

Study on the effects of using a carbon dioxide atmosphere on the properties of vine shoots-derived biochar

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HIGHLIGHTS

- Using CO₂ instead of N₂ did not result in any decrease in the yield of biochar.
- Biochars had similar fixed-carbon contents and molar H:C and O:C ratios.
- The yield of CO significantly increased at the expense of the yield of produced CO₂.

ABSTRACT

This study analyzes the effects of using a different atmosphere (pure N₂ or pure CO₂) at two levels of absolute pressure (0.1 and 1.1 MPa) on the pyrolysis of vine shoots at a constant peak temperature of 600 °C. Recycling CO₂ from residual flue gases into the pyrolysis process may be economically beneficial, since CO₂ can replace the use of an expensive N₂ environment. In addition, the use of a moderate pressure (e.g., 1.1 MPa) can result in higher carbonization efficiencies and an improvement in the pyrolysis gas (in terms of yield and composition). Results from our study suggest that the use of CO₂ instead of N₂ as pyrolysis environment led to similar carbonization efficiencies (i.e., fixed-carbon yields) and mass yields of biochar. The chemical properties related to the potential stability of biochar (i.e., fixed-carbon content and molar H:C and O:C ratios) were very similar for both pyrolysis atmospheres. Under an atmosphere of CO₂, the yield of produced CO₂ was drastically decreased at the expense of an increase in the yield of CO, probably as a consequence of the promotion of the reverse Boudouard reaction, especially at high pressure. The enhanced reverse Boudouard reaction can also explain the relatively high BET specific surface area and the macro-porosity development observed for the biochar produced under a CO₂ environment at 1.1 MPa. In summary, the pressurized pyrolysis of biomass under an atmosphere of CO₂ appears as a very interesting route to produce highly stable and porous biochars and simultaneously improving the yield of CO.

KEYWORDS

Vine shoots; Pyrolysis; Biochar; CO₂ Atmosphere; Pressure

1. Introduction

The Mediterranean basin countries generate a large amount of vineyard pruning residues (vine shoots and leaves). In 2015, almost 968 kha were cultivated with vineyards in Spain [1]. Considering a waste yield of 1.9 ton ha⁻¹ (dry basis) [2], around 1840 thousand tons of vine shoots are harvested per year in Spain. The disposal of vine shoots usually consists in shredding and burying them. However, this current practice can lead to negative effects in the health of vineyards due to the potential risk of increased inoculum [3].

Producing biochar from vine shoots, a residual lignocellulosic biomass from vine pruning, is an interesting pathway to manage this waste and simultaneously generate environmental and agronomic benefits. Among the different thermochemical processes, slow pyrolysis can retain the feedstock carbon in stable biochar with high value-added as a soil-applied carbon sequestering agent [4].

It is well known that the pyrolysis process parameters and the feedstock nature require continuing research because of their influence on the physicochemical properties of the produced biochar [5-7]. One of these parameters to study in depth is the type of pyrolysis atmosphere. In terms of energy efficiency, recycling CO₂ from residual flue gases into the pyrolysis process may be economically beneficial, since CO₂ can replace the use of an expensive N₂ environment leading to important cost savings [8]. For instance, the flue gas generated by combustion of pyrolysis gas and vapors can be used as pyrolysis gas environment. Through this approach, which can be implemented in small-scale and farm-based systems, the production of biochar could significantly be improved in terms of economic feasibility, environmental impact and thermal efficiency. However, research is needed to analyze the effects of modifying the inert environment (i.e., from pure N₂ to a flue gas containing CO₂) on the pyrolysis products' distribution as well as on the biochar properties. Special attention should be paid to those properties that are related to the potential stability of biochar (i.e., carbon sequestration

potential). In this sense, the fixed-carbon content and the molar H:C and O:C ratios appear as useful rough indicators of the stability of biochar [4-7].

Despite the fact that the slow pyrolysis of biomass has been widely studied since many years, the effect of using a moderate pressure (0.5–5.0 MPa) has received relatively little attention. Moreover, the effect of the pressure has usually been measured as a combined effect with the gas residence time. In other words, the gas residence time within the reactor was increased when the pyrolysis system was pressurized. Thus, most of the earlier studies have reported on an increment of the char and gas yields, at the expense of tar (i.e., organic condensable fraction), when both the pressure and gas residence time had been increased [9-13]. Particularly interesting are the results obtained at the Hawaii Natural Energy Institute (University of Hawaii at Manoa, USA), where a Flash Carbonization (FC) system was used to carbonize a number of agricultural residues. Using the FC process, which employs air in a downdraft reactor to force the flame to move upward through the feed, the researchers from the Hawaii Natural Energy Institute have recently reported very high biochar and fixed-carbon yields at pressures of 2.17 MPa [14]. Nevertheless, and coming back to regular pyrolysis systems (i.e., fixed-bed reactors with inert pyrolysis environments), other studies have found a negligible or even negative effect of the pressure on the yield of char [15-20]. It is interesting to point out that two of these works [19, 20] have analyzed the effect of the pressure when the residence time of the inert gas (N₂) within the pyrolysis reactor was kept constant. Qian et al. [20] observed for the pyrolysis of rice husk (at a peak temperature of 700 °C in a fixed-bed reactor) that the yields of char and gas increased with elevating the pressure from 0.1 to 1.0 MPa at the expense of a reduction in the tar yield; nevertheless, these effects became insignificant when the pressure was further elevated from 1.0 to 5.0 MPa. Manyà et al. [19] reported on a statistically significantly decreased yield of char when the pressure was increased from 0.1 to 1.0 MPa during the pyrolysis of two-phase olive mill waste in a lab-scale fixed-bed reactor at a peak temperature in the range of 400–600 °C. A possible explanation for this finding could be that an increased pressure could enhance the

kinetics of the steam gasification reaction. In any case, serious doubts still exist about the intrinsic effect of the pressure on the yields of the pyrolysis products.

The specific aim of this study is to investigate the effects of using a different atmosphere (100% N₂ and 100% CO₂) at two levels of absolute pressure (0.1 and 1.1 MPa) and at a constant peak temperature of 600 °C on the yield of biochar and its properties (especially those related to the potential stability). The gas residence time within the pyrolysis reactor was kept constant by adjusting the mass flow rate at NTP conditions of the pressurizing agent (i.e., N₂ or CO₂). The composition of the pyrolysis gas was also determined and compared in order to establish the influence of the tested operating conditions.

2. Material and methods

2.1. Materials

The used vine shoots (VS) were supplied by a winery located in the Spanish region of Aragon. The as-received VS (with particle sizes in the range of 0.1–1.0 cm diameter and 1.0–3.5 cm long) were pyrolyzed without using any additional milling and sieving step. The reason for such choice in particle size is that the efficiency of carbonization can be improved for large particles as compared with small, leading to charcoals with higher fixed-carbon contents [7, 21]. This is related to the major role of the secondary charring reactions that occurred at the intra-particle level. In other words, increasing the particle size is a means to extend the contact time between the volatile species with the solid in the interior of the particle, leading to an increase in the fixed-carbon content and a decrease in the molar H:C and O:C ratios of the produced char. In addition, processing relatively large particles of biomass in industrial-scale slow pyrolysis systems can lead to considerable savings on the costs of biomass pretreatment.

Proximate analyses were performed in quadruplicate according to ASTM standards (D3173 for moisture, D3174 for ash, and D3175 for volatile matter), whereas elemental analyses were carried out using a Leco TruSpec Micro CHNS analyzer (Leco Corporation, USA). Moreover, an

ADVANT'XP+ XRF spectrometer (Thermo ARL, Switzerland) was used to measure the ash composition on the basis of the weight fractions of the equivalent oxides (according to ASTM standard D4326-04). Table 1 lists the results from the above-mentioned analyses.

2.2. Experimental system

Pyrolysis experiments under both CO₂ and N₂ atmospheres and at 0.1 and 1.1 MPa were conducted by triplicate using a fixed-bed reactor that was operated at a peak temperature of 600 °C, since we observed in a previous study [7] that, for peak temperatures ranging from 400 to 600 °C, operating at the highest temperature led to the highest percentages of aromatic carbon in biochar as well as the lowest molar H:C and O:C ratios (i.e., highest potential stability of produced biochar). The pyrolysis device consists of a cylindrical and vertical reactor (140 mm ID; 465 mm long) made of Sandvik 253 MA™ stainless steel and heated by two electric resistances of 2.1 kW with proportional integral derivative (PID) temperature control. The total volume was 6 L and a basket of 4 L made of Monel™ alloy was used to put the biomass into the reactor. 400 g of feedstock was used per test, which represents around 90 % of the basket volume with a bed height of around 350 mm. The temperature inside of the bed was measured using four thermocouples placed into a thermowell in different heights, three in contact with the bed (bottom, middle and top) and one in the freeboard (see Figure S1 of the Supplementary Information for further details). During the experiments, the sample was heated at an average heating rate of 5 °C·min⁻¹ up to the peak temperature (600 °C) with a soaking time of 60 min at this temperature. A back pressure regulator was used to maintain the pressure of the system at a desired value. The produced gas passed through a heated line, maintained at a temperature of around 280 °C, before being passed through a series of two glass traps that were immersed in ice-water baths. A schematic diagram of the whole experimental set-up is shown in Fig. 1.

The mass flow rate at NTP conditions of the carrier gas (N₂ or CO₂) was adjusted as a function of the absolute pressure (0.1–1.1 MPa) to keep the real flow rate of nitrogen or carbon dioxide within the reactor (at 600 °C) at a constant value of 1.85 L min⁻¹. After each experiment,

the biochar present in the reactor was collected and weighed. The pyrolysis liquid was recovered directly from the condensers without using any solvent as wash liquid. The glass traps were weighted before and after each pyrolysis run to estimate the total mass of liquid. The composition of the major components in the pyrolysis gas (N₂, CO₂, CO, CH₄, C₂H_x and H₂) was determined using a Varian micro gas chromatograph (model CP-4900) equipped with two analytical columns: a Molsieve 5A (using argon as carrier gas) and a PolarPlot Q (using helium as carrier gas).

2.3. Characterization of the pyrolysis products

The mass yields of biochar, liquid (including produced water) and produced gas (y_{char} , y_{liq} and y_{gas} , respectively) were calculated in a dry-ash-free (daf) basis. The biochars were characterized by proximate and elemental composition analyses according to the same procedures described in section 2.1. The fixed-carbon yield (y_{FC}) was used to measure the carbonization efficiency, according to earlier studies [6, 11]. The y_{FC} was calculated as follows:

$$y_{FC} = x_{FC, bc} \cdot y_{char} \cdot \left(\frac{100}{100 - \% \text{ feed ash}} \right) \quad (1)$$

where $x_{FC, bc}$ is the mass fraction of fixed-carbon in the biochar and $\% \text{ feed ash}$ is the percentage ash content of the vine shoots.

The specific surface area of the biochars was analyzed using N₂ physisorption data recorded at a temperature of -196 °C on a TriStar 3000 gas adsorption analyzer (Micromeritics, USA). The surface area (S_{BET}) was calculated using the Brunauer–Emmet–Teller (BET) model from adsorption data obtained at relatively low relative pressures (0.05–0.20).

3. Results and discussion

3.1. Carbonization efficiency and distribution of the pyrolysis products

For the experiments conducted under N₂ (three replicates at 0.1 MPa and three replicates at 1.1 MPa), the mass of produced gas was calculated from the N₂ content in the outlet gas stream, which was used as an internal standard. For these specific runs, the overall mass balances were closed with reasonable accuracy (> 95%). For the pyrolysis runs conducted within CO₂ environment, the mass of produced gas was calculated by difference. The axial temperature profiles are shown in Supplementary Information. Note that the axial temperature gradients were very high for the specific pyrolysis runs conducted under atmospheric pressure (see Figs. S2 and S3). As the pressure was increased, the temperature became more homogeneous along the bed (see Figs S4 and S5), as a consequence of the enhanced convective heat transfer due to the higher N₂ or CO₂ mass flow rate (at NTP conditions) that passed through the reactor. Fig. 2 graphically shows the fixed-carbon yields as well as the normalized mass yields of the three main product fractions (y_{char} , y_{liq} , and y_{gas}).

From Fig. 2a, it can be seen that the fixed-carbon yield was quite constant regardless of the pressure and the pyrolysis environment used. This finding suggests that other operating parameters, such as the peak temperature (which was kept constant at 600 °C in the present study) and the particle size (relatively large particles were used here), could be the main factors affecting the carbonization efficiency. Relatively small differences were also observed for the yield of biochar (see Fig. 2b). For the pyrolysis experiments conducted under a N₂ atmosphere, a slightly decrease in y_{char} was observed when the pressure was increased. According to Manyà et al. [19], this trend could be explained by an enhancement of the kinetics of the steam gasification reaction leading to non-negligible reaction rates, even at relatively low temperatures. An additional explanation for the effect of pressure on the yield of biochar reported here could be the dilution of the pyrolysis volatiles. In this sense, an increase in the mass flow rate of N₂ for pressurized pyrolysis runs led to a reduction of the concentration of volatiles within the reactor,

possibly resulting in a lower extent of secondary charring reactions. The decrease in the yield of biochar with pressure is in disagreement with some previous studies, which have reported on a higher production of biochar when the pressure was increased [9-13] as a consequence of an enhancement of the secondary charring reactions. However, it should be noted that these previous studies were carried out at a constant mass flow rate of inert gas (at NTP conditions) and, thus, the gas residence time increased as the pressure rose. In other words, the reported increases in the char yield could exclusively be explained by the longer times for vapor-solid contact that occurred at high pressure.

Regarding the yields of total liquid, Figs. 2c and 2d indicate that an increase in the absolute pressure, for both pyrolysis environments, led to a decrease in y_{liq} at the expense of an increase in the yield of produced gas. As pointed out by Ragucci et al. [22], the vapor pressure of the precursors of volatiles increases with the absolute pressure, which can result in enhanced cross-linking reactions leading to a higher formation of char and gas at relatively low temperatures. However, at relatively higher temperatures (> 450 °C) the water gasification and the reverse Boudouard reactions (reaction #5 and reverse reaction #2 in Table 2, respectively) can play a non-negligible role at an absolute pressure of 1.1 MPa and taking into account the catalytic effect of the alkali and alkaline earth metallic species (AAEMs), which are inherently present in the feedstock (Table 1 reports a noticeable content of both Ca and K in the biomass ash). As a consequence of the extent of both heterogeneous reactions, a certain amount of biochar, the yield of which was initially favored at high pressure due to the restricted transport of volatiles, could be gasified leading to an additional increase in the yield of produced gas. An additional explanation for the higher production of gas at 1.1 MPa could be that decarboxylation during pyrolysis of both hemicellulose and cellulose was promoted at higher pressure [20].

Fig 2d also shows a certain increase in y_{gas} , for the pyrolysis of vine shoots at 0.1 MPa, when the atmosphere of N_2 was replaced by CO_2 . This increase in the yield of gas was accompanied by a decrease in the yield of biochar, whereas the yield of condensable products was remained

almost constant. Pilon and Lavoie [8] also observed an increase in y_{gas} for the pyrolysis at atmospheric pressure of switchgrass at a peak temperature of 500 °C. Nevertheless, the increase in the yield of gas observed by Pilon and Lavoie was at the expense of a decrease in the yield of liquid. This apparent discrepancy can be explained by several factors, including differences in peak temperature, biomass feedstock, particle size, and reactor configuration. In any case, a certain extent of the reverse Boudouard reaction when CO₂ was used as pyrolysis environment, even at 0.1 MPa, can explain our results.

3.2. Yields of gaseous species

3.2.1. Atmosphere of nitrogen

The cumulative yields of the main gaseous species are shown in Fig. 3. Within an environment of N₂, the yield of CO₂ was clearly enhanced with the increased pressure. This result is in agreement with that reported by Qian et al. [20] for the pressurized pyrolysis of rice husk. According to Qian et al. [20], decarboxylation of both hemicellulose and cellulose are promoted by higher pressure. Table 2 summarizes the main homogeneous (vapor phase) and heterogeneous (solid-vapor phase) reactions that can occur during the release of the produced gas. From a thermodynamics point of view, an increase in the absolute pressure from 0.1 to 1.1 MPa favors the production of CO₂ through reactions #2 and #6. The production of CH₄ via reactions #3, #4 and #6 is also thermodynamically favored by higher pressure. However, for an atmosphere of N₂, the production of methane at 1.1 MPa was just a little bit higher than that at 0.1 MPa as can be seen in Fig. 3. This could indicate that the rates of the methanation reactions were very low. In fact, the yield of CO (which is consumed in reactions #3 and #6) remained almost constant when the pressure was increased from 0.1 to 1.1 MPa. For its part, the yield of H₂ was significantly increased at higher pressure. This finding could be explained by two reasons. First, the rate of the water-gas shift (WGS) reaction (reaction #1 in Table 2) is expected to increase with raising the absolute pressure, as has already been observed by Hla et al. [23].

Second, and as has been stated before, the steam gasification reaction (reaction #5 in Table 2) could be kinetically enhanced at 1.1 MPa leading to an additional formation of H₂ and CO.

3.2.2. Atmosphere of carbon dioxide

For the experiments conducted under an atmosphere of CO₂, the produced CO₂ was calculated by subtracting from the total volume of CO₂ at the outlet the volume fed at the inlet. This approach, which assumes that the CO₂ fed to the system is an inert, allows us to obtain a reasonably good estimate of the yield of produced CO₂. Fig. 3 clearly shows that the yield of CO₂ was substantially lower in the CO₂ environment than in N₂, especially at high pressure. This decrease in the production of CO₂ was accompanied by a proportional increase in the yield of CO. This finding, which was also observed in previous studies [8, 24, 25], could confirm the above-mentioned hypothesis concerning the enhanced reverse Boudouard reaction under an atmosphere of carbon dioxide. Despite the fact that this reaction is an endothermic and very slow process at temperatures lower than 900 °C [26], the presence of Ni from stainless steel material and AAEMs from the feedstock can catalyze the reverse Boudouard reaction at low temperatures. At 1.1 MPa, the rate of the reverse Boudouard reaction can increase further leading to a higher consumption of CO₂, in spite of the thermodynamically favored reactions #2 and #6.

Fig. 3 also shows that the yield of CH₄ was significantly lower in the CO₂ environment than in N₂ at an absolute pressure of 1.1 MPa. In this sense, and as was suggested in earlier studies [8, 25], an enhancement of the dry reforming of CH₄ (reverse reaction #6 in Table 2) due to the high concentration of CO₂ could explain this result. In addition, the atmosphere of CO₂ can lead to a certain promotion of the reverse WGS reaction resulting in a lower production of H₂ (as can be seen in Fig. 3) and an additional production of CO.

From a practical point of view, it is interesting to compare the heating value of the produced gas under different operating conditions. In this respect, Fig. 4 shows the lower heating values of the produced gases (in a basis free of N₂ or CO₂ fed) as a function of the type of atmosphere and

pressure applied. As can be seen in the figure, the gas produced at 1.1 MPa within an environment of CO₂ had the highest heating value.

3.3. The properties of produced biochar

From the data reported in Table 3, it can be deduced that the potential stability (i.e., carbon sequestration potential) of all the biochars produced here is relatively high, given the high values of $x_{FC,bc}$ and the low values of both H:C and O:C ratios [4]. An increase in the absolute pressure led to a slight decrease in the molar H:C ratio, whereas the use of CO₂ instead of N₂ as pyrolysis atmosphere led to similar or even better results concerning the properties related to the potential stability of biochar (i.e., similar $x_{FC,bc}$ values and slightly lower H:C and O:C ratios).

Regarding the BET specific surface area, the results listed in Table 3 indicate that the highest porosity development (in the <2 nm – 50 nm range, that is, micro- and meso-pores) was attained at high pressure and using CO₂ as pyrolysis environment. According to Pilon and Lavoie [8], this result could be attributed to the extent of the reverse Boudouard reaction, which enhances the conversion of carbon leading to a successive emptying of pores. However, it should be pointed out that the technique used to measure the porosity (N₂ physisorption) does not provide any information about pores larger than meso-pore size (i.e., macro-pores). In fact, the SEM images in Fig. 5 revealed the presence of macro-pores in the biochars produced under an environment of CO₂. This macro-porosity development can significantly affect the mobility of biochar in the soil environment and its interaction with water and plants. As has recently been stated by Brewer et al. [27], an accurate characterization of the pore structure and pore size distribution of biochar is still challenging, because the pore sizes of biochars usually range over at least five orders of magnitude.

4. Conclusions

Based on the results presented above, the following conclusions can be drawn:

(1) For the type of biomass feedstock studied here (vine shoots), the use of CO₂ instead of N₂ as pyrolysis environment at a peak temperature of 600 °C resulted in similar carbonization efficiencies (i.e., fixed-carbon yields) and mass yields of biochar. Differences were especially small when the pressure was increased from 0.1 to 1.1 MPa.

(2) The small (in N₂ environment) or negligible (in CO₂ environment) effect of pressure on the yield of biochar, when the residence time of the feed gas was kept constant, seems to confirm that the effect of the vapor residence time within the pyrolysis reactor on the biochar yield is greater than that of pressure. Nevertheless, the dilution of volatiles when the mass flow rate of carrier gas was increased (i.e., pressurized experiments) can play a certain role in inhibiting the secondary charring reactions. Further studies are required to fully clarify this point.

(3) Under an atmosphere of CO₂, the yield of produced CO₂ was drastically decreased at the expense of an increase in the yield of CO. This can be explained by a non-negligible rate of the reverse Boudouard reaction, which was further increased at high pressure leading to a produced gas with high calorific value.

(4) The chemical properties related with the potential stability of biochar (i.e., fixed-carbon content and molar H:C and O:C ratios) were very similar for both pyrolysis atmospheres. In other words, the use of CO₂ as pyrolysis medium did not result in any decrease in the potential stability of produced biochars. Especially interesting was the relatively high BET specific surface area measured for the biochar produced under a CO₂ environment at 1.1 MPa.

(5) In summary, the use of CO₂ as pyrolysis environment instead of an expensive inert gas (N₂) during the pyrolysis of vine shoots is highly interesting for various reasons: (i) to reduce operating costs by replacing N₂ by residual flue gases, (ii) to produce a pyrolysis gas with higher energy recovery potential (especially for pressurized systems), and (iii) to obtain a similar yield

of biochar (as compared to the N₂ environment) with similar chemical properties and probably better porosity.

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Nomenclature

AAEMs = alkali and alkaline Earth metal species

LHV = lower heating value

NTP = normal temperature and pressure conditions (273 K; 101.3 kPa)

S_{BET} = Brunauer–Emmet–Teller specific surface area ($\text{m}^2 \text{g}^{-1}$)

SEM = Scanning Electron Microscopy

VS = vine shoots

WGS = water-gas shift

$x_{FC, bc}$ = mass fraction of fixed-carbon in the biochar

y_{char} = biochar yield in a dry and ash-free basis

y_{FC} = fixed-carbon yield in a dry and ash-free basis

y_{gas} = yield of produced gas in a dry and ash-free basis

y_{liq} = liquid yield in a dry and ash-free basis

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Table 1

Proximate, elemental and XRF analyses of vine shoots

Proximate (wt. %)	
Ash	0.99 ± 0.05
Moisture	7.97 ± 0.68
Volatile matter	68.1 ± 1.19
Fixed carbon	22.9 ± 1.91
Elemental (wt.%, daf basis)	
C	47.1 ± 0.14
H	5.29 ± 0.09
N	0.66 ± 0.05
S	0.56 ± 0.13
O	By difference
Inorganic matter (wt.% of ash) ^a	
CaO	58.3 ± 0.25
K ₂ O	18.4 ± 0.12
MgO	6.66 ± 0.14
SiO ₂	5.73 ± 0.08
Fe ₂ O ₃	3.51 ± 0.11
Al ₂ O ₃	2.57 ± 0.07
P ₂ O ₅	1.24 ± 0.04

^a Only listed components with a composition higher than 1%.

Table 2

Main reactions occurring during the release of the pyrolysis gas

No.	Reaction	ΔG^b (kJ mol ⁻¹)	
		600 °C and 0.1 MPa	600 °C and 1.1 MPa
1	$\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-0.2794	-0.2594
2	$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$	-1.648	-2.675
3	$3\text{H}_2 + \text{CO} \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	12.43	-10.29
4	$\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$	2.758	-14.05
5	$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$	-0.0604	1.486
6	$2\text{H}_2 + 2\text{CO} \rightleftharpoons \text{CO}_2 + \text{CH}_4$	10.99	-26.06

^b Calculated by Aspen Plus 8.8 using Peng-Robinson method and the Equilibrium Reactor (*Requil*) module. The initial concentration in molar fraction of reactants and products was taken equal to $1/n$, where n is the number of species involved.

Table 3

Characteristics of the produced biochars

Conditions	$x_{FC, bc}$	H:C molar ratio	O:C molar ratio	S_{BET} (m ² g ⁻¹)
N ₂ at 0.1 MPa	0.855 ± 0.013	0.401 ± 0.008	0.068 ± 0.008	109.3
CO ₂ at 0.1 MPa	0.861 ± 0.007	0.376 ± 0.021	0.054 ± 0.007	57.4
N ₂ at 1.1 MPa	0.856 ± 0.008	0.306 ± 0.004	0.061 ± 0.008	59.3
CO ₂ at 1.1 MPa	0.864 ± 0.006	0.290 ± 0.005	0.057 ± 0.002	197.0

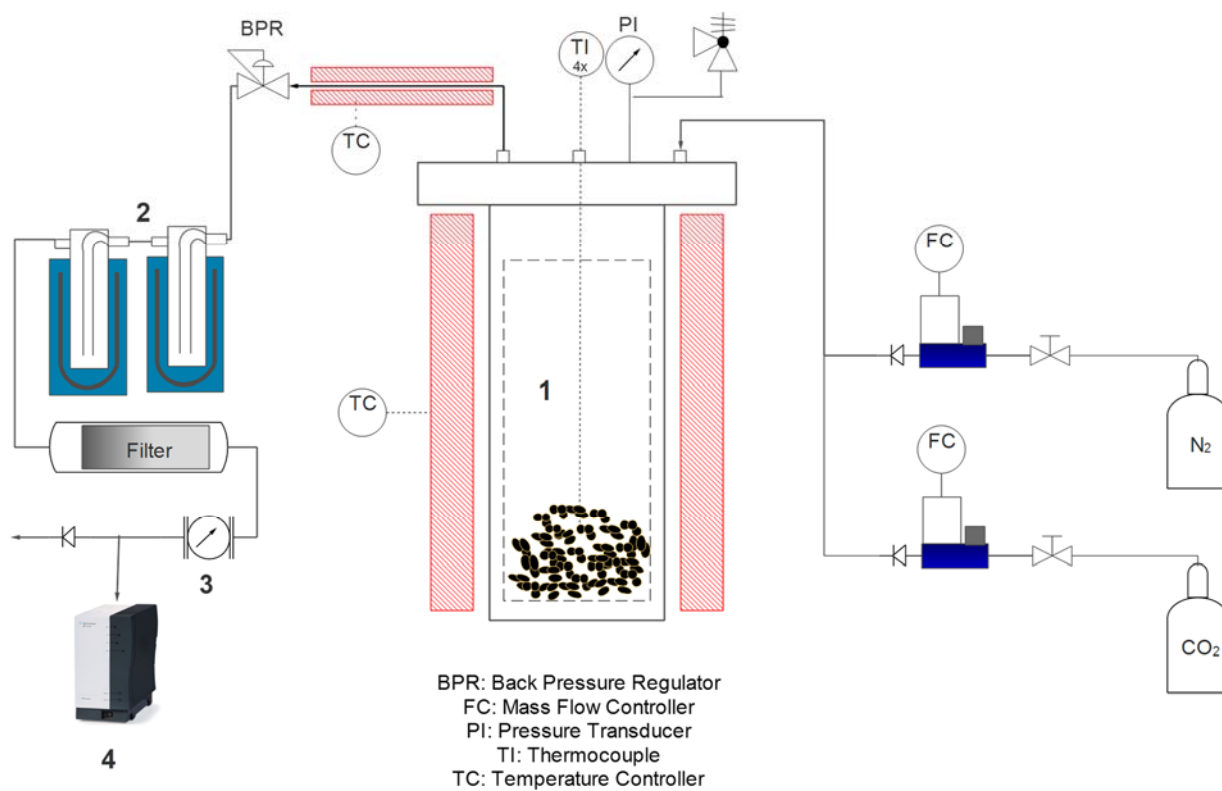


Fig. 1. Schematic layout of the experimental setup: (1) fixed-bed pyrolysis reactor, (2) pyrolysis liquid condensation system, (3) volumetric gas meter and (4) micro-GC.

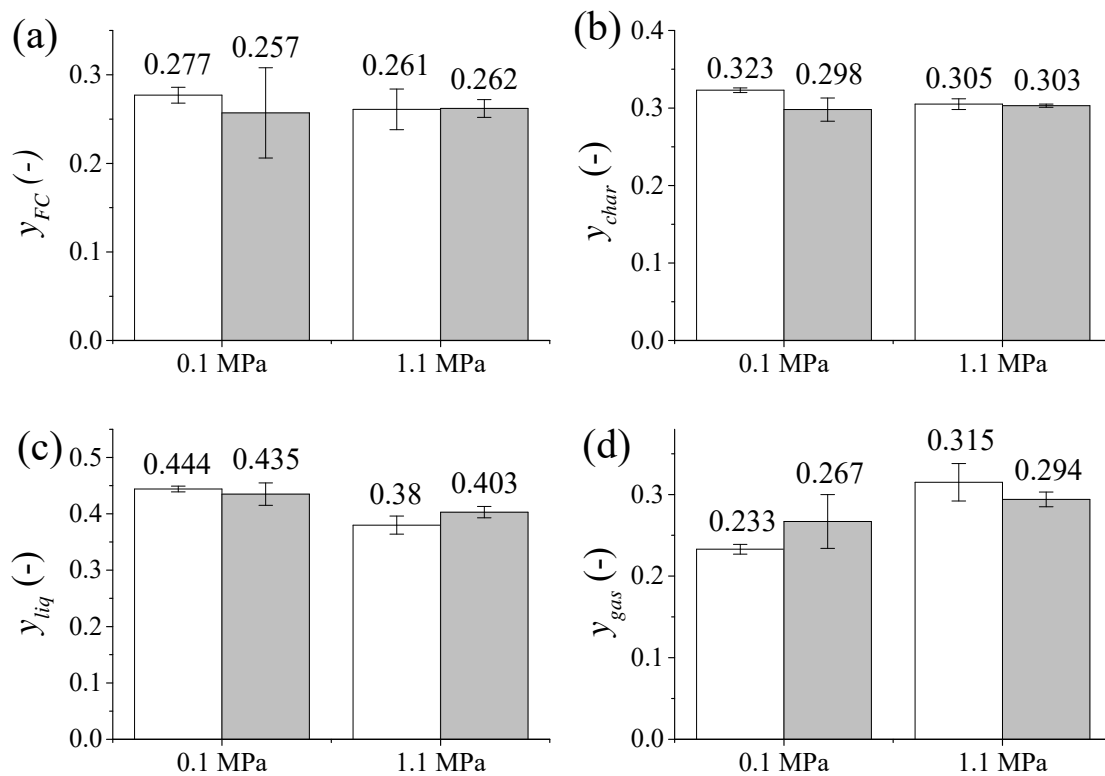


Fig. 2. Fixed-carbon yields (a) and mass yields (in a daf basis) of (b) biochar, (c) liquid, and (d) gas as a function of the pyrolysis atmosphere and pressure. White columns correspond to pyrolysis runs conducted with N₂, whereas light grey columns refer to runs conducted within a CO₂ environment.

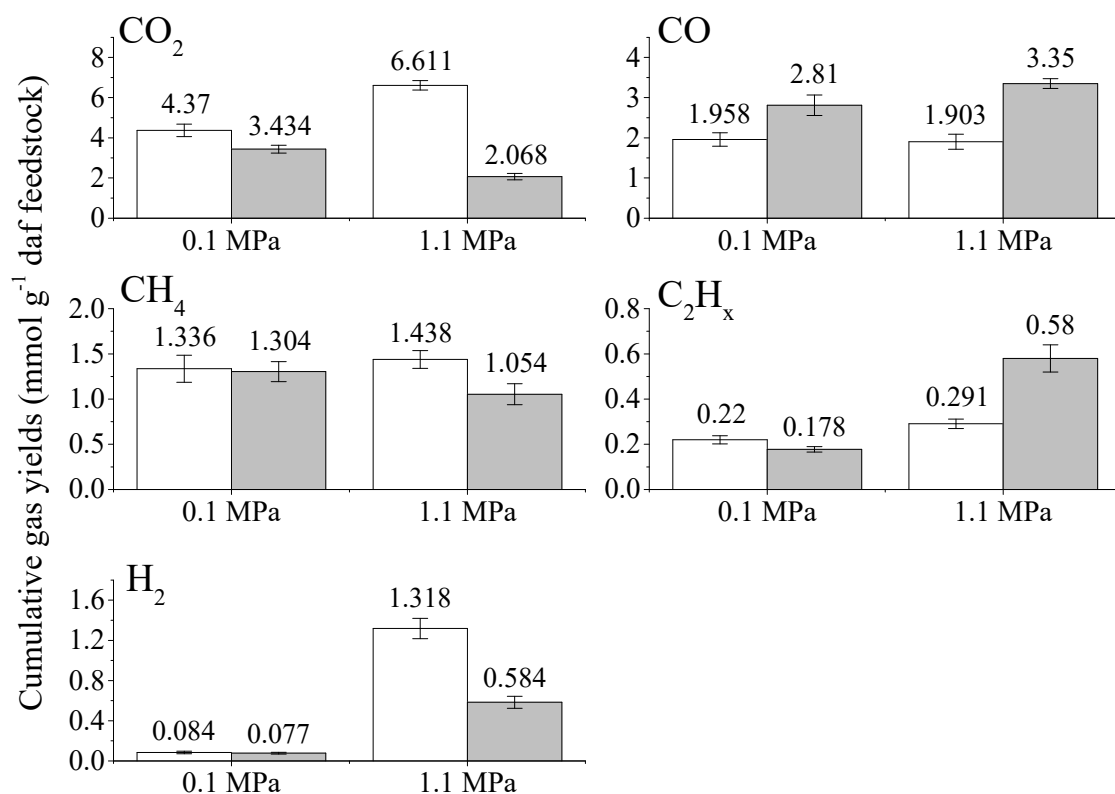


Fig. 3. Cumulative yields of the main gaseous compounds (mmol g⁻¹ of daf feedstock) as a function of the pyrolysis atmosphere and pressure. White columns correspond to pyrolysis runs conducted with N₂, whereas light grey columns refer to runs conducted within a CO₂ environment.

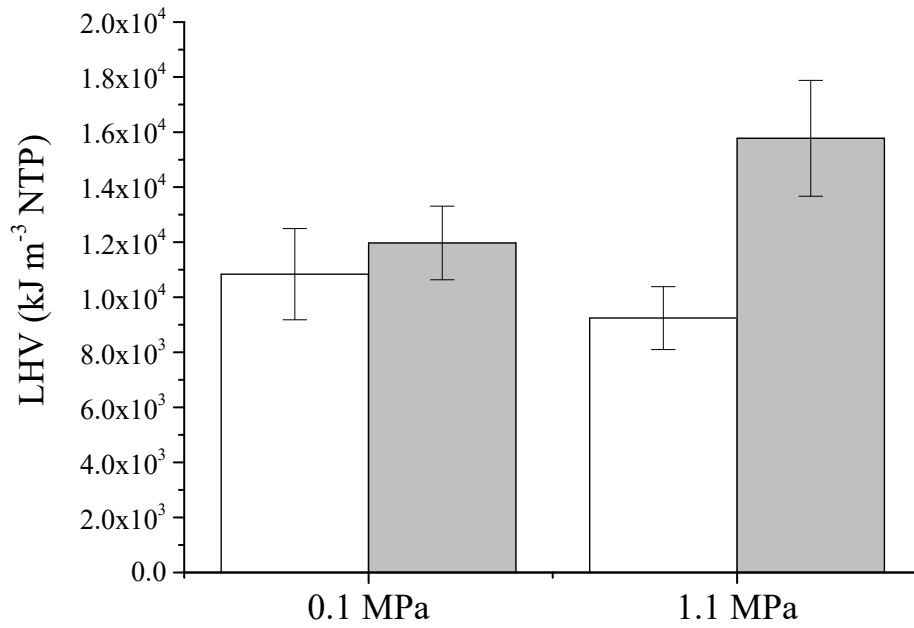
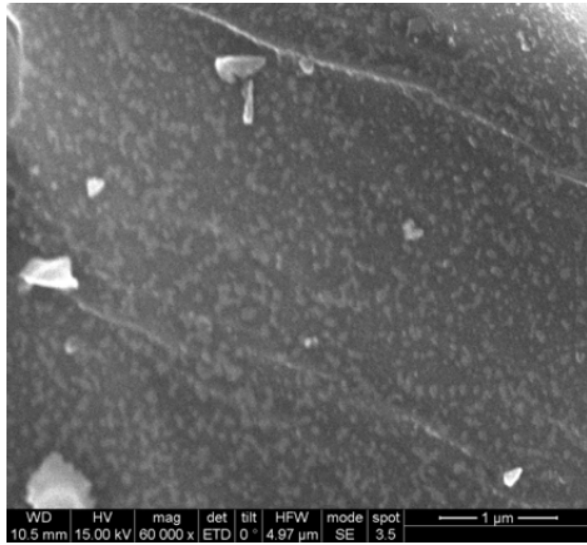
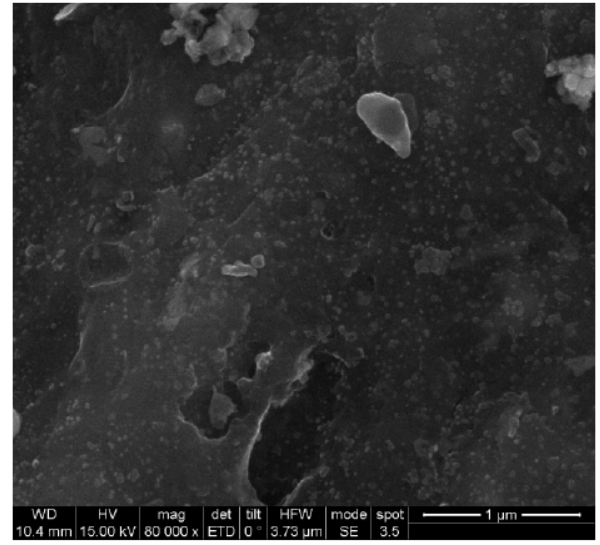


Fig. 4. Lower Heating Value (kJ m^{-3} NTP) as a function of the pyrolysis atmosphere and pressure. White columns correspond to pyrolysis runs conducted with N_2 , whereas light grey columns refer to runs conducted within a CO_2 environment.

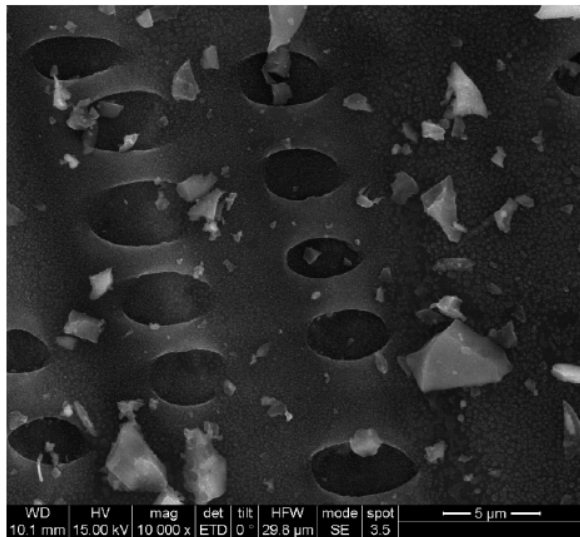
(a)



(b)



(c)



(d)

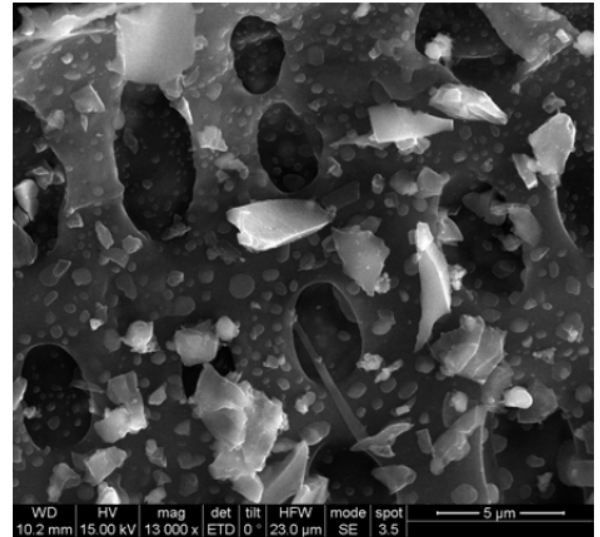


Fig. 5. SEM images of biochar samples: (a) atmosphere of N₂ at 0.1 MPa, (b) atmosphere of N₂ at 1.1 MPa, (c) atmosphere of CO₂ at 0.1 MPa, and (d) atmosphere of CO₂ at 1.1 MPa.