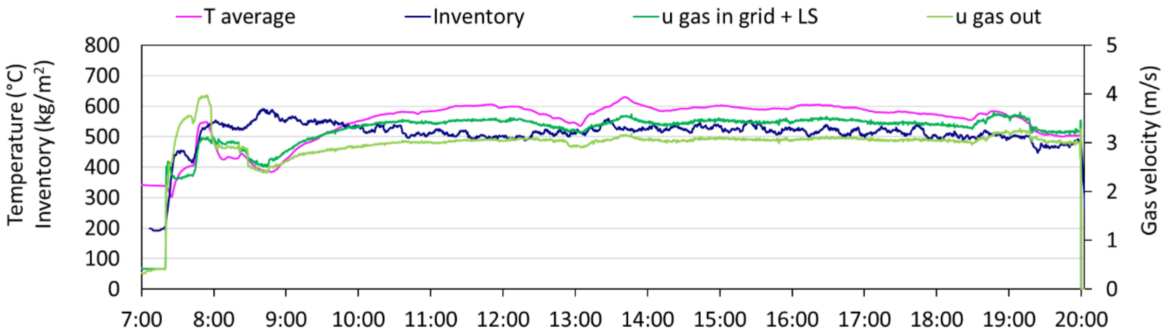

Figure A.88. Temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 29/02/24).

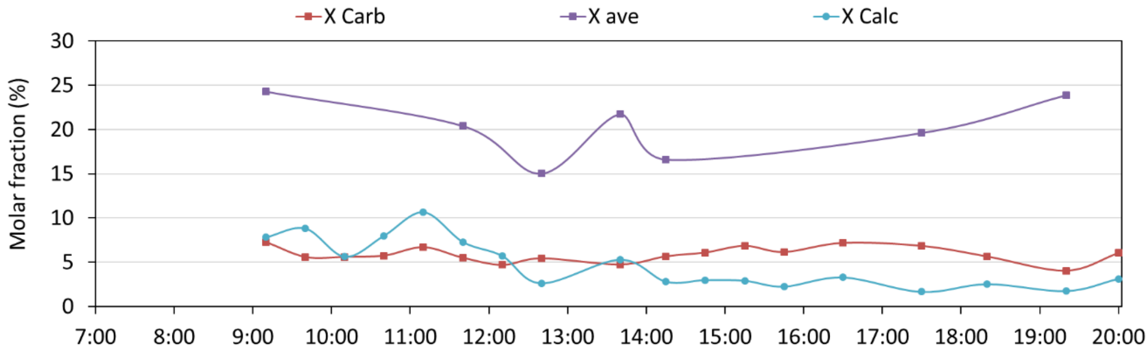

Figure A.89. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2carrying capacity of the solids (X_{ave}) (Experiment 29/02/24).

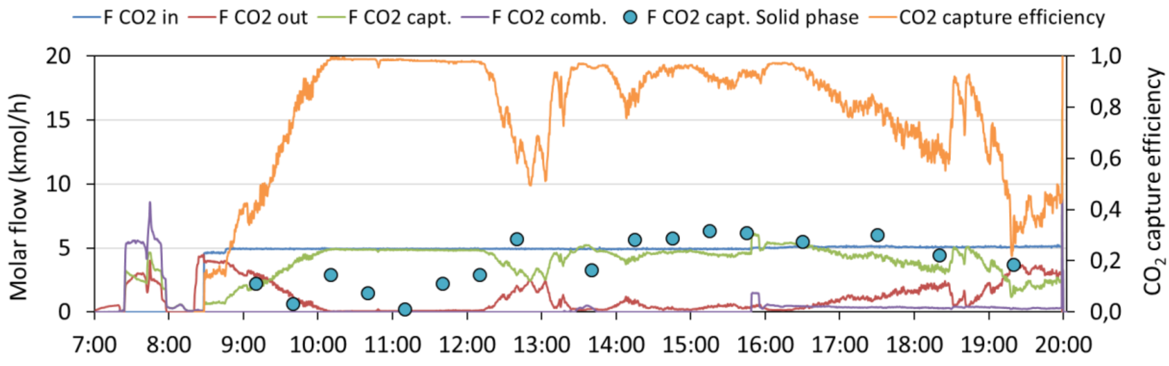

Figure A.90. Balance closure and CO_2 capture efficiency (Experiment 29/02/24).

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Experiment: 01/03/2024

In this experiment, four limestone feeding rates were tested. The calciner was operated under air combustion conditions while the carbonator was fed with a stream with a CO_2 concentration of 10.3%. As presented in Figure A.91, the calciner was operated in air mode and the O_2 in the outlet stream was maintained at an average value of 4.8 %. Figure A.92 shows the evolution of the average temperature, inventory, inlet and outlet gas velocities in the calciner. The temperature in the dense bed took an average value of 545 °C while in the upper section 820°C. The calciner inventory was stable during the experiment around 175 kg/m^2. The inlet gas velocity was 3.4 m/s while the outlet gas velocity of the gas stream leaving the calciner was 5.5 m/s. Limestone flow rates fed to the calciner were varied during the experiment, as shown in Figure A.93, four limestone flow rates were studied. Between 09:06 h and 10:12 h, 500 kg/h were fed to the reactor. Next, between 10:10 h to 15:00 h the flow rate was 300 kg/h and between 15:00 h to 16:00 h, the flow was reduced to 150 kg/h. Finally, from 16:00 h to 18:10 h limestone was put back on 300 kg/h.

Table A.15. Average values of experimental key variables between 08:41 h and 18:09 h

(Experiment 01/03/24).

Calciner data	
$T_{901\ dense\ bed}$ (°C)	544.9
$T_{out\ 906}$ (°C)	820.2
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.4
$O_{2\ in}$ (%)	21
$O_{2\ out}$ (%)	4.8
Limestone flow (kg/h)	302.0
Biomass flow (kg/h)	315.6
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	621.4
$T_{806\ out}$ (°C)	531.3
X_{ave}	0.254
$u_{gas\ in\ grid\ +\ LS}$	3.2
$CO_{2\ in}$ (%)	10.3
$CO_{2\ out}$ (%)	1.4

Regarding the carbonator, as illustrated in Figure A.94, it was fed with a stream with a CO_2 concentration of 10.3% and kept constant during the experiment. Figure A.95, presents the evolution of the average temperature. The average temperature in the upper section was 530 °C while in the lower part of the reactor, 620°C. The inlet gas velocity was 3.2 m/s while the outlet gas velocity 2.9 m/s. The maximum CO_2 carrying capacity of the solids and the $CaCO_3$ composition are illustrated in Figure A.96. The average X_{ave} value of the solids was 0.254. Lastly, in Figure A.97, it can be seen the CO_2 balance closure and the CO_2 capture efficiency.

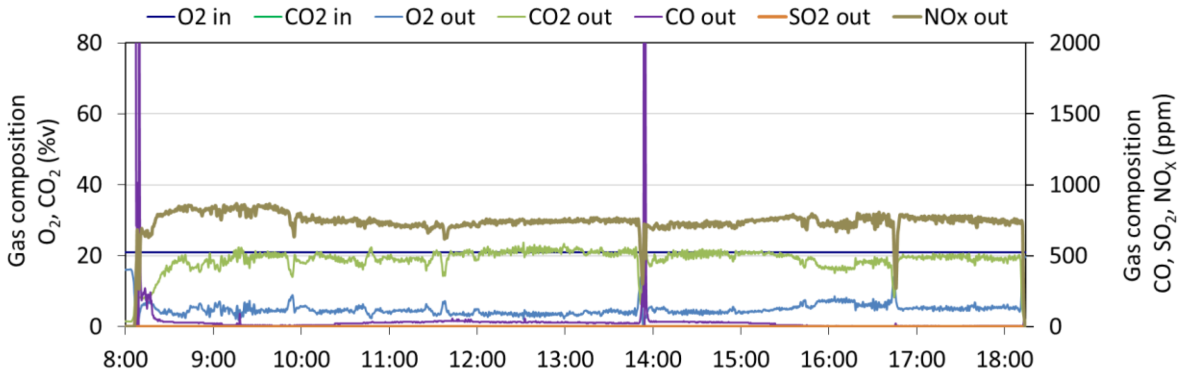

Figure A.91. Inlet and outlet gas composition in the calciner reactor (Experiment 01/03/24)

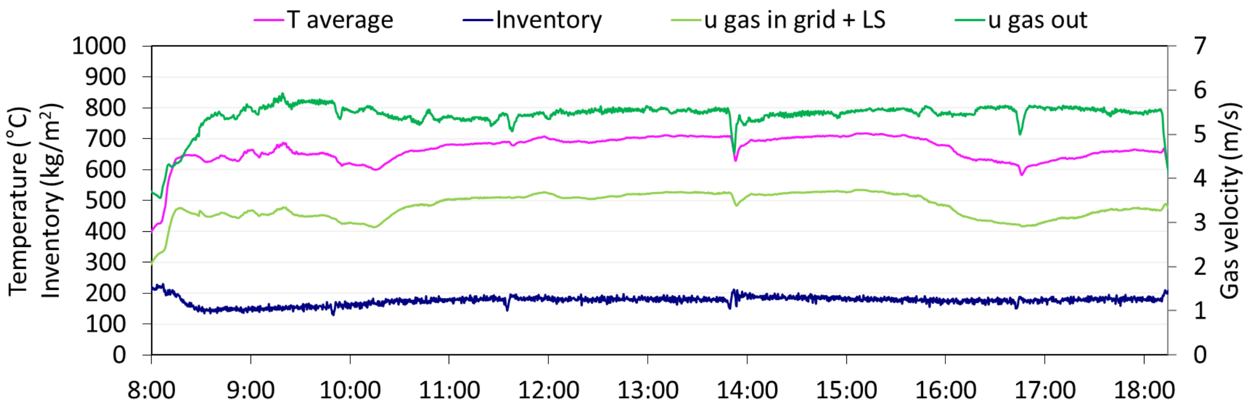

Figure A.92. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 01/03/24).

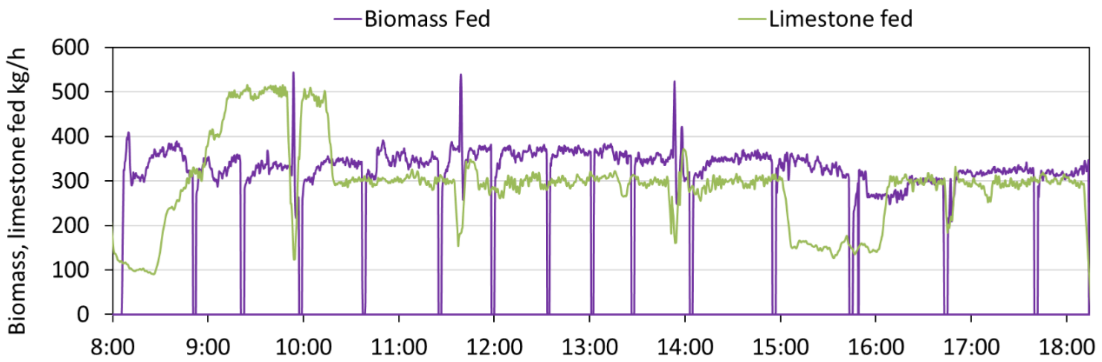

Figure A.93. Biomass and limestone feeding rates (Experiment 01/03/24).

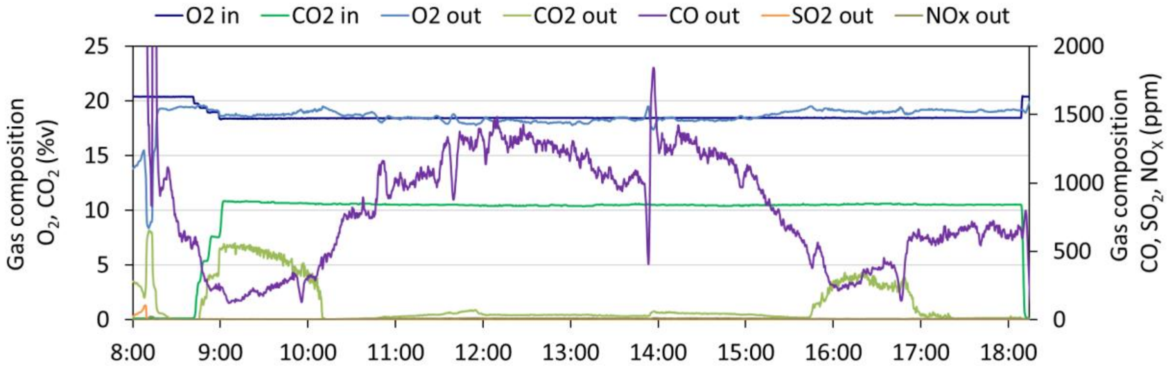

Figure A.94. Inlet and outlet gas composition in the carbonator reactor (Experiment 01/03/24).

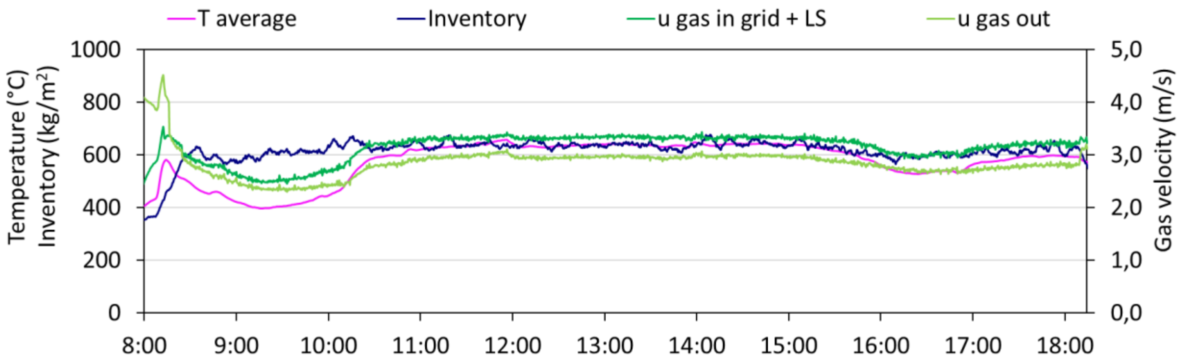

Figure A.95. Average temperature, inventory, inlet and outlet gas velocities in the carbonator (Experiment 01/03/24).

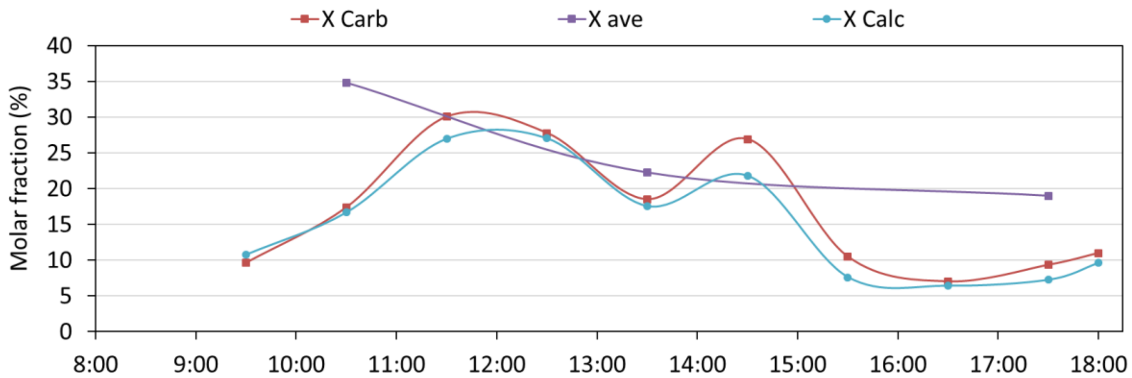

Figure A.96. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids in the carbonator (X_{ave}) (Experiment 01/03/24).

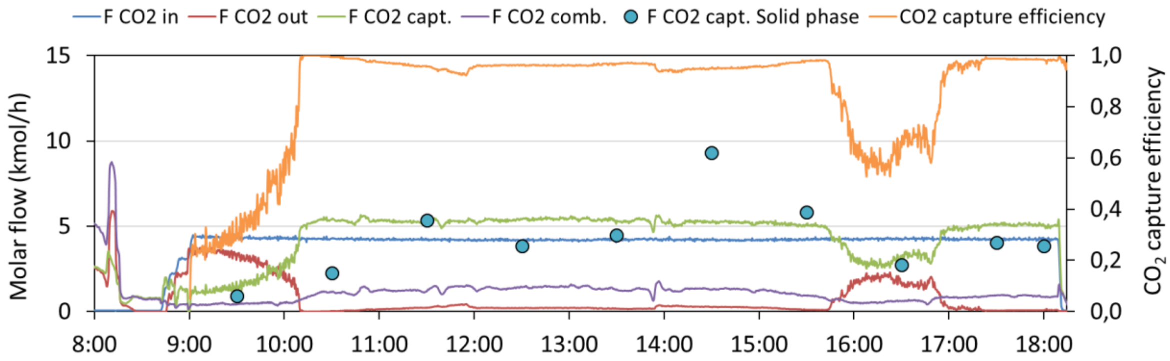

Figure A.97. CO_2 balance closure and CO_2 capture efficiency (Experiment 01/03/24).

Experiment: 05/03/24

This experiment corresponds to a series of three experiments trying to operate the pilot under steady conditions for at least 10 hours with different calciner temperatures. During these tests, fouling/corrosion probes were installed by SWF at the exit of the calciner (after the cyclone). The aim of this test was to operate the pilot plant under stable operating conditions so as to have a base case enabling for a comparison with the subsequent tests with an average calciner temperature of 910 ºC. A period of 12 hours with constant operating conditions was maintained.

This was conducted between 08:35 h and 20:45 h. As evidenced by Figure A.98, the calciner was operated under oxy-combustion conditions and was kept at an average temperature of 910 °C in the upper section of the fluidized bed reactor. Moreover, the inlet gas velocity at the calciner was 2.7 m/s whereas the outlet gas velocity was 3.2 m/s.

Limestone and biomass feeding rates are presented in Figure A.100. Since limestone rates must be sufficiently high in order to ensure reasonable circulation rates between reactors and homogeneous temperatures along the fluidized bed, limestone was kept constant and at high value during the experiment. Consequently, the average limestone feeding rate was 350 kg/h for this test. In regard to the fuel, the biomass flow varied between 300 kg/h and 450 kg/h, aiming for an oxygen concentration in the outlet stream of the calciner of 4 % and an average temperature in the reactor upper section of 910°C, as previously mentioned. The abrupt decreases to zero in the biomass flow also shown in Figure A.100, are owe to the refilling of the biomass hopper. A similar phenomenon occurs when the refilled hopper is the one corresponding to the limestone, there is a decrease in the limestone flow, but it also entails a sudden increment in the biomass flow. However, these punctual fluctuations do not affect the overall stability of the process.

Concerning the carbonator reactor, a synthetic flue gas stream with a CO_2 concentration of 10.9 % was introduced and not altered throughout the test. It can be seen in Figure A.101 that the CO_2 concentration in the outlet stream of the carbonator is below 1 %, since once in carbon capture conditions, as shown in Figure A.104, high capture efficiencies were reached within the carbonator during the experiment. In addition, as derived from Figure A.102, the average inlet gas velocity was 3.4 m/s while the average outlet gas velocity was 3.0 m/s. Besides, the average temperature in the reactor was 600°C. The molar composition of the solid samples in terms of $CaCO_3$ is illustrated in Figure A.103. It also can be seen the evolution of the maximum CO_2 carrying capacity of the particles measured experimentally through TG analysis, being 0.193 the average value of the samples taken between 09:15h and 19:45h.

Table A.16. Average values of the key variables of the experiment between 08:35 and 08:47.

Calciner data	
$T_{901\ dense\ bed}$ (°C)	811.1
$T_{out\ upper\ section}$ (°C)	909.0
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	2.7
$O_{2\ in}$ (%)	35.0
$O_{2\ out}$ (%)	4.7
Limestone flow (kg/h)	351.2
Biomass flow (kg/h)	315.2
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	638.0
$T_{806\ out}$ (°C)	556.7
X_{ave}	0.2
$u_{gas\ in\ grid\ +\ LS}$	3.4
$CO_{2\ in}$ (%)	10.9
$CO_{2\ out}$ (%)	0.8

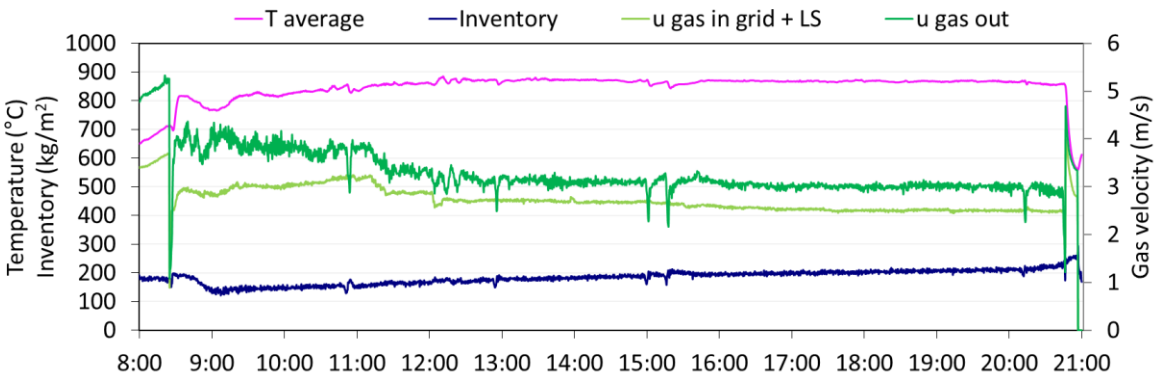

Figure A.98. Inlet and outlet gas composition in the calciner reactor (Experiment 05/03/24).

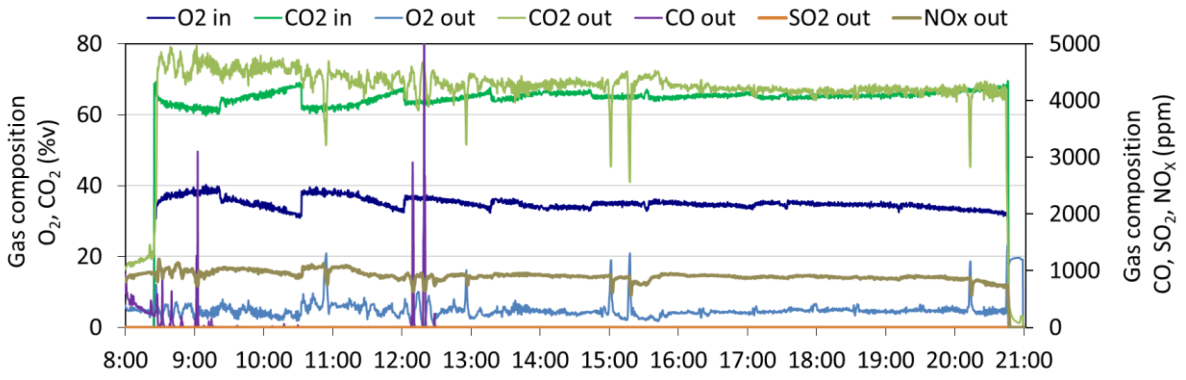

Figure A.99. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 05/03/24).

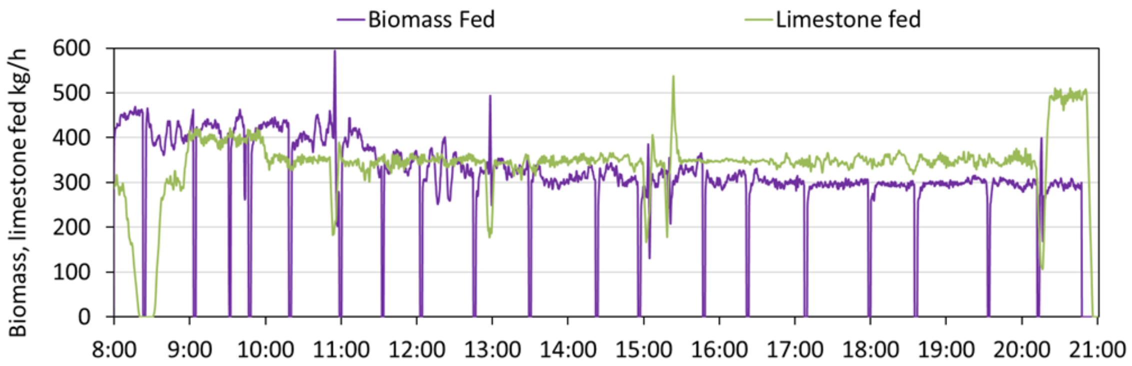

Figure A.100. Limestone and biomass feeding rates fed to the calciner (Experiment 05/03/24).

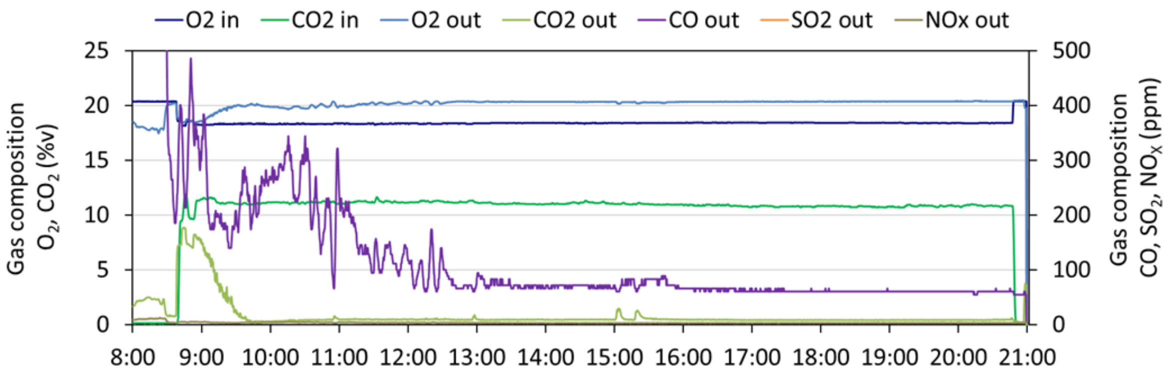

Figure A.101. Inlet and outlet gas composition in the carbonator reactor (Experiment 05/03/24).

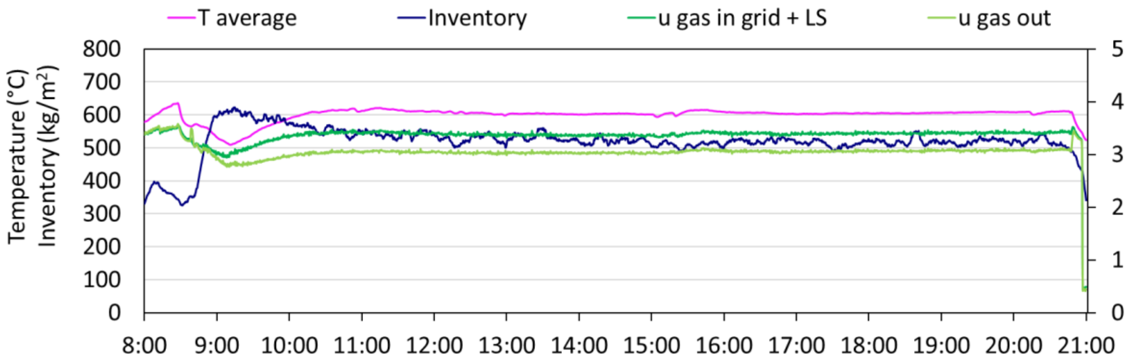

Figure A.102. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 05/03/24).

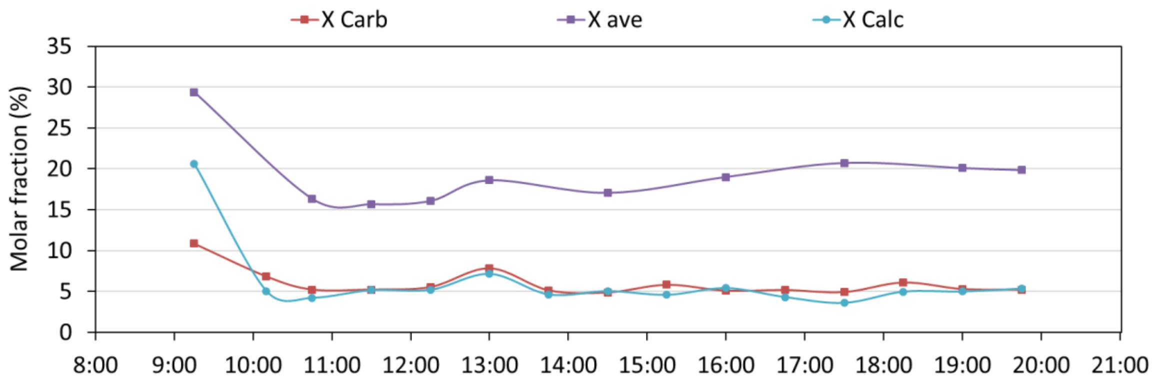

Figure A.103. $CaCO_3$ molar fraction of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity (X_{ave}) of the solids in the carbonator reactor (Experiment 05/03/24).

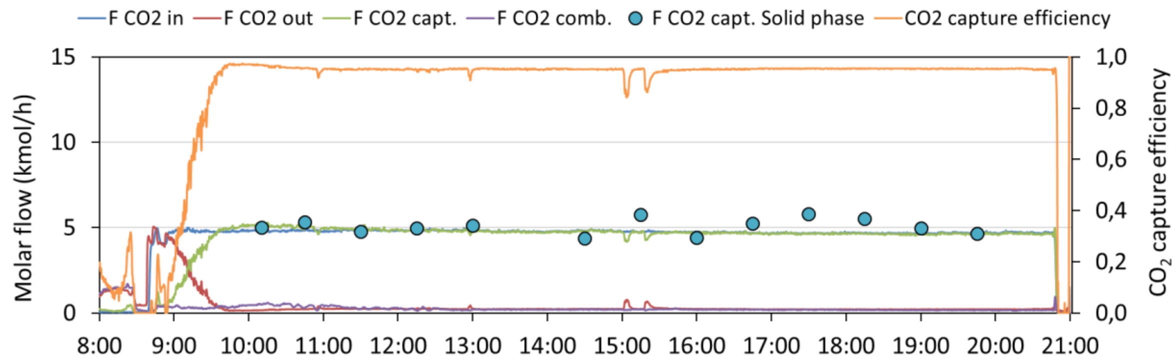

Figure A.104. CO_2 balance closure and CO_2 capture efficiency in the carbonator reactor (Experiment 05/03/2024).

Experiment: 06/03/24

During this experiment, a higher calciner temperature of 940 ºC was tested. A carbon capture experiment was conducted within a period of almost 11 hours with constant operating conditions between 08:00 h and 18:45 h. As presented in Figure A.105, the calciner was operated in oxy-combustion mode aiming for a temperature in the upper section of 940 °C. Regarding gas velocities, the inlet gas velocity at the calciner was 3.0 m/s whereas the outlet gas velocity was 3.7 m/s.

Figure A.107 depicts limestone and biomass feeding rates. Limestone rates must be sufficiently high in order to ensure reasonable circulation rates between reactors and homogeneous temperatures. Consequently, the average limestone feeding rate was 345 kg/h for this test, while the average biomass flow was 340 kg/h, endeavouring to achieve an oxygen concentration in the outlet stream of the calciner about 4 %, being the average value 4.8 %. Sharp decreases in the biomass flow are caused because of the refilling of the biomass and limestone hopper. Nevertheless, these punctual fluctuations do not affect the overall stability of the process.

The carbonator reactor, was operated at an average temperature of 610°C (Figure A.109). Besides, a synthetic flue gas stream with a CO_2 concentration of 11 % was introduced and not modified throughout the test. Once in carbon capture conditions, high capture efficiencies were reached. Hence, in Figure A.108 the CO_2 concentration in the outlet stream of the carbonator is below 1 % while high carbon capture efficiencies are illustrated in Figure A.111. The average inlet gas velocity was 3.4 m/s whilst the average outlet gas velocity was 3.03 m/s.

The $CaCO_3$ molar composition of the solid samples is illustrated in Figure A.110. It also shows the evolution of the maximum CO_2 carrying capacity of the particles measured experimentally through TG analysis, being 0.161 the average value of the samples taken between 09:00h and 18:00h.

Table A.17. Average values of the key variables of the experiment between 08:00 and 18:45.

Calciner data	
$T_{901\ dense\ bed}$ (°C)	804.6
$T_{out\ upper\ section}$ (°C)	937.3
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	3.0
$O_{2\ in}$ (%)	37.1
$O_{2\ out}$ (%)	4.8
Limestone flow (kg/h)	343.9
Biomass flow (kg/h)	339.7
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	651.7
$T_{806\ out}$ (°C)	564.4
X_{ave}	0.161
$u_{gas\ in\ grid\ +\ LS}$	3.4

$CO_{2\ in}$ (%)	11.0
$CO_{2\ out}$ (%)	0.7

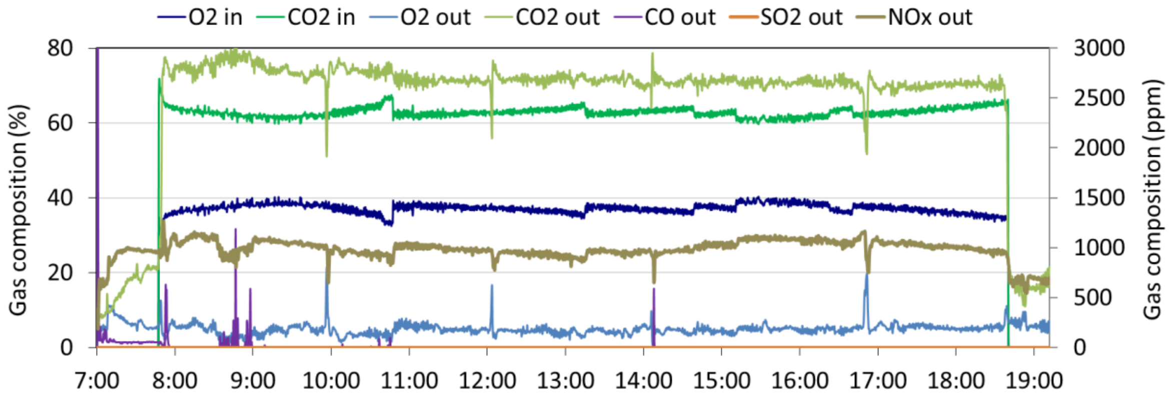

Figure A.105. Inlet and outlet gas composition in the calciner reactor (Experiment 06/03/24).

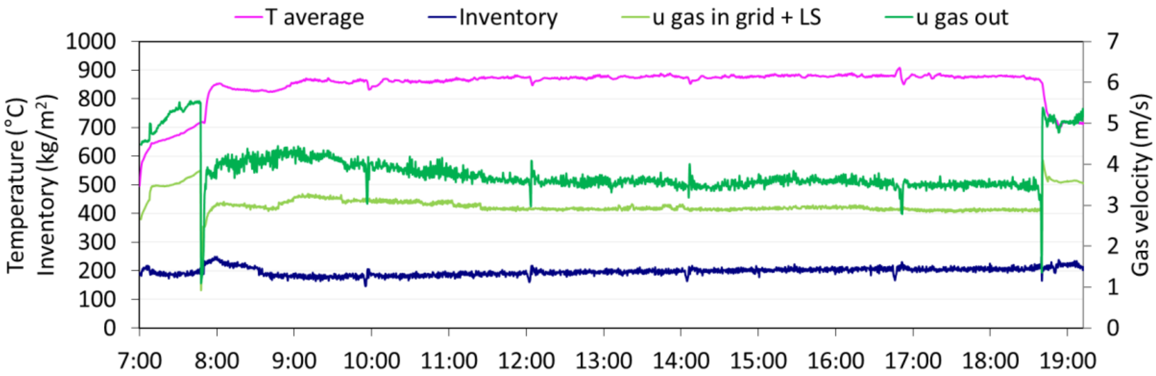

Figure A.106. Temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 06/03/24).

Figure A.107. Biomass and limestone feeding rates fed to the calciner reactor (Experiment 06/03/24).

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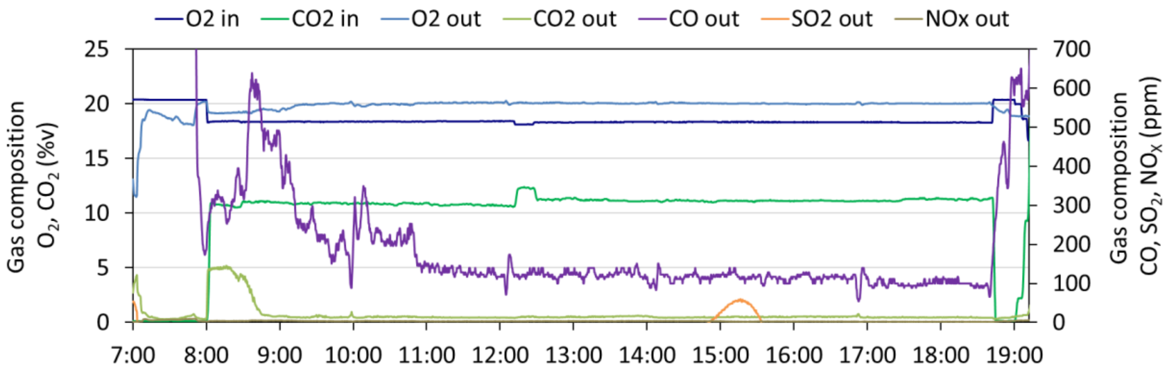

Figure A.108. Inlet and outlet gas composition in the carbonator reactor (Experiment 06/03/24).

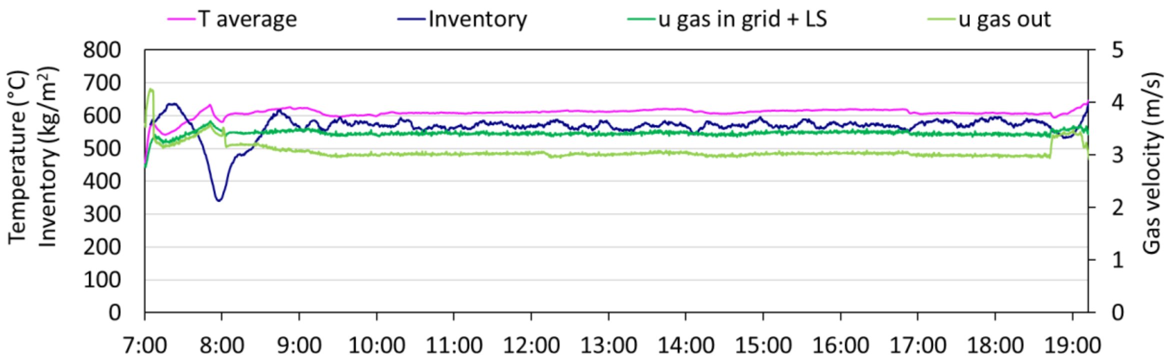

Figure A.109. Temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 06/03/24).

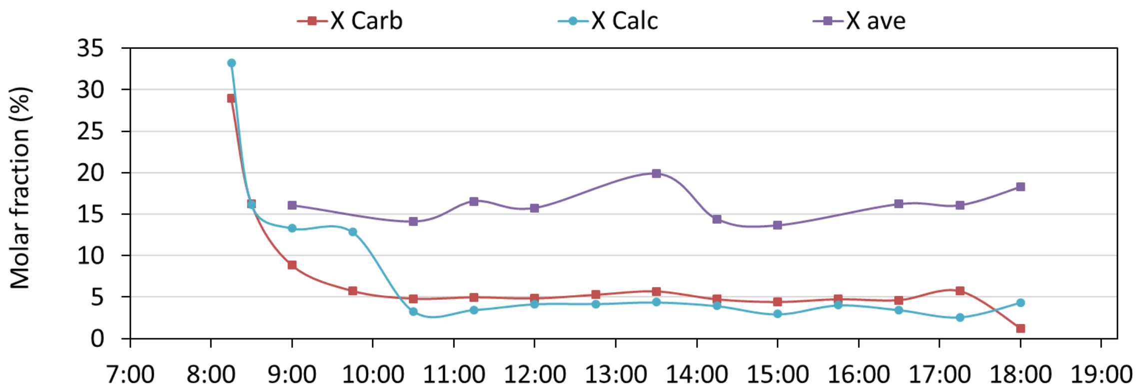

Figure A.110. $CaCO_3$ molar fraction of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the CO_2 maximum carrying capacity (X_{ave}) in the carbonator reactor (Experiment 06/03/24).

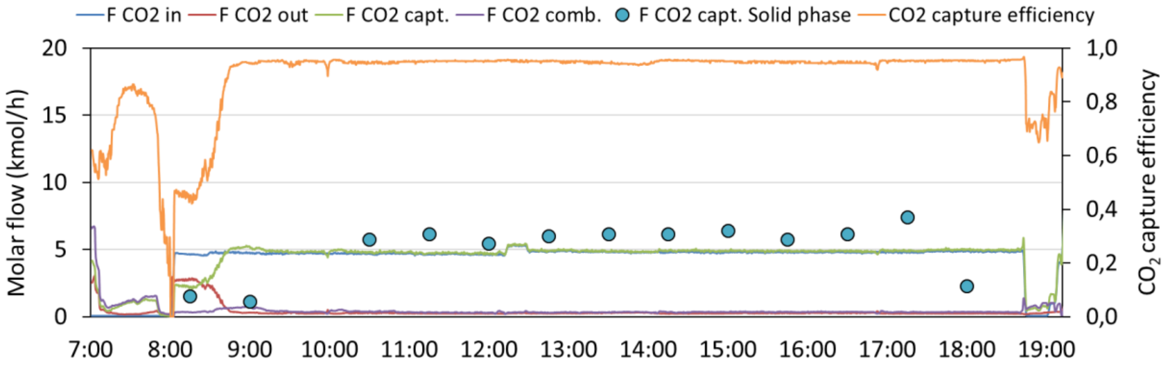

Figure A.111. CO_2 balance closure and CO_2 capture efficiency in the carbonator reactor (Experiment 06/03/24).

Experiment: 07/03/24

During this experiment a lower calcination temperature was tested (890 ºC). The pilot plant was maintained under stable operating conditions over a 10-hour period. The carbon capture experiment started at 07:55 h when a stream with 9.2% of CO_2 was fed to the carbonator and concluded at 18:11 h. As noticed in Figure A.112, the calciner was operated under oxy-combustion conditions and kept at an average temperature of 890 °C in the upper section of the reactor. Regarding gas velocities in Figure A.113, the inlet gas velocity at the calciner was 2.6 m/s whereas the outlet gas velocity was 2.8 m/s.

Limestone and biomass feeding rates are presented in Figure A.114. The average limestone feeding rate was 375 kg/h for this test, while the average biomass flow was 390 kg/h, being the desired oxygen concentration in the outlet stream of the calciner about 4 % and the temperature in the reactor upper section, 890°C.

Concerning the carbonator reactor, a synthetic flue gas stream with a CO_2 concentration of 9.2 % was introduced and not varied during the test. As illustrated in Figure A.115 the CO_2 concentration in the outlet stream of the carbonator is below 1 %. Therefore, high capture efficiencies near 99% were reached, as presented in Figure A.118. In addition, as derived from Figure A.116, the average inlet gas velocity was 3.2 m/s while the average outlet gas velocity was 3.2 m/s. Besides, the average temperature in the reactor was 590°C.

The molar composition of the solid samples in terms of $CaCO_3$ is illustrated in Figure A.117. It also can be seen the evolution of the maximum CO_2 carrying capacity of the particles measured experimentally through TG analysis, being 0.208 the average value of the samples taken between 08:30h and 17:45h.

Table A.18. Average values of the key variables of the experiment between 07:55 and 18:10.

Calciner data	
$T_{901\ dense\ bed}$ (°C)	834.5
$T_{out\ upper\ section}$ (°C)	887.4
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	2.6
$O_{2\ in}$ (%)	36.6
$O_{2\ out}$ (%)	4.2
Limestone flow (kg/h)	375.4
Biomass flow (kg/h)	290.1
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	625.9
$T_{806\ out}$ (°C)	548.0
X_{ave}	0.208
$u_{gas\ in\ grid\ +\ LS}$	3.5
$CO_{2\ in}$ (%)	9.2
$CO_{2\ out}$ (%)	1.4

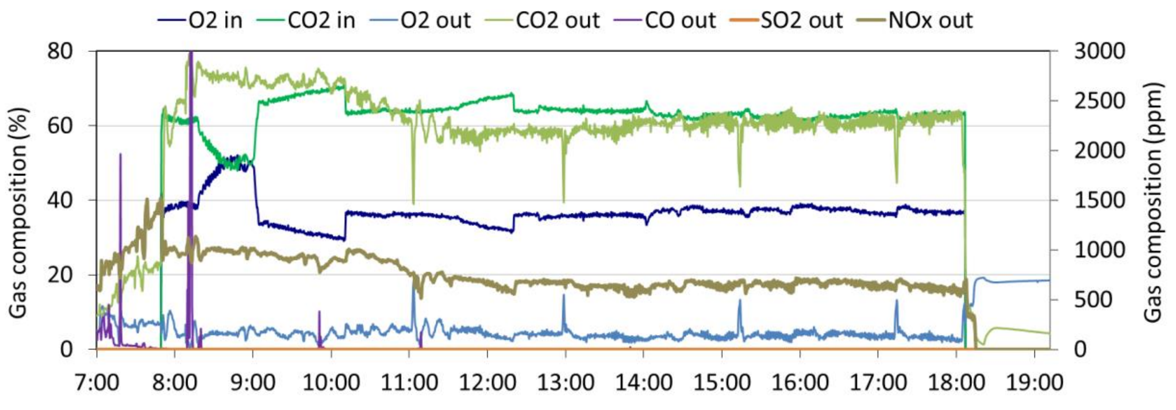

Figure A.112. Inlet and outlet gas composition in the calciner reactor (Experiment 07/03/24).

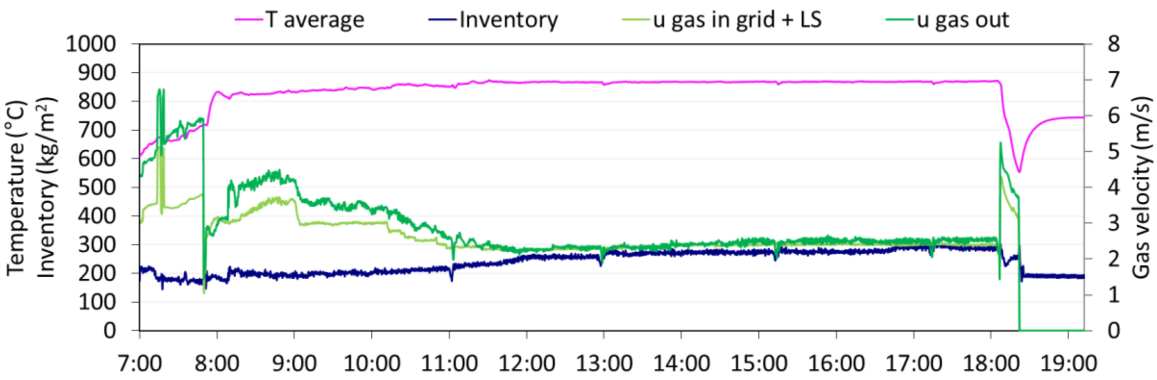

Figure A.113. Temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 07/03/24).

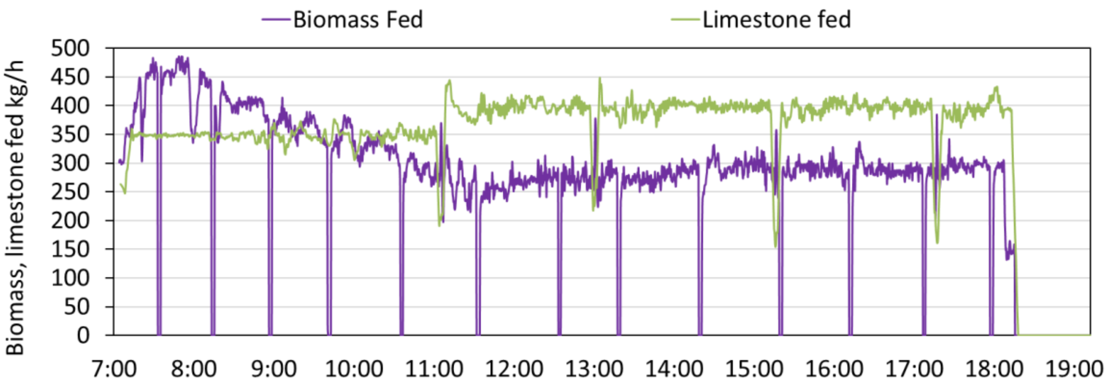

Figure A.114. Biomass and limestone feeding rates fed to the calciner reactor (Experiment 07/03/24).

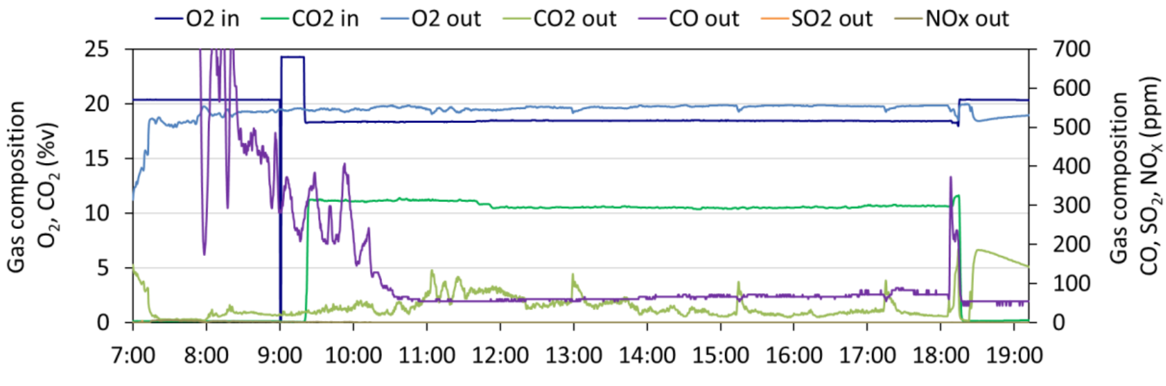

Figure A.115. Inlet and outlet gas composition in the carbonator reactor (Experiment 07/03/24).

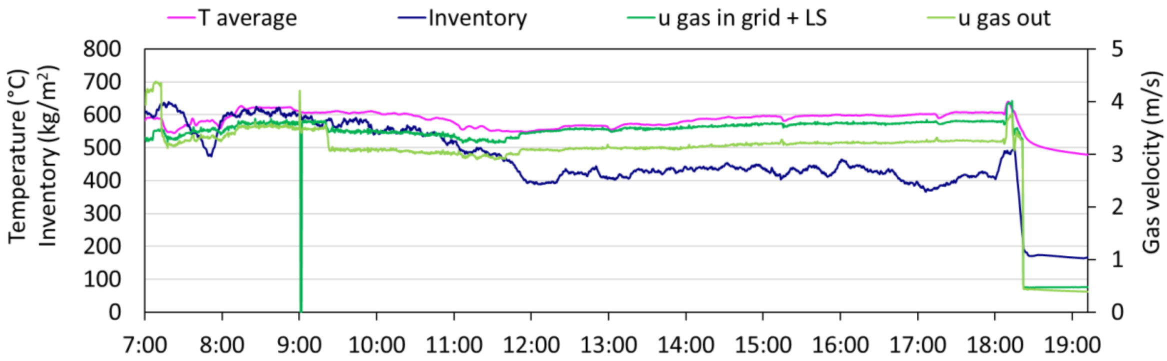

Figure A.116. Temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 07/03/24).

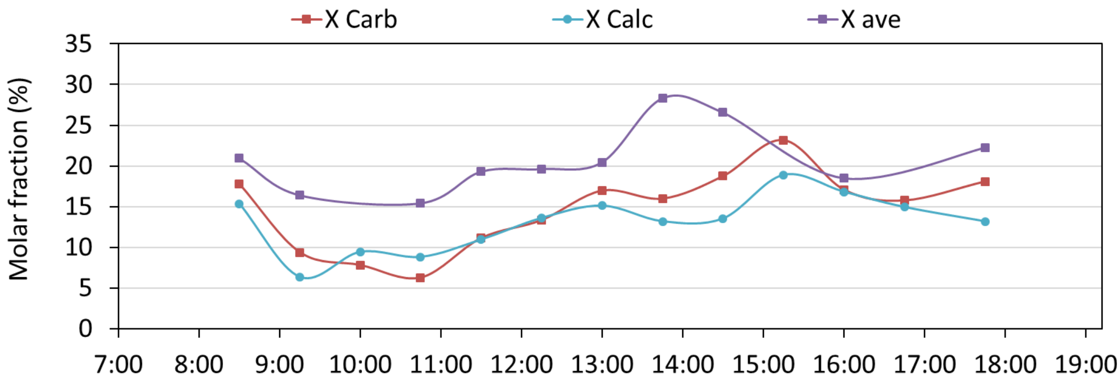

Figure A.117. $CaCO_3$ molar composition in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids in the carbonator reactor (X_{ave}) (Experiment 07/03/24).

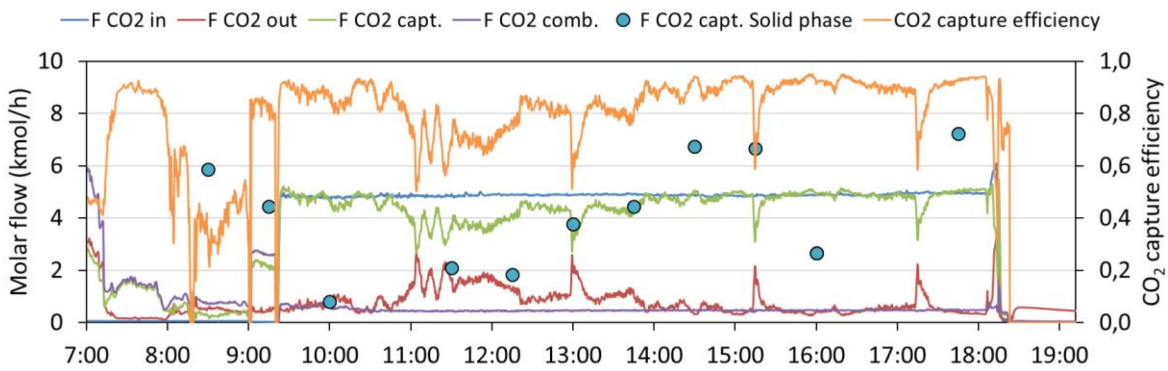

Figure A.118. CO_2 balance closure and CO_2 capture efficiency in the carbonator reactor (Experiment 07/03/24).

Experiment: 08/03/24

The experiment consisted in a dynamic test where the effect of four variables on the system was studied, namely the CO_2 concentration in the synthetic flue gas, the air flow to the carbonator, the O_2 concentration in the inlet stream of the calciner and the biomass flow. Table A.20 offers an insight into the experiment timeline and the variables studied.

The test was developed between 07:50 h and 19:10 h. Reference conditions were stablished enabling for comparison between tests. The calciner was operated under oxy-combustion conditions, being the average temperature sought in the upper section, 910°C and, limestone flow 350 kg/h, ensuring an adequate circulation between reactors. Concerning the carbonator, the reference inlet flow was 1400 kg/h and the concentration of CO_2 in the inlet stream 10,4%.

The concentration of carbon dioxide in the synthetic flue gas stream was altered throughout the test in order to study the flexibility of the system towards load changes. The reference CO_2 concentration was 10,4%. It can be seen in Figure A.122 that, between 10:00 h and 11:00 h a stream with 15% CO_2 was introduced and these conditions were maintained for an hour. Then, at 11:00 h, the synthetic flue gas went back to reference conditions. At 12:00 h another disturbance was forced, by introducing a stream with 4.5% of CO_2 to the reactor. Finally, at 13:00 h the plant went back at the CO_2 concentration of reference.

Table A.20. Experiment timeline

Time (h)	*Conditions*
09:00 - 10:00	*Reference*
10:00 - 11:00	15% $CO_{2\ \mathrm{in\ CB}}$
11:00 - 12:00	*Reference*
12:00 - 13:00	4.5% $CO_{2\ \mathrm{in\ CB}}$
13:00 - 14:00	*Reference*
14:00 - 15:00	+ 20 % gas flow $_{\mathrm{in\ CB}}$
15:00 - 16:00	*Reference*
16:00 - 17:00	+ 20 % gas flow $_{\mathrm{in\ CC}}$
17:00 - 18:00	*Reference*
18:00 - 19:00	- 20 % biomass flow

As derived from Figure A.125, the capture efficiency decreased during the period when the CO_2 concentration of the synthetic flue gas fed to the carbonator reactor was 15 %, compared to the other two concentrations tested. Thus, the capture efficiency between 10:00 and 11:00 was 0.87, in contrast to 0.97 in the previous hour and 0.95 between 12:00 and 13:00.

Another variable whose effect on the system was evaluated was the flow rate entering the carbonator. During the whole test the average value of this parameter was 1400 kg/h, whereas from 14:00 to 15:00 that parameter was aimed to be increased a 20%. Therefore, the average gas flow entering the carbonator during that period of time was 1680 kg/h. A drop of considerable proportions in the carbonator inventory can be observed in Figure A.123 at 14:00. The aforesaid phenomenon is due to the fact that the solids tend to accumulate in the reactor with less velocity. In addition, the average carbonator inlet gas velocity was 3.2 m/s, while the average outlet gas velocity was 3.08 m/s. In addition, the average temperature in the reactor was 606.5°C.

The calciner was operated under oxy-combustion conditions and was kept at an average temperature of 910 °C in the upper section. It can be noticed in Figure A.120, that the average temperature in the calciner took values around 867°C, since the calculation of the average temperature involves the upper section and the dense bed. The inlet gas velocity at the calciner was 2.8 m/s whereas the outlet gas velocity was 3.6 m/s.

From 16:00 to 17:00, a change in O_2 concentration was forced while the O_2 flow remained constant. The average O_2 concentration in the calciner inlet flow increased from 35% to 42%, as seen in Figure A.119. Therefore, temperatures in the calciner suffered from a remarkable increment. Consequently, the average temperature in the upper section in this period was 928.4 °C, in comparison with the value that the referred variable took the previous hour, which was 909.5°C. This led to an improvement in carbon capture efficiencies, while the carbonator temperature remained unaltered.

Limestone and biomass feeding rates are presented in Figure A.121. The average limestone feeding rate was 345 kg/h for this test. The average biomass flow was 315 kg/h, aiming for an oxygen concentration in the outlet stream of the calciner about 4 %.

At 18:00 a 20% decrease in the biomass flow was tested. The average flow during that period was 255 kg/h. Hence, temperatures in the calciner upper section decrease from 911 °C to 895°C, due to the fact that there was an excess of oxygen in the system, resulting in an increment on the O_2 concentration in the outlet stream of the calciner 7.7%. In addition, the mentioned change had also an impact on the carbonator reactor. Temperatures decreased and CO_2 in the outlet stream also rose till 2.5%.

The molar composition of the solid samples in terms of $CaCO_3$ is illustrated in Figure A.124. It also can be seen the evolution of the maximum CO_2 carrying capacity of the particles measured experimentally through TG analysis, being 0.172 the average value of the samples taken between 10:00h and 19:00h.

Table A.19. Average values of experimental key variables between 07:50 and 19:15.

Calciner data	
$T_{901\ dense\ bed}$ (°C)	805.3
$T_{906\ out}$ (°C)	908.6
$u_{gas\ in\ grid + LS}$ (m/s)	2.8
$O_{2\ in}$ (%)	35.7
$O_{2\ out}$ (%)	4.9
Limestone flow (kg/h)	343.7
Biomass flow (kg/h)	316.8

Carbonator data	
$T_{801\ dense\ bed}$ (°C)	650.2
$T_{806\ out}$ (°C)	559.0
X_{ave}	0.172
$u_{gas\ in\ grid + LS}$	3.2
$CO_{2\ in}$ (%)	11.3
$CO_{2\ out}$ (%)	1.4

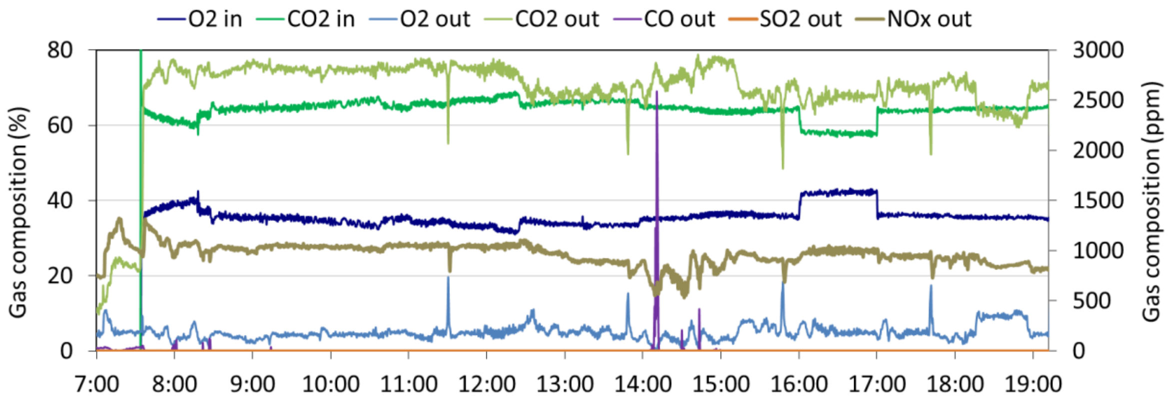

Figure A.119. Inlet and outlet gas composition in the calciner reactor (Experiment 08/03/24).

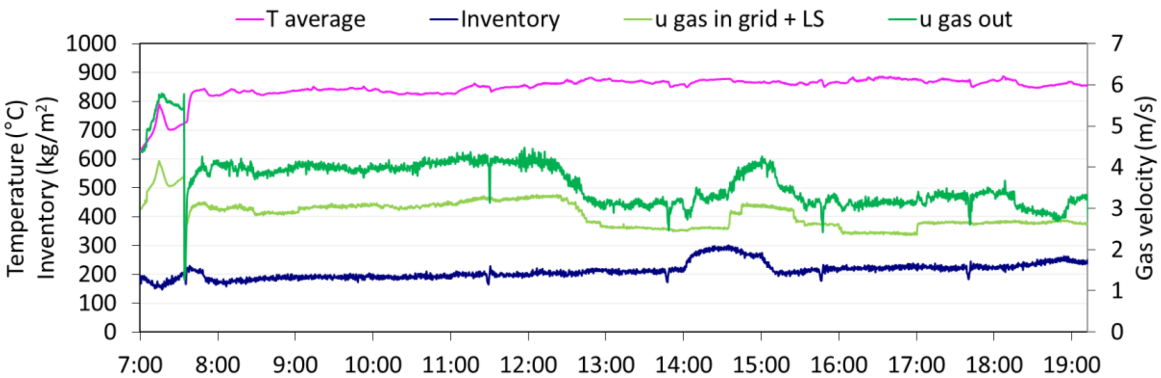

Figure A.120. Temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 08/03/24).

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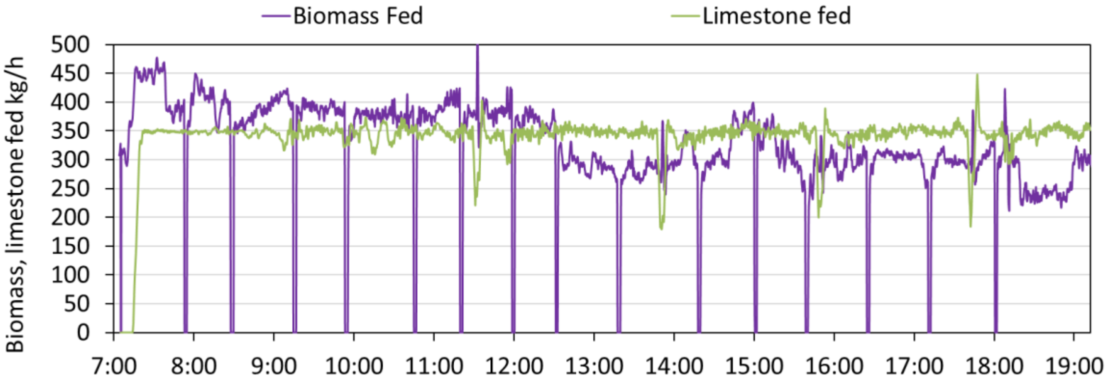


Figure A.121. Limestone and biomass feeding rates fed to the calciner reactor (Experiment 08/03/24).

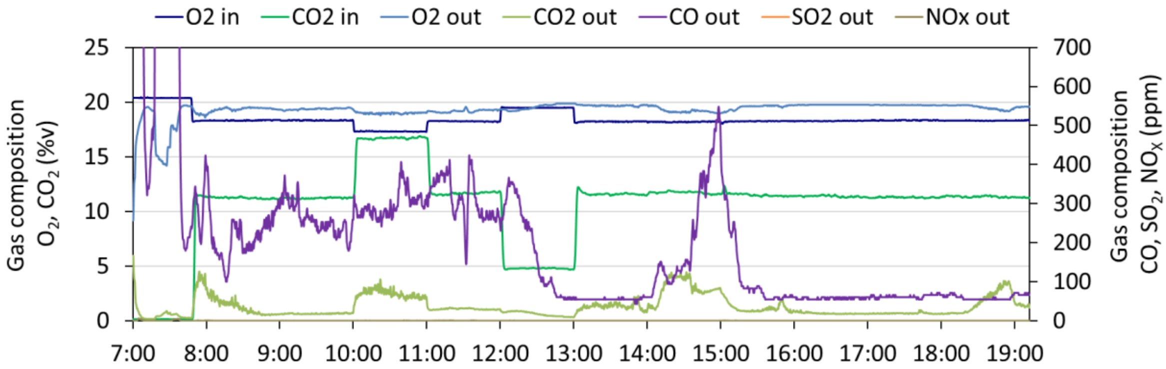


Figure A.122. Inlet and outlet gas composition in the carbonator reactor (Experiment 08/03/24).

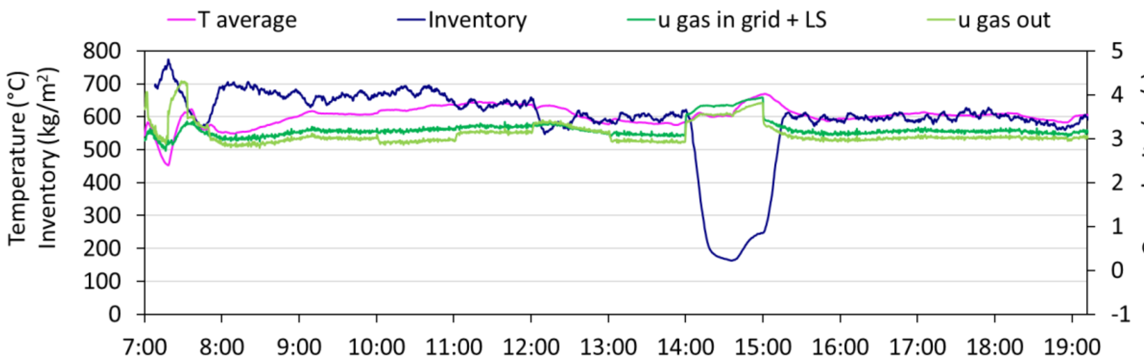


Figure A.123. Temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 08/03/24).

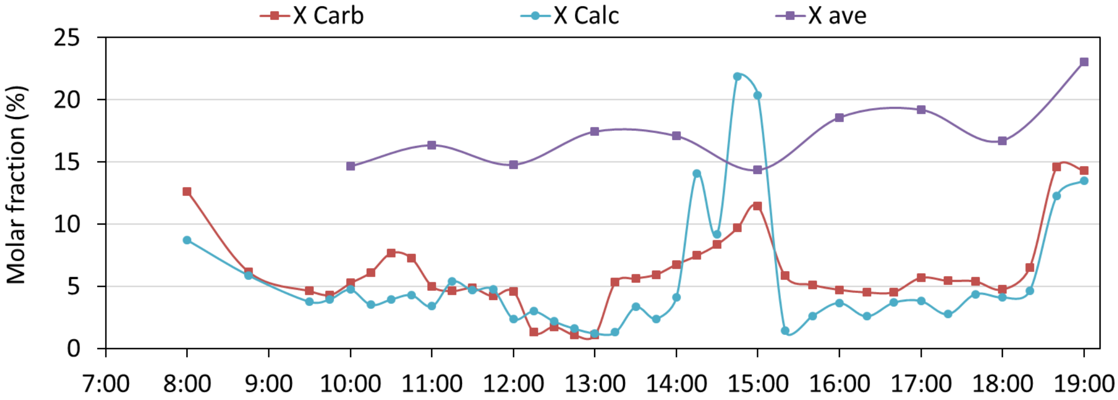


Figure A.124. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum CO_2 carrying capacity of the solids (X_{ave}) in the carbonator reactor (Experiment 08/03/24).

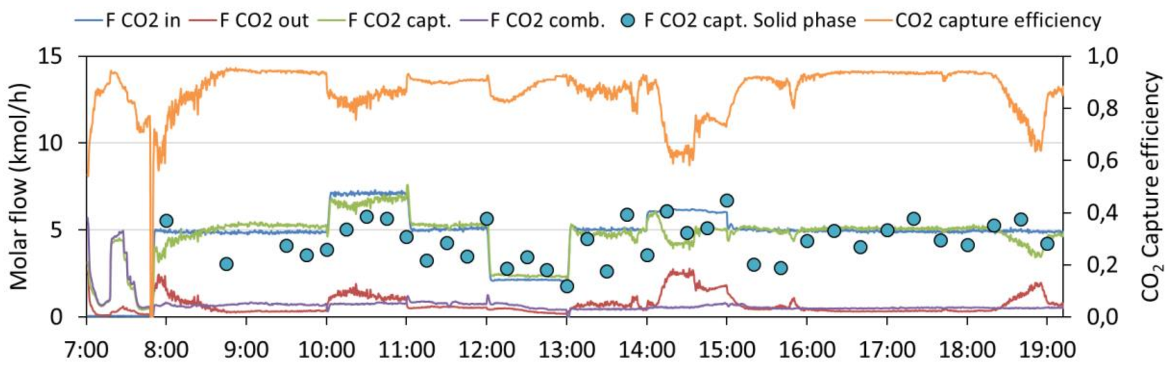


Figure A.125. CO_2 balance closure and CO_2 capture efficiency (Experiment 08/03/24).

Experiment 05/06/2024

This experiment corresponds to the first test aimed to study the fate of Cl and F in the calciner. For this test, periods were alternated in which a fixed flow of polymeric material (PVC as source of Cl and PTFE as source of F) was fed to the calciner. Between 09:00 h and 14:00 h, 3.4 kg/h of PVC was continuously fed into the calciner. Then, between 14:30 h and 19:49 h, 2.23 kg/h of Teflon was fed, before PVC was introduced again at a rate of 3.5 kg/h between 19:49 h and 20:04 h.

The calciner reactor, as shown in Figure A.126, was operated in enriched-air conditions. The average O_2 in the outlet stream of the calciner was 6.0 %. In Figure A.127, it can be seen the evolution of the average temperature in the calciner. In the dense bed the average temperature was 584.5 °C and in the upper section 815.0 °C. The inlet gas velocity was 2.8 m/s while the average outlet gas velocity was 4.5 m/s. The evolution of the biomass and limestone fed during the experiment is illustrated in Figure A.128. Biomass started to be fed continuously at 07:52 h, being the average flow during the experiment 262.9 kg/h. In order to ensure good circulation rate between reactors, limestone was fed with a high average flow of 446.3 kg/h.

Concerning the carbonator reactor, on this test no synthetic flue gas was introduced to the reactor. Regarding temperatures, depicted in Figure A.129, in the dense bed 533.6 °C was reached, while in the upper section 467.0 °C. The average inlet gas velocity was 3.1 m/s and the outlet average gas velocity was 3.3 m/s. In Figure A.131 is presented the evolution of the CaCO3 molar composition of the samples taken from both reactors. In addition, it illustrates the maximum carrying capacity of the solids in the carbonator reactor being the average value of this parameter 0.561.

Table A.20. Average values of experimental key variables between 08:00 h and 20:00 h

(Experiment 05/06/24)

Calciner data	
$T_{901\ dense\ bed}$ (°C)	584.5
$T_{out\ 906}$ (°C)	815.0
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	2.8
$O_{2\ in}$ (%)	23.3
$O_{2\ out}$ (%)	6.0
Limestone flow (kg/h)	446.3
Biomass flow (kg/h)	262.9
Carbonator data	
$T_{801\ dense\ bed}$ (°C)	533.6
$T_{806\ out}$ (°C)	467.0
X_{ave}	0.561
$u_{gas\ in\ grid\ +\ LS}$	3.1
$CO_{2\ in}$ (%)	0.0
$CO_{2\ out}$ (%)	0.0

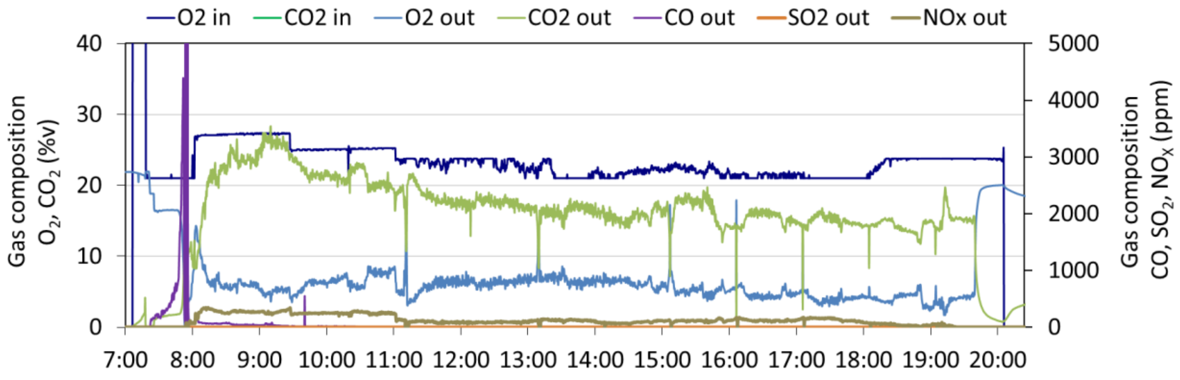


Figure A.126. Inlet and outlet gas composition in the calciner reactor (Experiment 05/06/24).

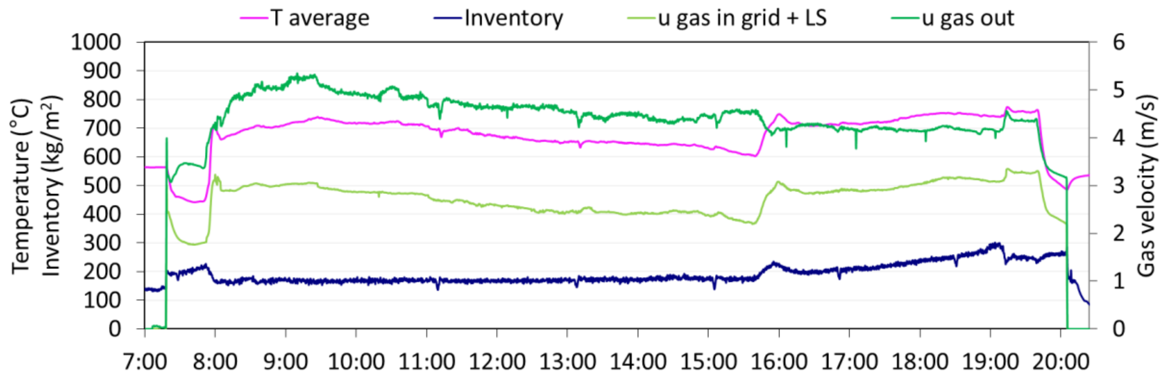


Figure A.127. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 05/06/24).

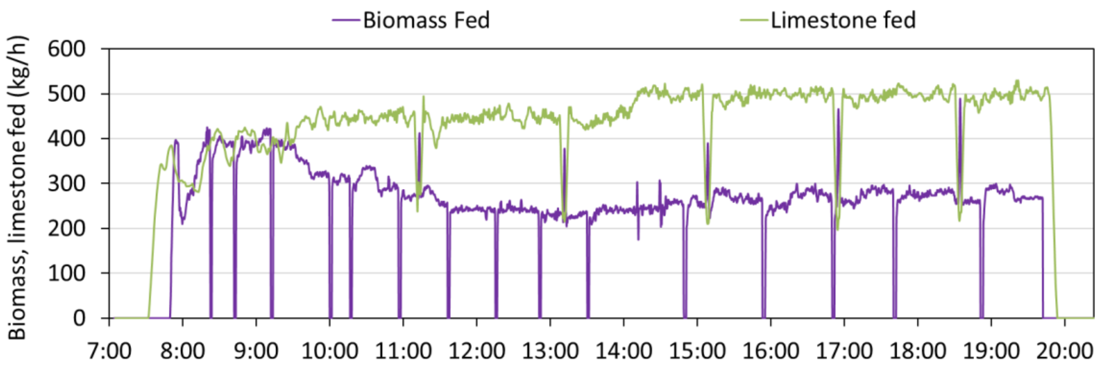


Figure A.128. Biomass and limestone feeding rate (Experiment 05/06/24).

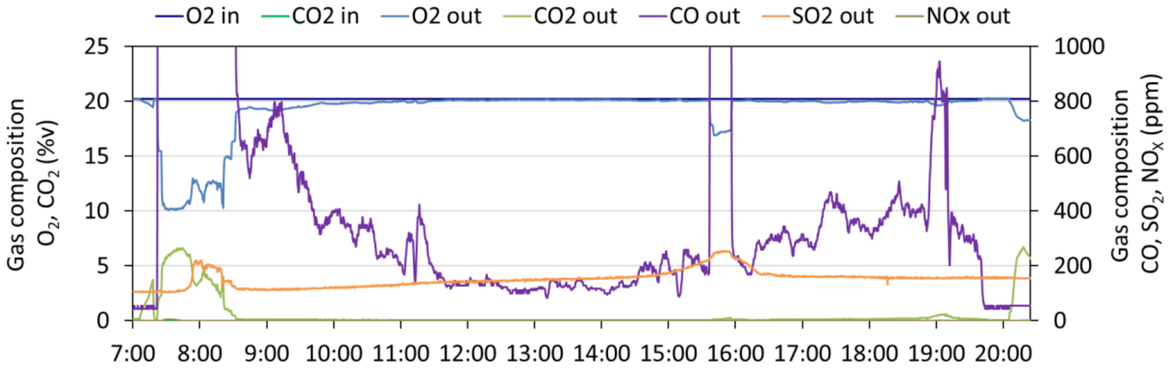


Figure A.129. Inlet and outlet gas concentration in the carbonator reactor (Experiment 05/06/24).

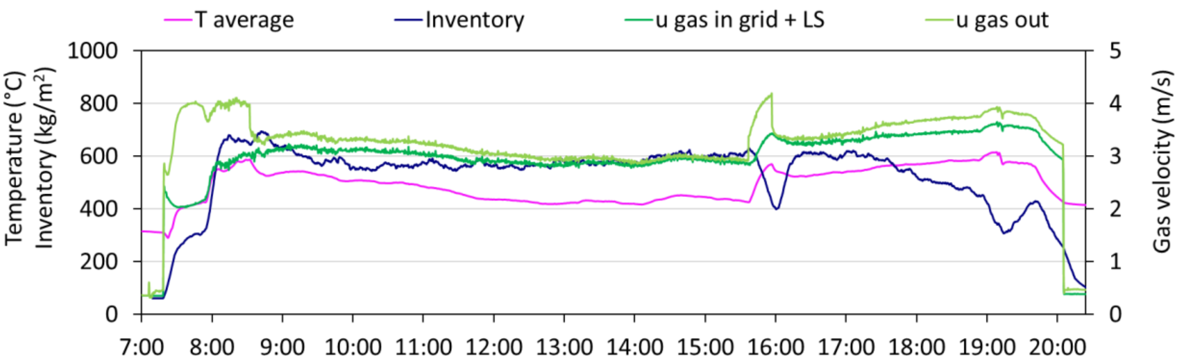


Figure A.130. Average temperature, inventory, inlet and outlet gas velocities in the carbonator reactor (Experiment 05/06/24).

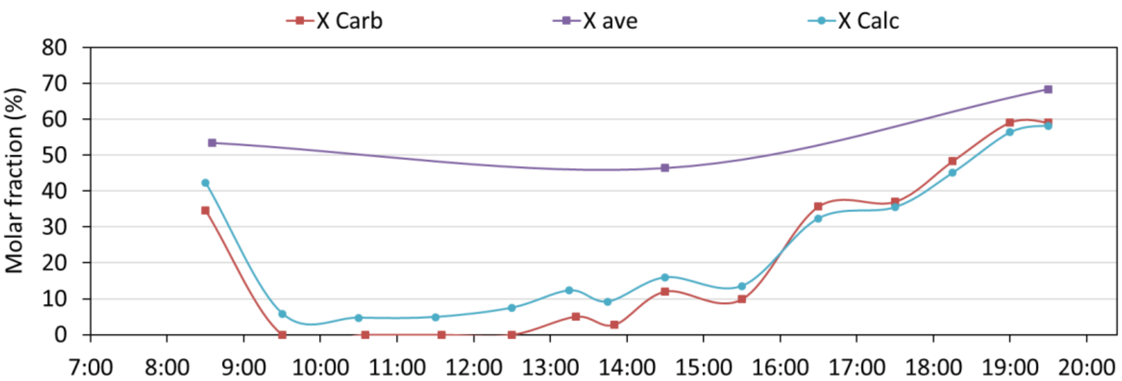


Figure A.131. $CaCO_3$ molar composition of the solids in the carbonator (X_{Carb}) and in the calciner (X_{Calc}), along with the maximum carrying capacity of the solids in the carbonator reactor (X_{ave}) (Experiment 05/06/24).

Experiment 04/07/2023

During the period of July 2023, experiments were carried out at La Pereda Pilot Plant by operating only the calciner reactor. Therefore, the solids from the cyclone return back to the calciner reactor in the form of an internal recycle. These experimental campaigns were developed by operating the calciner under two different modes, air-combustion and oxy-combustion. This experiment corresponds to an air-calcination tests

Table A.21. Average values of experimental key variables between 14:00 h and 18:00 h

(Experiment 04/07/23)

Calciner data	
$T_{901\ dense\ bed}$ (°C)	786.8
$T_{out\ 906}$ (°C)	839.1
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	4.7
$O_{2\ in}$ (%)	21.0
$O_{2\ out}$ (%)	4.7
Limestone flow (kg/h)	276.6
Biomass flow (kg/h)	294.7

As can be seen in Figure A.132, the calciner was operated in air-mode, and the O_2 composition at the outlet stream of the calciner was 4.7 %. In Figure A.133, it can be seen the evolution of the average temperature in the calciner, between 14:00 h and 18:00 h, the period when stable operation was reached, the average temperature in the dense bed was 736.8°C while in the upper part of the reactor it was 839.1 °C. Besides, the average value of the inventory in the aforementioned period was 561.4 kg/m^2. In addition, the average inlet gas velocity was 4.7 m/s while the average outlet gas velocity was 6.2 m/s. Regarding biomass and limestone feeding rates shown in Figure A.134, the average biomass feeding rate was 294.7 kg/h and the limestone rate 276.6 kg/h, although from 16:00 h to the end of the experiment limestone was kept constant at 500 kg/h. The evolution of the $CaCO_3$ molar composition of the solids is presented in Figure A.135. Furthermore, the average maximum carrying capacity of the solids was 0.372.

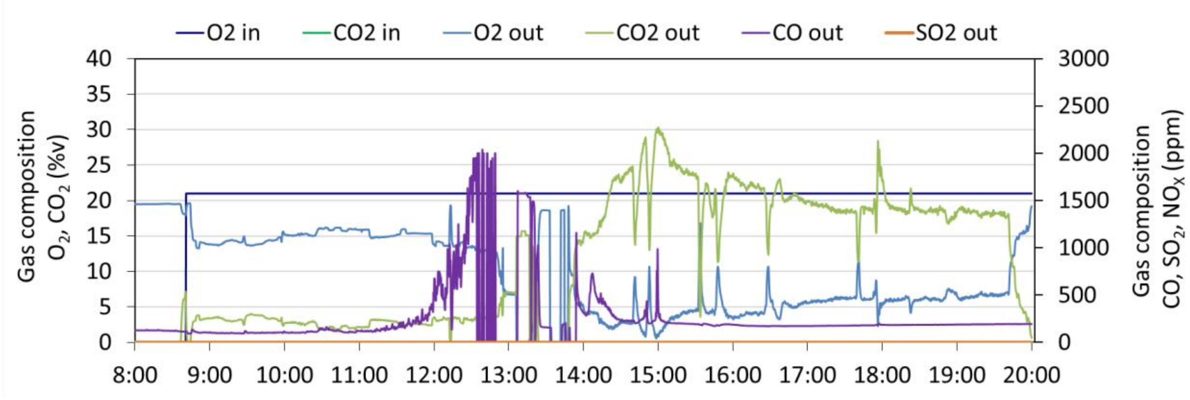


Figure A.132. Inlet and outlet gas composition in the calciner reactor (Experiment 04/07/23).

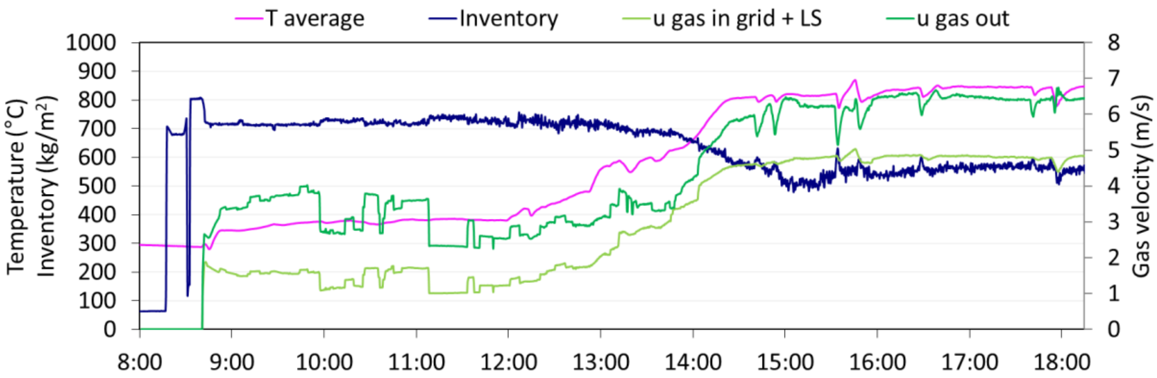


Figure A.133. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 04/07/23).

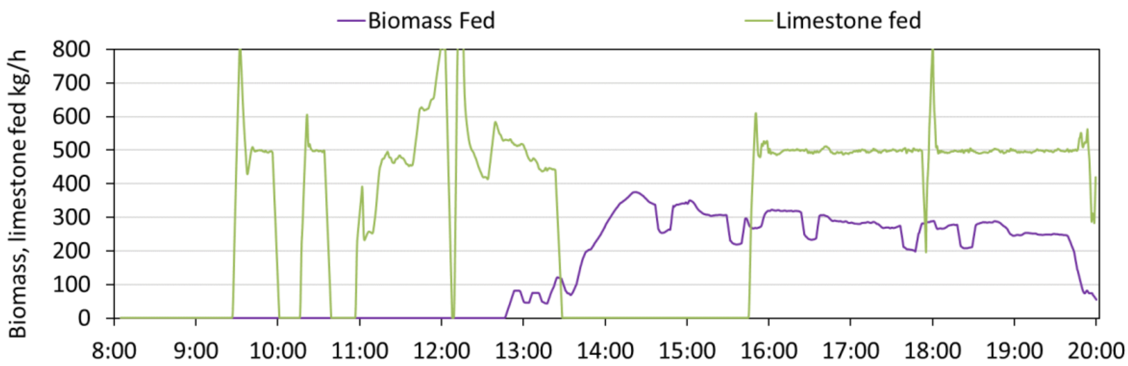


Figure A.134. Biomass and limestone feeding rates (Experiment 04/07/23).

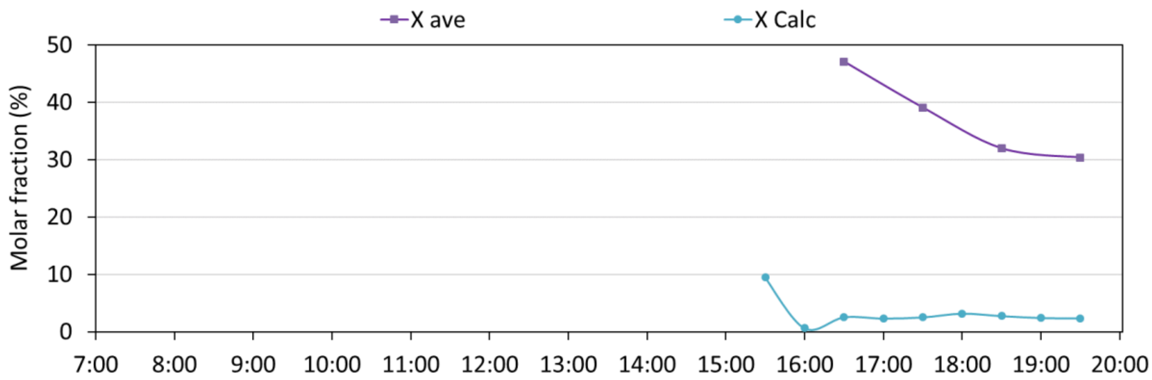


Figure A.135. $CaCO_3$ molar composition of the solids in the calciner (X_{Calc}) and maximum CO_2 carrying capacity of the solids in the calciner reactor (X_{ave}) (Experiment 04/07/23).

Experiment 05/07/2023

This is an air-calcination experiments. As can be seen in Figure A.136, the average O_2 composition at the outlet stream of the calciner was 5.1 %. In Figure A.137, it can be seen the evolution of the average temperature in the calciner. From 09:00 h to 16:50 h, the average temperature in the dense bed was 783.2 °C while in the upper part of the reactor it was 891.6 °C.

Table A.22. Average values of experimental key variables between 09:00 h and 16:50 h

(Experiment 05/07/23)

Calciner data	
$T_{901\ dense\ bed}$ (°C)	783.2
$T_{out\ 906}$ (°C)	891.6
$u_{gas\ in\ grid\ +\ LS}$ (m/s)	4.2/6.0
$O_{2\ in}$ (%)	21.0
$O_{2\ out}$ (%)	5.1
Limestone flow (kg/h)	591.5
Biomass flow (kg/h)	287.0

The inventory during that period was 517.2 kg/m^2. The average inlet gas velocity was 4.7 m/s while the average outlet gas velocity was 6.2 m/s. Biomass and limestone were continuously fed to the reactor since 09:00 h as shown in Figure A.138, the average biomass feeding rate was 287.0 kg/h and the limestone rate 591.5 kg/h. In Figure

A.139, is presented the $CaCO_3$ molar composition of the solid samples taken from the calciner during the test. Regarding the average maximum carrying capacity of the solids, it was 0.264 for this experiment.

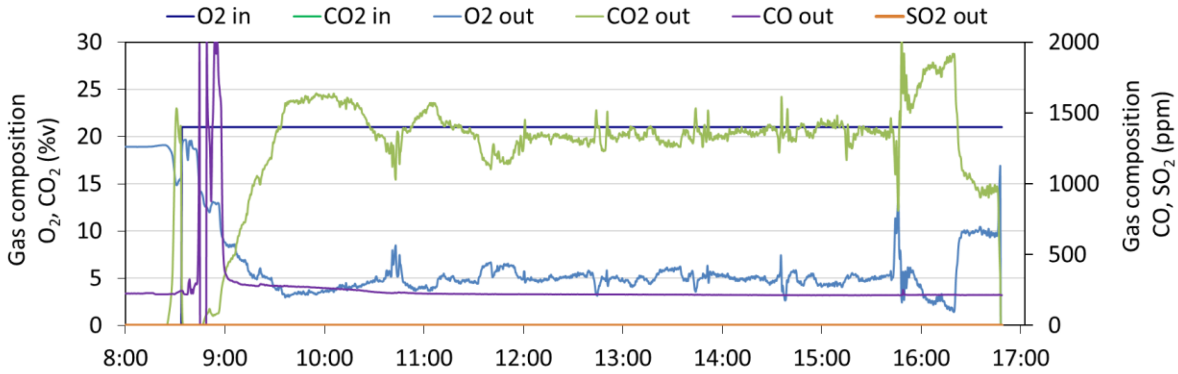


Figure A.136. Inlet and outlet gas composition in the calciner reactor (Experiment 05/07/23).

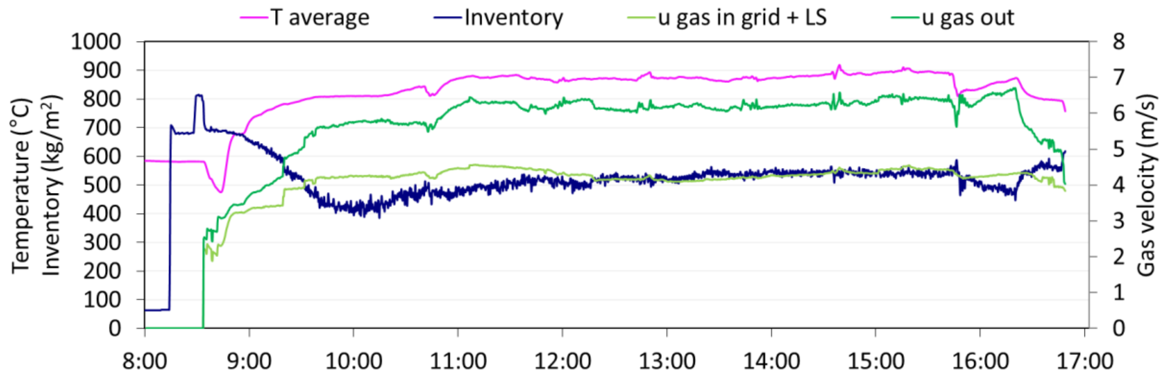


Figure A.137. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 05/07/23).

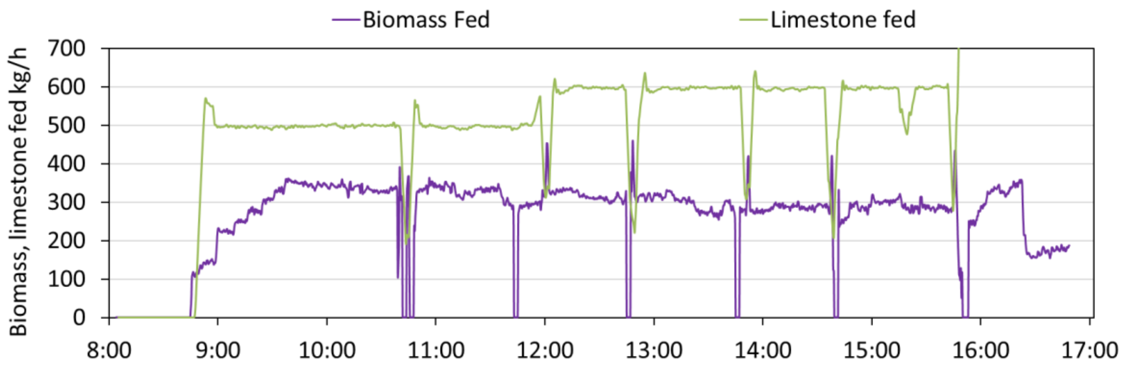
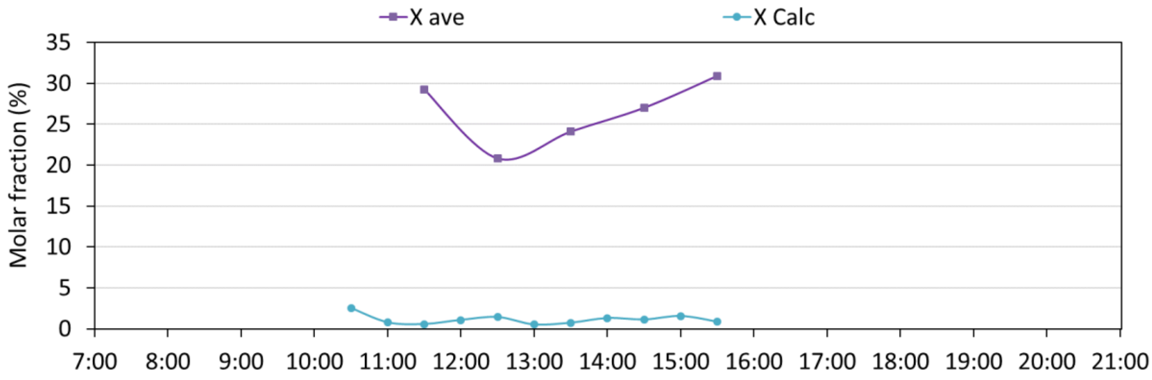


Figure A.138. Biomass and limestone feeding rates (Experiment 05/07/23).

Figure A.139. $CaCO_3$ molar composition of the solids in the calciner (X_{Calc}) and maximum CO_2 carrying capacity of the



solids in the calciner reactor (X_{ave}) (Experiment 05/07/23).

Oxy-calcination experiment 25/07/2023

For this test, as shown in Figure A.140, the calciner was operated under oxy-combustion conditions, while aiming to maintain the oxygen at the outlet stream of the reactor near a 4 % - 5% range. The average oxygen concentration in the outlet stream was 4.9%, therefore meeting the operational objective. The average temperature in the calciner, is presented in Figure A.141, between 12:00 h and 16:50 h, the average temperature in the dense bed was 907.2 °C while in the upper section of the reactor was 920.8°C. These temperature values are higher compared to those achieved in the air experiments. This is due to the fact that under oxy-combustion conditions the reactor is operated at higher temperatures. The average inventory value between 12:00 h and 16:50 h was 499.1 kg/m^2. Taking a closer look to Figure A.141, it can be noticed at 11:33 h a drop in the inventory due to a blower shutdown when trying to switch to oxy-mode. However, this problem was solved and from 11:40 h to 16:50 h, the calciner was operated in oxy-combustion conditions. Biomass and limestone illustrated in Figure A.142, were continuously fed to the reactor since 09:00 h. The average biomass feeding rate was 270.2 kg/h and the limestone rate 670.5 kg/h. Finally, in Figure A.143, is presented the $CaCO_3$ molar composition of the solid samples taken from the calciner during the test. The average maximum carrying capacity of the solids for this test was 0.241.

Table A.23. Average values of experimental key variables between 12:00 h and 18:00 h

(Experiment 25/07/23)

Calciner data	
T $_{901\ dense\ bed}$ (°C)	907.2
T $_{out\ 906}$ (°C)	920.8
u $_{gas\ in\ grid\ +\ LS}$ (m/s)	3.3/5.1
O_2 $_{in}$ (%)	29.6
O_2 $_{out}$ (%)	4.9
Limestone flow (kg/h)	670.5
Biomass flow (kg/h)	270.2

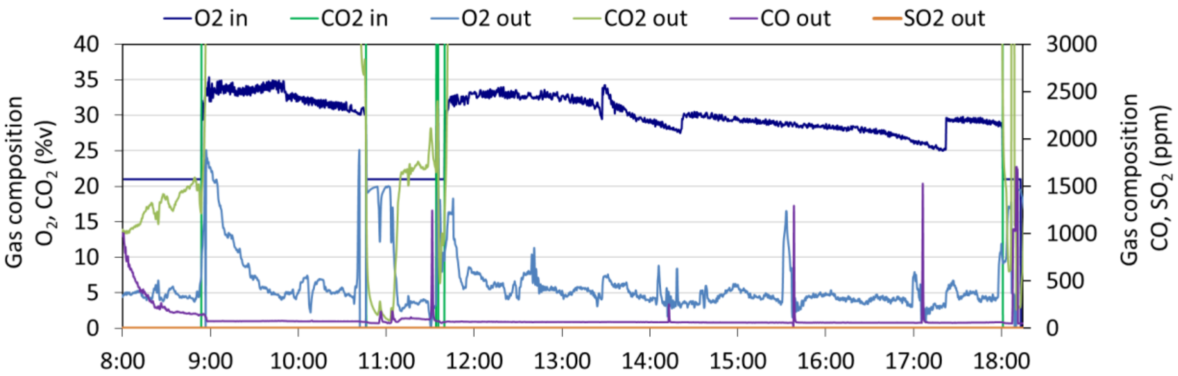


Figure A.140 Inlet and outlet gas composition in the calciner reactor (Experiment 25/07/23).

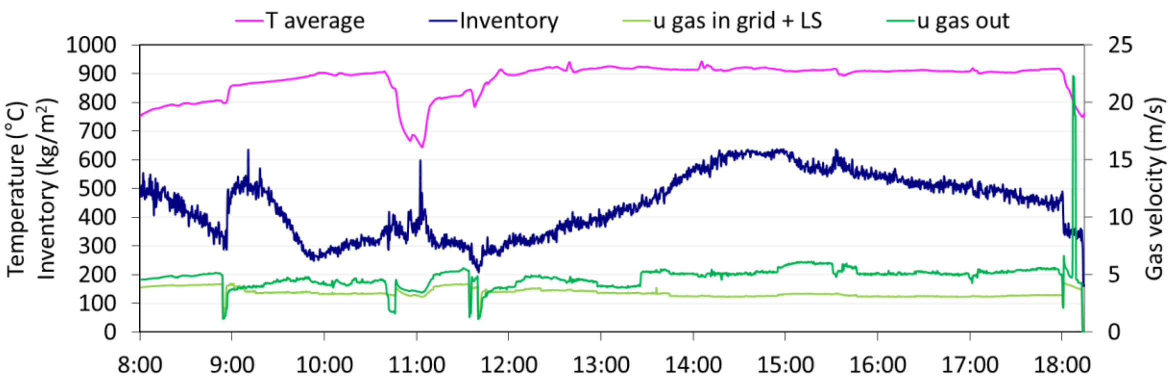


Figure A.141. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 25/07/23).

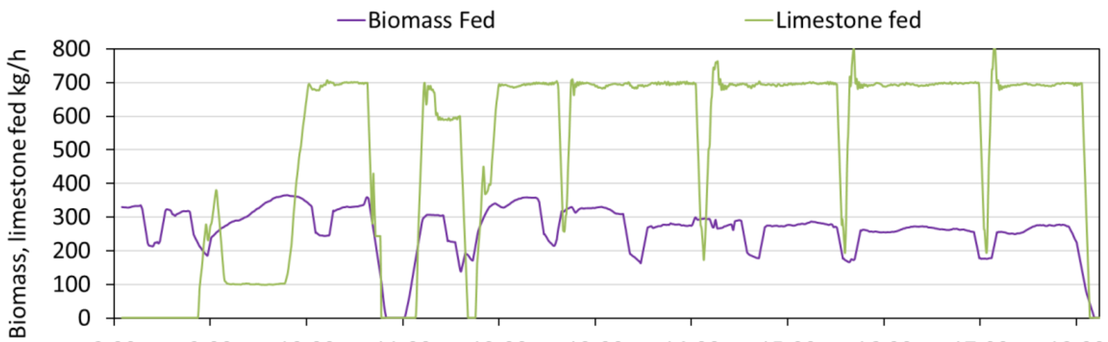


Figure A.142. Biomass and limestone feeding rates (Experiment 25/07/23).

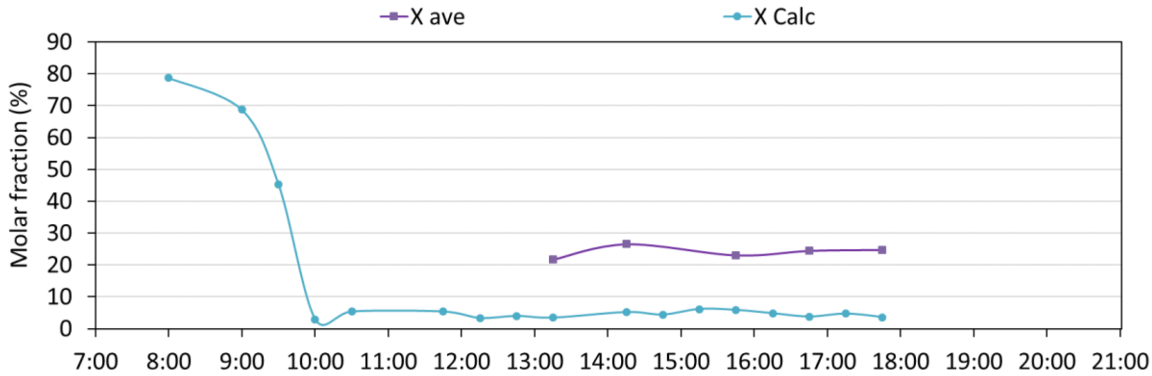


Figure A.143. $CaCO_3$ molar composition of the solids in the calciner (X_{Calc}) and maximum CO_2 carrying capacity of the solids in the calciner reactor (X_{ave}) (Experiment 25/07/23).

Oxy-calcination experiment 26/07/2023

The aim of this experiment was to operate the calciner under oxy-combustion conditions while maintaining a low level of oxygen in the outlet stream of the calciner. As presented in Figure A.144, the reactor operated in oxy-mode from 10:45 h to the end of the experiment, except for short periods between 12:36 h and 12:53 h, 14:25 h and 14:39 h, 15:50 h and 16:10 h, <u>where the reactor was switch to air conditions due to blockages in the feeder system of the solids that was causing operational problems on this day</u>. The average oxygen concentration in the outlet stream was 6.4 %. In Figure A.145, the evolution of the average temperature, inventory and gas velocities are depicted. The average temperature in the dense bed was 853.4 °C while in the upper section 906.6 °C. The average inlet gas velocity was 4.4 m/s and the outlet 7.4 m/s. In regard to the inventory, the average value was 241.7 kg/m^2. Biomass and limestone feeding rates are shown in Figure A.146. The average biomass rate was 275.5 kg/h and the average limestone rate fed to the reactor was 537.5 kg/h. Concerning the solid samples, the $CaCO_3$ molar composition is presented in Figure A.147 and the average maximum carrying capacity was 0.308.

Table A.24. Average values of experimental key variables between 10:45 h and 18:00 h

(Experiment 26/07/23)

Calciner data	
T $_{901\ dense\ bed}$ (°C)	853.4
T $_{out\ 906}$ (°C)	906.6
u $_{gas\ in\ grid\ +\ LS}$ (m/s)	4.4/7.4
$O_{2\ in}$ (%)	26.8
$O_{2\ out}$ (%)	6.4
Limestone flow (kg/h)	537.5
Biomass flow (kg/h)	275.5

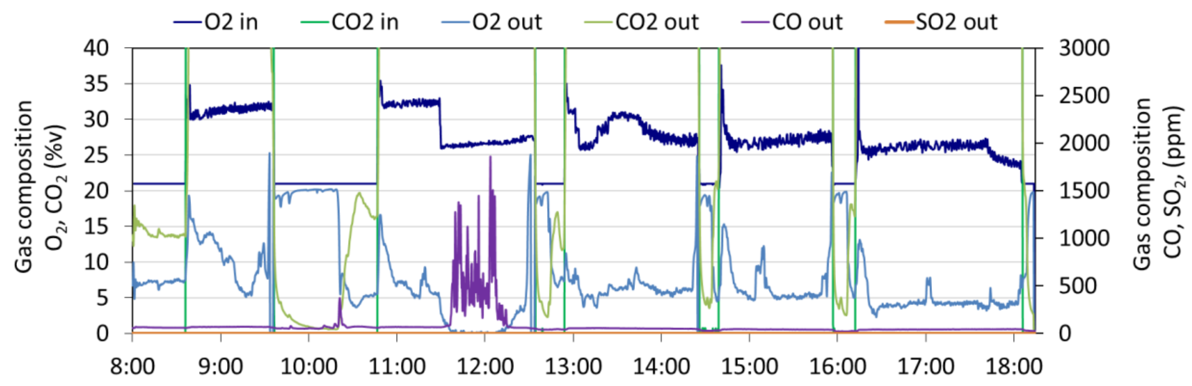


Figure A.144. Inlet and outlet gas composition in the calciner reactor (Experiment 26/07/23).

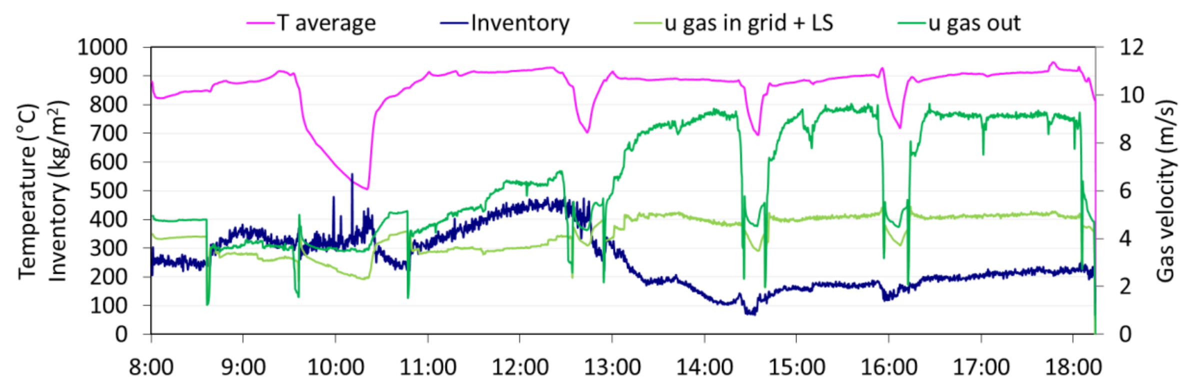


Figure A.145. Average temperature, inventory, inlet and outlet gas velocities in the calciner reactor (Experiment 25/07/23).

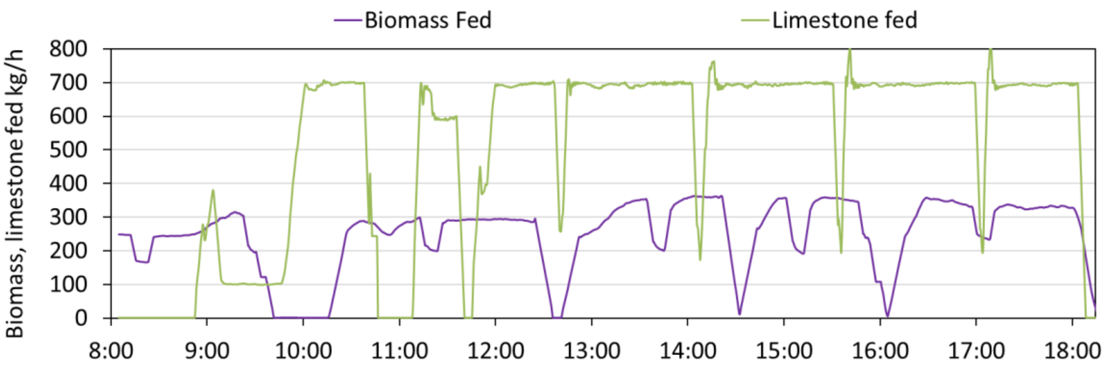


Figure A.146. Biomass and limestone feeding rates (Experiment 26/07/23).

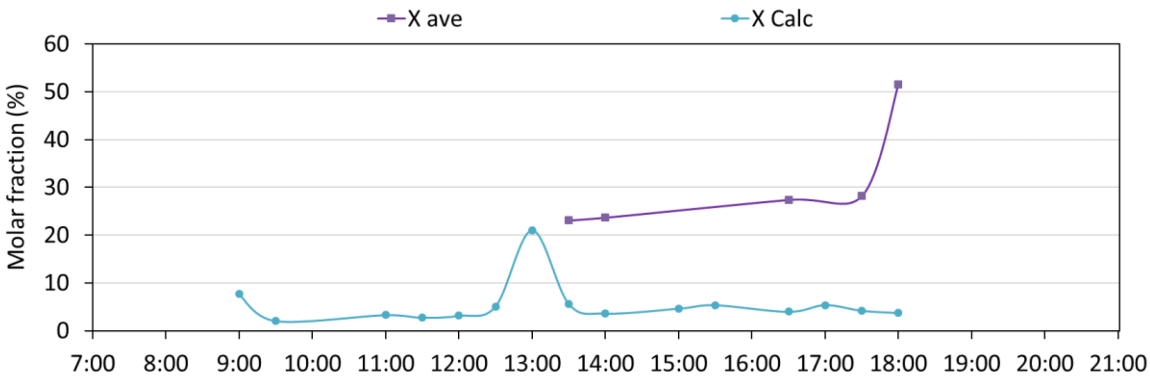


Figure A.147. $CaCO_3$ molar composition of the solids in the calciner (X_{Calc}) and maximum CO_2 carrying capacity of the solids in the calciner reactor (X_{ave}) (Experiment 26/07/23).

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Funded by the European Union under the Horizon Europe Framework Programme (Project name: CaLby2030; grant number: 101075416). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor the granting authority can be held responsible for them.The project is also supported by the UK Research and Innovation (UKRI).