

Biogas upgrading by wood combustion ash accelerated carbonation

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Abstract

Purpose. In this work wood ash, generated by the combustion of wood in a central heating plant, was used to capture CO₂ from simulated biogas, by means of accelerated carbonation. The process was studied in relation to the possibility of removing the CO₂ contained into biogas, with the aim of producing biomethane, i.e. as an alternative to the conventional upgrading technologies available on the market.

Methods. The process was investigated at laboratory scale by setting up a facility for realizing the direct contact between the wood ash and the simulated biogas in a fixed bed reactor.

Results. The process is able to completely capture the CO₂, in its starting phase. After about 30 hours the CO₂ starts to appear again in the exiting stream and rapidly increases. The specific CO₂ uptake is about 200 g/kg of dry wood ash.

Conclusions. The found uptake value is much higher than the values found for bottom ash, in similar experiences, for which the specific CO₂ uptake was in the range of 10-20 g/kg. Presently, further developments are ongoing, related to the use of the results obtained from the experimental phase for evaluating the process from the economic, energy and environmental points of view.

Keywords: biogas, carbon dioxide, biomethane, accelerated carbonation, alkaline residues, wood ash

1. Introduction

Several technologies are available for the upgrading of biogas produced during the anaerobic digestion (AD) of biowaste. The main aim is the gas cleaning from CO₂ with subsequent concentration of CH₄ up to minimum 95-96% in volume to obtain biomethane, which can substitute natural gas by grid injection or/and transport use.

Presently, several processes are commercially available for biogas upgrading [1-3], including absorption by chemical solvents, physical absorption, cryogenic separation, membrane separation and CO₂ fixation by biological or chemical methods [4]. The most commonly applied methods are high pressure water scrubbing (HPWS), amine scrubbing, and pressure swing adsorption (PSA) [5-6]. Generally the upgrading technologies available on the market are economically sustainable only for large plants (>300-500 Nm³/hour of entering biogas), thus the development of low cost solutions devoted to small biogas plants - or for processing the surplus biogas which cannot be converted to power - seems to be a topic of interest.

Among the several possibilities studied worldwide to remove CO₂, accelerated carbonation has been considered an interesting process for Carbon Capture and Storage (CCS) since a long time [7]. In addition to natural rocks, some industrial residues are suitable for capturing CO₂ through accelerated carbonation, thanks to some appropriate characteristics, i.e. calcium and magnesium oxide contents [8]. Bottom Ash (BA) from municipal solid waste incineration was

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already proposed for this purpose with the aim of producing biomethane from landfill gas or biogas [9-15].

In this work the attention is focused on wood ash (WA), generated by the combustion of wood in a central heating plant. The WA accelerated carbonation process was studied in relation to the possibility of removing the CO₂ contained into biogas, with the aim of producing biomethane. The process was first investigated at laboratory scale by setting up a facility for realizing the direct contact between the WA and the simulated biogas in a fixed bed reactor. Presently, further developments are ongoing, related to the use of the results obtained from the experimental phase for evaluating the process from the economic, energy and environmental points of view.

2. Materials and methods

2.1 Experimental setup

The experimental facility mainly consists of the WA fixed bed reactor and the measuring systems.

The WA fixed bed reactor is a 27 l stainless steel cylindrical tank (internal diameter: 26.5 cm, height: 66 cm) (Figure 1a). The reactor can be opened from the top, by means of a semispherical cap, for loading and unloading the WA; the gas seal is ensured by a series of twelve bolts. The gas flows into the reactor from the bottom to the top (upflow configuration). The ashes are located on a drilled plate sustained from a dedicated support and covered by a geotextile fabric which retains the small particles and allows the passage of the gas avoiding the formation of preferential gas paths (Figure 1b). For the external thermal insulation, the reactor's body is provided with a 19 mm insulating material layer (not shown in Figure 1a).

Before the gas flowed into the WA reactor, nitrogen is flushed in order to purge air/O₂ from the reactor [10]. The nitrogen supply is stopped when the oxygen content in the output gas is lower than 0.2% by volume, and then the simulated biogas is fed to the fixed bed reactor.

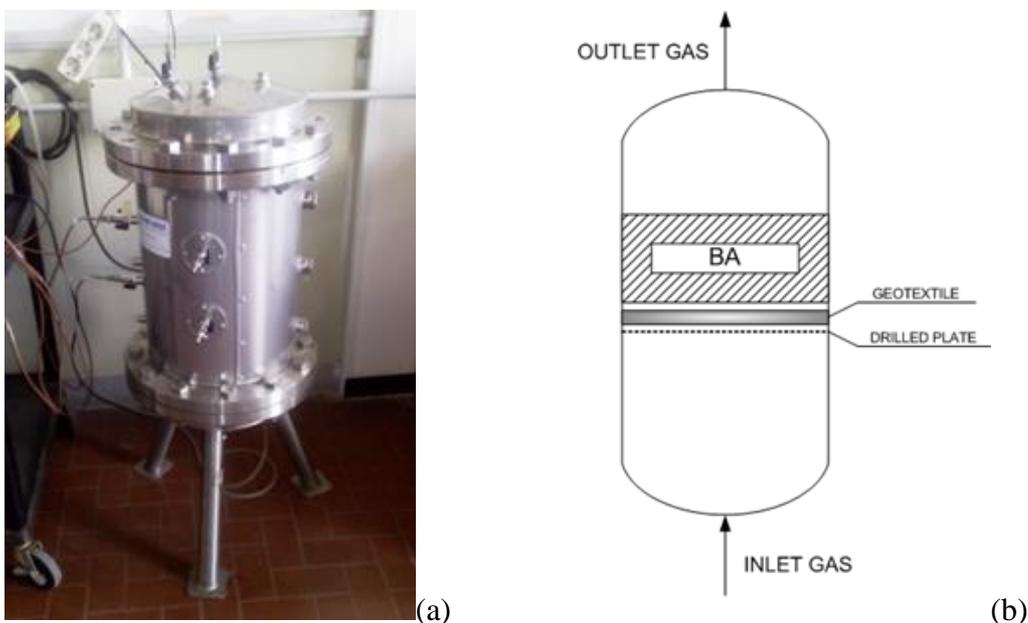


Figure 1. Fixed bed reactor: a) external view, b) schematic view of the internal arrangement.

Input and output gas flow rates to/from the WA fixed bed reactor are measured by means of CKD Small size flow sensors (FSM2-NVF010-S063), able to measure in the range 0-1000 ml/min with accuracy of $\pm 3\%$ f.s. and repeatability $< \pm 1\%$ f.s..

The differential pressure of the input and output gas streams to/from the reactor is measured by a differential piezoresistive pressure transducer (Delta Ohm-HD 408T) able to work in the range from -100 to +2000 mbar relative to the atmospheric pressure with accuracy of $\pm 0.5\%$ f.s. at 20°C.

Atmospheric pressure is measured by means of a barometric pressure transducer (Delta Ohm HD 9908 BARO) able to work in the range from 700 to 1100 mbar, with accuracy of ± 0.5 mbar at 20°C and resolution 1 mbar.

The inlet/outlet gas temperature and the temperature inside the reactor are measured by electronic thermocouples, produced by T.C. Direct (T405-125, T405-128), able to measure in the range da -50 a +150°C with precision of ± 0.3 °C and resolution 0.0001 °C.

The inlet and outlet gas flows pass through two cylindrical settling chambers (diameter: 15 cm, height: 16 cm) where the above parameters are measured.

The gas flow rate, pressure and temperature are measured at a sampling rate of 1 khz, the average of the measured values is registered every 10 minutes. The measurement instruments are controlled by a programmable automation controller NI-USB 6008 National Instruments with 8 analog inputs (12-bit, 10 kS/s); 2 analog outputs (12 bit, 150 S/s); 12 I/O digital; 1 counter 32 bit; programming software Labview 10.0.

Additionally the CO₂ volumetric concentration in the gas flow at the reactor exit was measured every 30 minutes by means of a portable gas analyzer (PGD3-IR - ENMET Corporation), able to reveal CH₄ and CO₂ by infra-red absorption ($\pm 3\%$ absolute accuracy for $>15\%$ vol.) and O₂ by internal electro-chemical cells.

Besides, the experimental facility is equipped with a gas mixing device (Witt-Gasetechnik, MG 50-3ME (Ex) PvDu), able to produce CO₂/CH₄/N₂ gas mixtures of different compositions. The device allows setting the desired volumetric concentration for 5% steps with an accuracy of $\pm 2\%$ abs. For a schematic view of the laboratory facility see Figure 2 (where Q is the gas flow rate; T is the temperature and P is the pressure measured respectively by flow meters, thermocouples and pressure transducers).

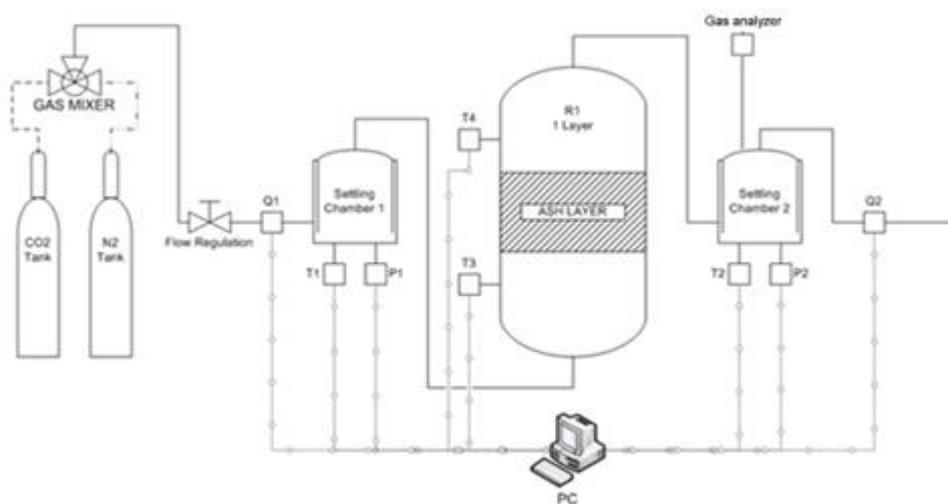


Figure 2. Schematic view of the experimental layout.

WA moisture was measured weighing the sample before and after drying at 105 °C, for 24 hours.

WA pH was measured mixing 10 mg of WA, after drying at 105 °C for 24 hours, with 100 mL of distilled water, according to UNI EN 12457-2, with a liquid/solid ratio equal to 10. Mixing was kept for 24 hours by electromagnetic agitator. The mix was then filtered using Buchner filter with diameter 0.45 µm and a paper filter. The pH was measured in the obtained eluate by a pH-meter.

Moisture and pH were measured for the WA before and after the carbonation process.

2.2 Materials

The WA used in the experiments originated from wood chips combustion in the boiler serving the central heating network supplying heat to the buildings of the Fondazione Edmund Mach in San Michele all'Adige (TN), Italy.

CO₂ and N₂ were provided in gas cylinders by SOL S.p.A. with a purity of respectively 99.999% (Level 5) and 99.9999% (Level 6).

2.3 Experimental tests

Biogas composition was simulated preparing appropriate mixtures of CO₂ and N₂, using the gas mixing device. N₂ was used as a substitute to CH₄ in the laboratory tests for safety reasons. The substitution of CH₄ with N₂, however, does not influence the reliability of the performed tests, since previous experimental results showed that CH₄ does not interact with WA, as well as N₂ does not [10]. The tests were carried out imposing a fixed composition: nitrogen 60% by volume and carbon dioxide 40% by volume. For each test the gas was flowed through the reactor until, in the exiting flow, the CO₂ concentration remained lower than 4% in volume (i.e. in CH₄/CO₂ biogas mixture, CH₄ higher than 96% in vol.).

Two types of moisture conditions for WA (20 and 30% in mass) were set in the tests, as reported in Table 1. Each test was repeated two times, adopting the same value for the specific gas flow/solid ratio through the WA fixed bed - equal to $4 \text{ Nm}^3/(\text{h} \cdot t_{\text{BA}})$ - which resulted as preferable value in previous investigations [10]. The appropriate amount of WA was loaded in the reactor after moisturizing. WA as received moisture was measured resulting 2% in mass. On this basis, we calculated the amount of water to be added to reach target moisture content of about 20 and 30% in mass, as two possible conditions. After the water addition, the moisture was measured again and effective obtained values are reported in the results section. The amount of moisturized WA placed into the reactor for each test was equal to 6 kg. To keep the target specific gas flow/solid ratio equal to $4 \text{ Nm}^3/(\text{h} \cdot t_{\text{BA}})$, the entering gas flow rate must be kept at 24 NL/h. However, the gas flow rate was not completely steady during the tests, with average values of entering gas flow rate generally higher than the target one, as reported in the results section.

The laboratory tests were carried out during the day for about 10-12 consecutive hours. At the time of facility closure, the tests were stopped, meaning stopping the inlet gas flow rate, closing the entrance and the exit of the reactor and stopping the acquisition system. Then the tests were started again the following morning.

Table 1. Main target conditions of the experimental tests.

Test	Gas composition		WA [kg]	WA moisture [% mass]	Gas flow rate [NI/h]
	CO ₂ [% v/v]	N ₂ [% v/v]			
WA_m20_i WA_m20_ii	40	60	6	20	24
WA_30_i WA_30_ii	40	60	6	30	24

The amount of captured CO₂ was estimated by means of a mass balance, i.e. from the difference between the entering and the exiting volume of gas, at a given time of the experiment, since the captured gas is only CO₂. Thus the results are obtained by using the equation 2:

$$CO_{2,Captured} = \frac{(V_{IN,t} - V_{OUT,t})}{V_m} * M_{CO_2} \quad (2)$$

Where: $V_{IN,t}$ is the volume of the gas flowed in, at the time t (reported at normal conditions of pressure = 101325 Pa and temperature = 273 K; expressed in Nm³); $V_{OUT,t}$ is the volume of the gas flowed out at the time t (expressed in Nm³); V_m is the volume of a kmol of ideal gas at normal conditions (equal to 22.414 Nm³/kmol); M_{CO_2} is the CO₂ molar weight (equal to 44 kg/kmol). $CO_{2,captured}$ is the mass of captured CO₂ at a given time and it is expressed in kg.

3. Results and discussion

The main results of the experimental tests are reported in following.

Fig. 3 shows the trends of the measured CO₂ volumetric concentration at the exit of the reactor, plotted against the time of the experiments, for tests at respectively 20 and 30% of moisture.

The process is able to completely capture the CO₂, in its starting phase, as already observed in previous experimental tests with other types of alkaline residues [10-15]. As more gas flows through the WA fixed bed, CO₂ concentration in the exiting stream progressively starts to increase, due to the fact that the solid loading capacity is gradually reduced with time. After about 30 hours the CO₂ starts to appear again in the exiting stream and rapidly increases. If the aim of CO₂ capturing is producing biomethane, a maximum of 4% in vol. CO₂ at the exit is acceptable. However, if one likes to process more gas, the gas flow should be stopped, the WA in the fixed bed should be replaced with a new amount and the gas flow should be started again.

Test WA_m20_ii was stopped before the CO₂ increase over 4% in vol. in the exiting stream could be observed, because of external time constraints.

Table 2 reports the average values of the measured entering volumetric flow rate of gas for each test. The target value for this stream was originally set at 24 NI/h, corresponding to a specific flow rate equal to 4 Nm³/(h·t_{BA}), but the measured average values resulted higher and in the range of 23-24 NI/h, corresponding to a specific flow rate equal to 3.5-4 Nm³/(h·t_{BA}). Similarly, also the entering gas composition was not really constant and the measured CO₂ volumetric concentration average values resulted 41-45 % in vol.

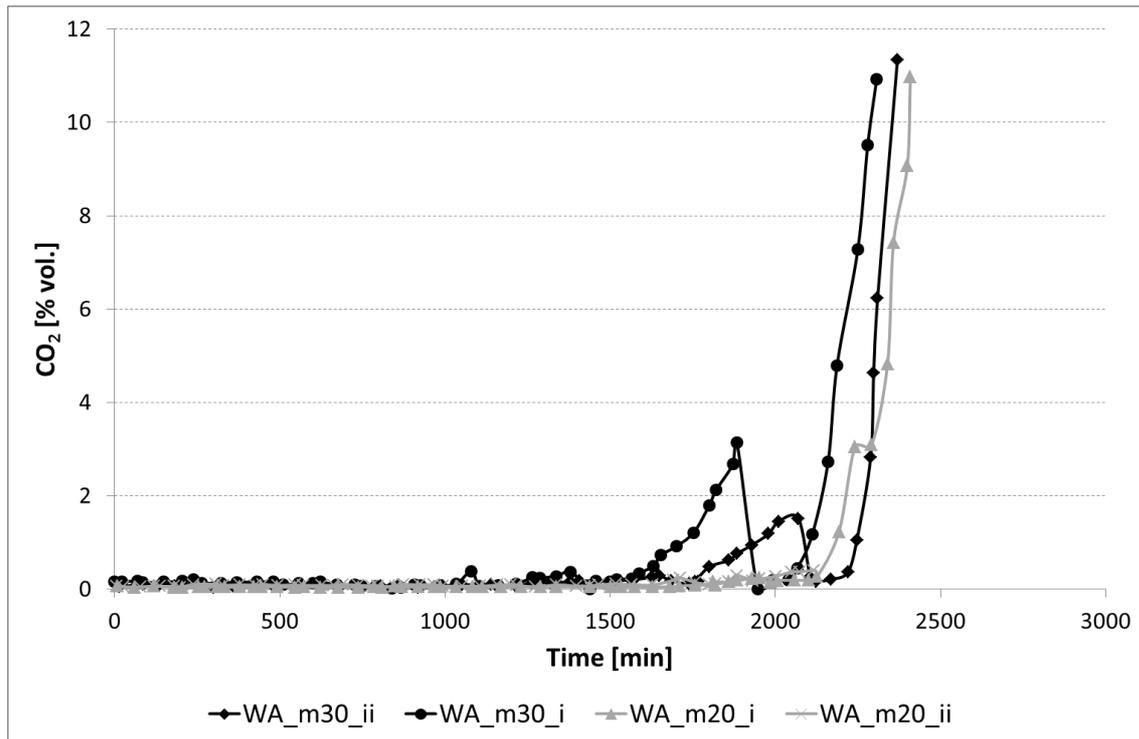


Figure 3. Measured CO₂ volumetric concentration at the exit of the reactor, plotted against the time of the experiments, for tests at respectively 20 and 30% moisture.

Table 2. Average values of the measured entering volumetric flow rate of gas for each test and the corresponding obtained specific flow rate.

Test		Mean entering flow rate [Nm ³ /h]	Mean entering CO ₂ concentration [% vol.]	Specific flow rate [Nm ³ /(h·t _{BA})]
WA_m20	WA_m20_i	23.24	44.06	3.9
	WA_m20_ii	23.83	45.42	4.0
WA_m30	WA_30_i	23.22	41.10	3.9
	WA_30_ii	22.97	43.91	3.5

Table 3 reports the value of the time, the processed volume, the WA specific requirement (expressed in kg/Nm³ of entering volume) and the specific CO₂ uptake per unit of mass of WA, for each test, at the condition of 4% of CO₂ in the exiting gas.

To compare the two different moisture conditions we report in Fig. 4 the calculated specific CO₂ uptake per unit of mass of dry WA for the four tests, plotted against the cumulative entering volume of simulated biogas. Since the CO₂ concentration in the entering flow was not really steady, i.e. different amount of CO₂ came into contact with WA, we plotted also the calculated specific CO₂ uptake per unit of mass of dry WA for the four tests, against the cumulative entering volume of CO₂ in Fig.5. From Fig. 4 and 5 it appears that the tests with higher moisture reached a slightly higher uptake of CO₂, which is more than 200 g/kg of dry WA.

Thus, even if with slight difference, working with higher moisture allows better performance of the process from CO₂ capture point of view. However, when thinking to a possible process on industrial scale, we should consider that higher the moisture, the higher the water request and weight of the WA at the exit of the process, which is directly linked to the eventual further disposal costs.

Table 3. Time duration of the process, volume of processed gas, WA specific requirement and specific CO₂ uptake per unit of mass of WA. Parameters calculated at the time when the CO₂ reached 4% in volume in the exiting stream.

Test		Time [min]	Volume of processed gas [NI]	Wet WA specific requirement [kg/Nm ³]	Specific CO ₂ uptake [kg _{CO2} /kg _{WA}]
WA_m20	WA_m20_i	2230	864	6.9	205
	WA_m20_ii	-	-	-	-
WA_m30	WA_30_i	2170	845	7.1	201
	WA_30_ii	2290	877	6.8	216

Table 4. Measured moisture and pH.

Test		Initial moisture [% mass]	Final moisture [% mass]	Initial pH	Final pH
WA_m20	WA_m20_i	19.79	19.82	14.49	13.02
	WA_m20_ii	18.40	18.90	14.49	13.43
WA_m30	WA_30_i	29.31	29.99	14.49	13.26
	WA_30_ii	28.85	29.30	14.49	12.80

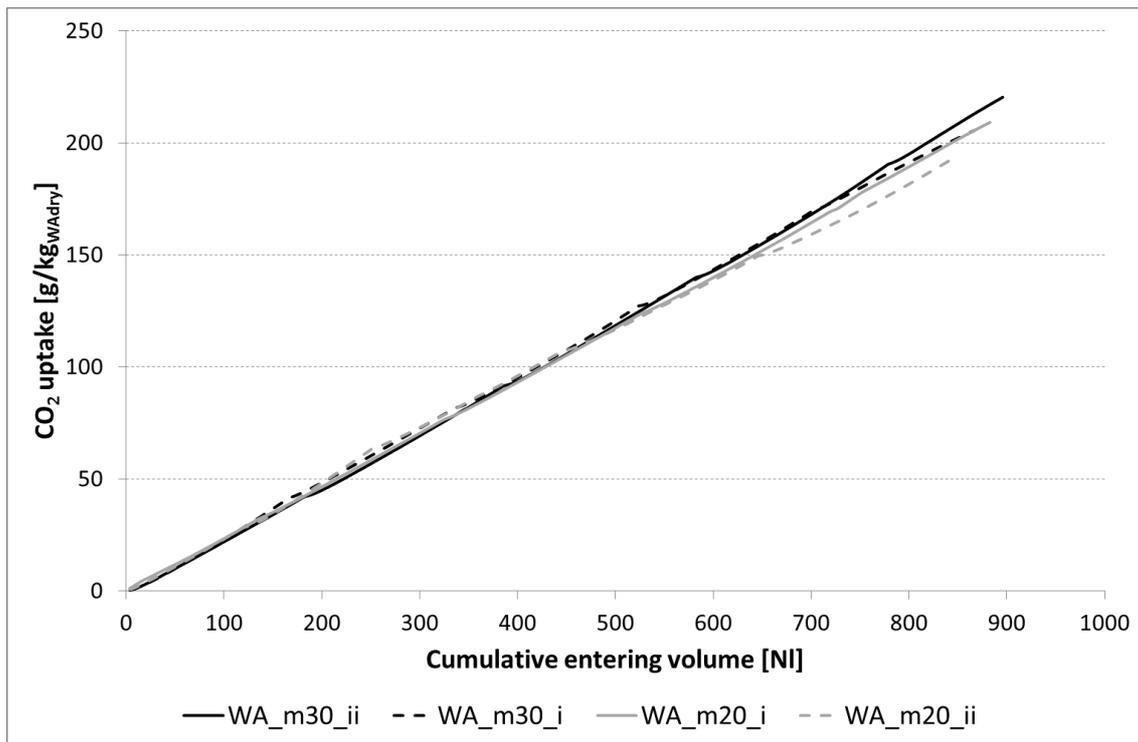


Figure 4. Calculated specific CO₂ uptake per dry unit of mass of WA, plotted against the entering volume of gas into the reactor, for tests at respectively 20 and 30% moisture.

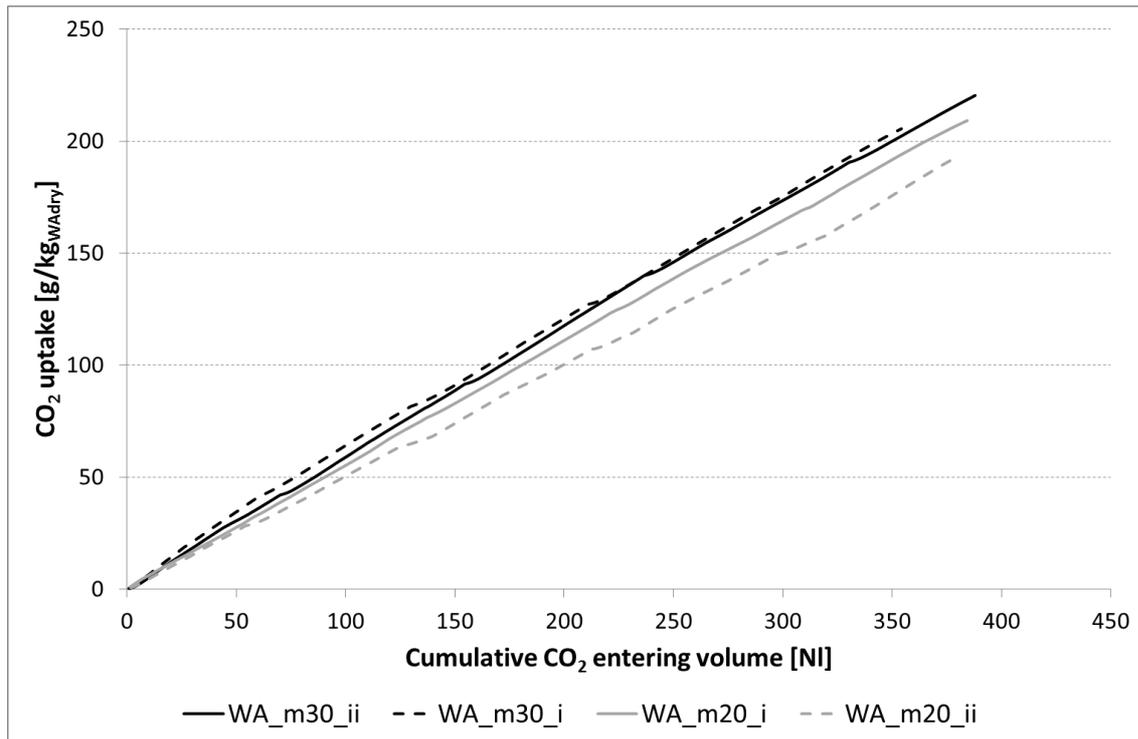


Figure 5. Calculated specific CO₂ uptake per dry unit of mass of WA, plotted against the entering volume of CO₂ into the reactor, for tests at respectively 20 and 30% moisture.

It is worth to make a preliminary comparison with the same type of results obtained in previous experiment using a different type of alkaline solid residues, that BA.

In the case of using pure CO₂ as entering gas – after flowing about 150-200 NI of entering pure CO₂, the specific uptake was about 20-40 g/kg of BA [12]. In that case, average BA moisture was about 30%, thus the specific uptake per unit of mass of dry BA is about 27-57 g/kg of BA. This is not directly comparable with the present results. However, from Fig. 5, we can estimate that after flowing about 200 NI of CO₂ through the reactor, the uptake is about 100-120 g/kg of dry WA, much higher than the BA case. We should also consider that in the BA case experiment, the use of pure CO₂ stream is a better conditions for the reaction to take place (i.e. higher CO₂ partial pressure), with respect to the 40-45% vol. concentration. We can also observe that, in the BA experiments, after flowing about 150-200 NI of entering pure CO₂, the specific uptake curve starts to be quite flat (thus a significative increase in the uptake is not expected for more CO₂ flowing through the reactor).

Direct comparison can be made with another previous experience using BA, in this case in a pilot reactor fed with real landfill gas [10]: in this case the CO₂ specific uptake was 10.2–22.9 g CO₂/kg_{BA}, which is definitely lower than the WA uptake obtained in this study.

4. Conclusions

In this study a simple process of direct contact – in a fixed bed reactor - between wood ash and simulated biogas was investigated at laboratory scale. The aim was to capture the CO₂ contained into the simulated biogas, to reduce its content at level acceptable for biomethane (i.e. CO₂ lower than 4% in vol. and CH₄ higher than 96% in vol.). The process is able to completely capture the CO₂, in its starting phase. As more gas flows through the wood ash fixed bed, CO₂

concentration in the exiting stream progressively starts to increase, due to the fact that the solid loading capacity is gradually reduced with time. After about 30 hours the CO₂ starts to appear again in the exiting stream and rapidly increases. When the tests were stopped, according to the criteria of CO₂ at the exit higher than 4% in vol. the specific CO₂ uptake was about 200 g/kg of dry WA. This is much higher than the values found for another type of alkaline solid residues, previously investigated, that is bottom ash, for which the specific CO₂ uptake was in the range of 10-20 g/kg.

Presently additional laboratory tests are ongoing. At the same time a preliminary sizing for a hypothetical industrial plant is under development, with the aim of performing an economic analysis of the treatment cost, in order to compare with conventional upgrading technologies. Life cycle assessment of the process and its comparison with conventional processes is under development as well.

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