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Effects of CO_2 on biomass fast pyrolysis: Reaction rate, gas yields and char reactive properties

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HIGHLIGHTS

- The CO_2 impacts the biomass pyrolysis process.
- Introducing CO_2 results on a higher CO yield and lower char yield.
- Char reactivity, chemical and textural properties are different in a CO_2-containing atmosphere.
- TPO analysis reveals different oxidation profile for CO_2-chars.

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ABSTRACT

The effect of CO_2 introduction in a biomass fast pyrolysis process at 850 °C was investigated. It was found that CO_2 impacts the final gas yield and composition, and the char yield and properties. Introducing CO_2 in the pyrolysis medium alongside nitrogen enhanced CO production as a result of homogeneous and heterogeneous reactions of CO_2 with gases, tars and char. The char yield was lower compared to a reference char yield in pure nitrogen. The char obtained in a CO_2-containing atmosphere has its surface area increased nearly sixfold and has a chemical composition different from that of chars obtained in N_2 atmosphere. However, the reactivity of the two chars towards H_2O, CO_2 and O_2 was almost the same. Temperature-programmed oxidation experiments on both chars – those obtained in pure nitrogen and those obtained in a CO_2-containing atmosphere – revealed quite different oxidation profiles and peak temperatures. Taken together, these results tend to confirm that CO_2 is impacting the biomass fast pyrolysis process. In the light of these results and of the literature findings, we propose a mechanism illustrating the role of CO_2 during fast pyrolysis of biomass.

1. Introduction

Biomass pyrolysis is a thermal decomposition of the biomass into gas, liquid, and solid [1]. The yields and distribution of the pyrolysis product depend on various parameters such us the physico-chemical characteristics of the biomass (origin, chemical composition, ash and moisture contents, particle size) and the operating conditions (reactor design, temperature, residence time). The production trends of pyrolysis products as a function of temperature and heating rate are reported in Di Blasi's review [2].

For instance, high temperature and small particle size promote gas production and decrease the char yield [3]. Higher residence times in the reactor are also required to maximise the tar thermal cracking to gas. The particle heating rate – which depends on the particle size and shape, as well as on the operating conditions in the reactor (temperature and gas flow) – is a key parameter which influences the pyrolysis product yields and the char properties [1,4].

Despite the huge amount of study devoted to biomass pyrolysis and dealing with issues related to the aforementioned parameters, noticeably few papers focus on the gas surrounding the solid and its potential effects on the pyrolysis reaction.

For instance, Zhang et al. [5] investigated the effect of the composition of the pyrolysis medium in the biomass fast pyrolysis process in a fluidized bed gasifier at 550 °C. The pyrolysis mediums were N_2, CO_2, CO, CH_4 and H_2. The authors found that the liquid yield, composition and higher heating value depend on the composition of the pyrolysis bath gas. The pyrolysis in a CO_2 atmosphere was seen to produce less char than in the other atmospheres. The CO_2 yield also decreased compared to the yield obtained in an N_2 atmosphere. With regard to the liquid product distribution, the CO_2 atmosphere led to the highest yield of acetic acid compared to the other atmospheres. The acid products yield under N_2 was 9% while it increased to 16% under CO_2. Ketones yield also

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increased slightly from 15% to 17% while the phenol yield decreased from 33% to 26%. The authors explained these observations by alluding to two possible mechanisms: either the CO_2 reacted with the active volatiles or with the biomass char. The former assumption seems to be more plausible in view of the pyrolysis temperature.

In a recent study, Kwon et al. [6], observed that introducing CO_2 in the macro-algae pyrolysis process resulted in a breakdown of a significant amount of chemical species. The gas yield was enhanced while the oil yield decreased. The same authors performed another study of the pyrolysis of styrene butadiene rubber [7] and found that the CO_2 enhances C4 hydrocarbon cracking in addition to impeding the gas phase addition reaction by which benzene derivatives are formed. Tyre pyrolysis experiments at 650 °C in free and in CO_2-containing atmospheres showed that the amount of condensable hydrocarbons decreased by 30–50% when introducing CO_2. There was also a modification of the end products.

Other studies focused more on the effect of the pyrolysis atmosphere on the char properties. Hanaoka et al. [8] found that preparing chars in a $N_2/CO_2/O_2$-containing atmosphere leads to a more developed surface area and a higher reactivity towards pure CO_2, especially in a 18% N_2/41% CO_2/41% O_2 atmosphere. The char yield was similar to that obtained under nitrogen. The authors observed an increase in the BET surface area from 275 m^2/g in pure nitrogen to 417 m^2/g in a 18% N_2/41% CO_2/41% O_2 atmosphere. The char reactivity towards CO_2 also increased by a factor of 1.7 to 2.5 for chars prepared in a CO_2-containing atmosphere.

Jamil et al. [9] performed coal pyrolysis experiments in a wire-mesh reactor respectively under *He* and CO_2 with slow and high heating rates. The authors found that the nascent char obtained after a fast heating is very reactive to CO_2. The authors proposed that the char gasification with CO_2 occurs simultaneously with the thermal cracking during fast heating. The CO_2 would mainly react with radicals generated at the char surface, which systematically induces an extra mass loss compared to the inert atmosphere.

In a quite recent study, Gao et al. [10] studied the influence of CO_2 in the lignite pyrolysis process. The authors found that CO_2 impacts the lignite pyrolysis process on different levels. They concluded that the introduced CO_2 promotes the occurrence of coal pyrolysis by enhancing the cracking of the benzene ring and the fracturing of hydroxyl, methyl and methylene groups. Further gasification by CO_2 caused the char to have a higher specific surface area and enhanced the gas yield.

Borrego et al. [11] performed pyrolysis experiments on pulverised wood (particle size of 36–75 μm) in a drop tube furnace at 950 °C under N_2 and CO_2. They performed textural characterisation of the residual chars and found similar specific areas: 277 and 331 m^2/g under N_2 and CO_2. The char reactivity towards air at 550 °C in a TG device was also the same. The residence time was estimated at 0.3 s.

Other studies have focused more on coal pyrolysis but it is still interesting to analyse their results as a means of comparison with biomass pyrolysis. For instance, Gil et al. [12] performed pyrolysis experiments on pulverised coal chars in a drop tube furnace under N_2 and CO_2 atmospheres at 1000 °C. The authors observed an enhanced volatile yield in the CO_2 atmosphere in comparison with the N_2 atmosphere.

Other studies highlighted the role of CO_2 in oxy-fuel conditions. Rathnam et al. [13] studied the reactivity of pulverised coals in air (N_2/O_2) and oxy-fuel conditions (CO_2/O_2). Experiments were performed in an entrained flow reactor at 1400°C and the residence time was estimated to be 0.62 s. The authors observed that replacing 79% N_2 by 79% CO_2 alongside O_2 results in a higher volatile yield. The char specific area and reactivity also increased with the introduction of CO_2. The authors imputed these results to the char-CO_2 reaction occurring simultaneously with the pyrolysis and the combustion reactions.

Thus, according to the literature, the surrounding gas impacts the pyrolysis reaction and product yields. However, very little information about the phenomena involved is available in the literature. The aim of the present study is to assess the effect of the presence of CO_2 in the surrounding gas on the pyrolysis reaction and to deepen understanding of its potential impacts. The present study concerns biomass fast pyrolysis at a high temperature of 850 °C. These experimental conditions come close to those encountered in fluidized bed gasifiers. The potential effects of CO_2 are assessed through the pyrolysis reaction rate, the pyrolysis product yields and composition and the char properties.

2. Materials and methods

2.1. Parent wood sample

The biomass samples were beech wood-chips provided by the French company SPPS. Raw samples were initially sieved. Biomass particles with a size in the range of 4–5 mm and a thickness of about 1 mm were selected to perform the pyrolysis experiments. Proximate and ultimate analysis of the biomass samples are presented in Table 1. The results are given on a dry basis. The moisture content of the wood-chips was 10% ± 1%.

2.2. Experimental devices and procedures for wood-chips pyrolysis

2.2.1. The macro-thermogravimetry experimental device and procedure

The thermal degradation of the wood-chips in a macro-thermogravimetry device (M-TG) was used to determine the pyrolysis rate and final char yield. Experiments were performed under two atmospheres: N_2 and 20% CO_2 in N_2 at 850 °C.

2.2.1.1. M-TG apparatus. The new M-TG device is described in detail in our previous work on char gasification in mixed atmospheres of CO_2 and H_2O [14]. In general terms, the experimental apparatus consists of a 2-m long, 75-mm i.d. alumina reactor that is electrically heated, and a weighing system comprising an electronic scale having an accuracy of ±0.1 mg, a metallic stand placed over the scale on which three hollow ceramic tubes are fixed, each having a length of 1 m and a 2.4 mm external diameter. These ceramic tubes hold up a platinum basket in which the biomass particles are placed. The gas flow rates are controlled by means of mass flow-meters/controllers. The gas flow inside the reactor is laminar and flowing at an average velocity of 0.20 m/s. This device allows fast heating of the biomass particles as they are introduced in the hot furnace within less than 15 s.

2.2.1.2. Experimental procedure. A load of 20 to 25 wood-chips with a total weight of about 0.5 g was placed in the platinum basket and uniformly spaced to avoid thermal and chemical interactions. The biomass particles were submitted to a thermal shock as if they had been placed in a fluidized bed gasifier. For this purpose, a new rapid sample introduction procedure – involving a blank test –

Table 1
Proximate and ultimate analysis of the beech wood-chips (% dry basis).

Proximate analysis			Ultimate analysis			
VM	Ash	FC	C	H	O	N
88.1	0.4	11.5	46.1	5.5	47.9	0.1

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had to be developed in order to run short duration experiments. During the heating of the platinum basket and the ceramic tubes, the flowing gas dynamic pressure (force exerted on the basket) in addition to the drag forces along the ceramic tubes caused the displayed mass value to change. Once a thermal equilibrium was reached inside the reactor, and the gas flow around the basket and the ceramic tubes had stabilized, the displayed mass remained constant. Blank tests (without wood-chips in the basket) were performed to correct the mass decay. The reproducibility of the blank tests was verified and an experimental protocol was established so that the pyrolysis tests were always performed in the same way. For data processing, we subtracted the blank test mass record from that of the pyrolysis experiment. Fig. 1 shows reproducibility pyrolysis test results with 20% CO_2 in N_2 after correcting the mass record. The mass loss is recorded via the electronic scale every 0.1 s.

Pyrolysis experiment results were very reliable after 13.5 s; before this time, results remained acceptable except at 2–3 s when lifting the device and at 11–12 s when stopping the motion of the device. One can note a time delay of approximately 8 s before the particle mass loss began, which was attributed to the heating of the metal basket.

2.2.2. The horizontal tubular reactor experimental device and procedure

To determine the effect on the gas yield and composition of introducing the CO_2, pyrolysis experiments were performed on the wood-chips in a Horizontal Tubular Reactor (HTR) at 850 °C under three different atmospheres: N_2, 20% CO_2 in N_2 and 40% CO_2 in N_2.

2.2.2.1. HTR apparatus. The Horizontal Tubular Reactor (HTR) consists of a double-walled quartz pipe. The length and inside diameters are respectively 850 mm and 55 mm for the inner tube, and 1290 mm and 70 mm for the outer tube. Nitrogen and carbon dioxide flow rates are controlled by means of mass flow-meters/controllers. The major part of the incoming gas flow (75%) is introduced on right hand-side of the reactor and passes through the annular space to be heated before reaching the biomass samples. The rest of the gas flow is injected on the left hand-side to cool the injection spoon when pooled out from the hot zone and to prevent a backward flow of the pyrolysis gases. The pyrolysis experimental device is presented in Fig. 2.

2.2.2.2. Experimental procedure. A load of 20–25 wood-chips with a total weight of about 0.5 g was placed in a basket made with a stainless-steel grid of 0.5 mm thickness and attached to the end of a mobile stick made of Pyrex. The wood-chips were spaced widely enough to avoid chemical and thermal interactions. The mobile stick bearing the basket containing the biomass samples was kept in the non-heated zone until the stabilization of the reactor atmosphere. The flow rate of the pyrolysis gas medium (pure nitrogen or mixtures of carbon dioxide and nitrogen) was set to 2 l/min (STP). Part of the gas flow was initially deviated to a SERVOMEX paramagnetic analyser to quantify the oxygen. Once the O_2 concentration reached zero, the pyrolysis experiment could start. At $t = 0$, the reactor outlet was connected to a Tedlar gas sampling bag. Then, the mobile stick was introduced in the hot reactor until the grid basket reached the entry of the isothermal zone, which had a length of 40 cm and a temperature of 850 ± 10 °C. The gas collection time was set to 3 min according to preliminary pyrolysis tests showing that the pyrolysis reaction lasts less than 1 min. When CO_2 was introduced alongside nitrogen, the stainless-steel basket was pulled out in the cooled zone after 1 min to avoid char gasification by CO_2. CO_2, CO, H_2, CH_4, C_2H_4 and C_2H_2, which are the major permanent gases emitted during pyrolysis, were subsequently analysed with a micro-chromatograph analyser (Agilent 3000 μGC). As the pyrolysis emitted a considerable amount of water (0.10–0.17 g/g wood (db)), calculations and precautions were made to ensure that the water partial pressure in the bag was below its saturation pressure to avoid water condensation inside the bag, which could distort the measurements. We also filled the bag periodically with air to force any eventually condensed water to evaporate.

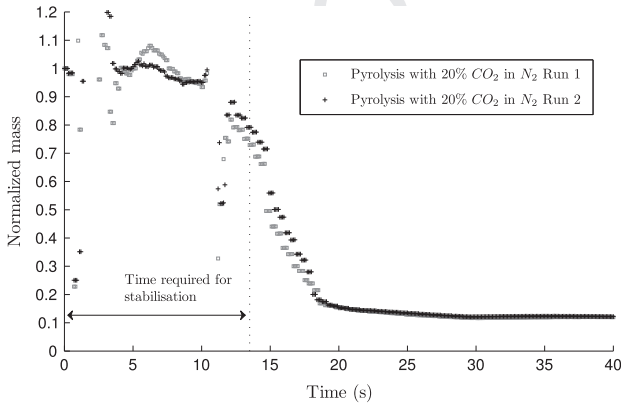


Fig. 1. Repeatability tests of high-temperature flash pyrolysis experiments.

2.2.2.3. Pyrolysis product yields. N_2 was used as a gas tracer. As the quantity collected in the bag was known, and its molar fraction was given by the μGC, it was possible to determine the total moles of gas in the bag:

$$n_{tot} = \frac{n_{N_2}}{x_{N_2}} = \frac{Q_{N_2(STP)} \times \rho_{N_2(STP)} \times t_{sampling}}{M_{N_2} \times x_{N_2}} \quad (1)$$

and to calculate the molar quantity of the aforementioned gaseous species:

$$n_i = x_i \times n_{tot} \quad (2)$$

With: n_{tot}: total gas moles [moles], n_{N_2}: nitrogen moles [moles], x_{N_2}: nitrogen molar fraction, $Q_{N_2(STP)}$: nitrogen flow rate [l/min], $rho_{N_2(STP)}$ nitrogen density [kg/m^3] and $t_{sampling}$: sampling duration [min].

The results are given hereafter as mass yields on a dry ash-free basis (kg gas/ kg wood (dafb)). The total gas yield represents the mass of permanent gases emitted during the pyrolysis (daf):

$$Y_{gas}\ (\%) = \frac{m_{gas}}{m_{wood\ (dafb)}} \times 100 = \frac{\sum m_i}{m_{wood\ (dafb)}} \times 100 \quad (3)$$

The energy content of the gas is assessed through the variable CGE (cold gas efficiency). This variable represents the ratio between the energy content of the permanent gas (HHV_{gas}) and the energy content of the initial biomass feedstock ($HHV_{wood(dafb)}$) without taking into account the heat input in the reactor:

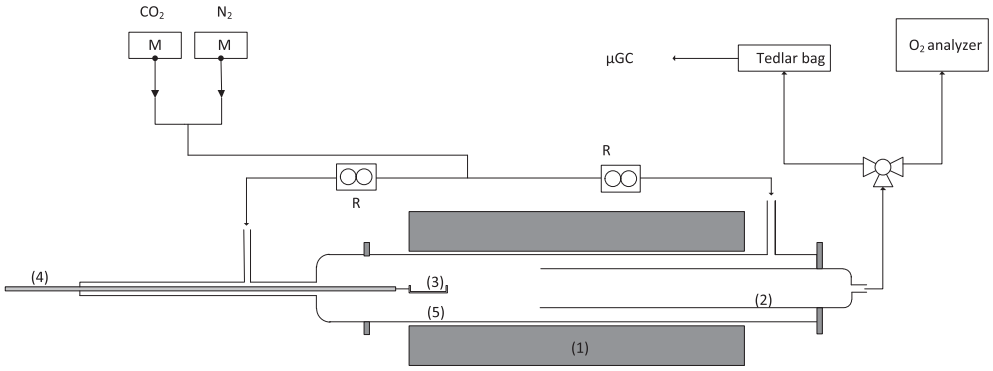
$$CGE = \frac{HHV_{gas}}{HHV_{wood(dafb)}} \quad (4)$$

At the and of the experiment the residual chars were weighed and stored in a sealed recipient for further characterisation. The char yield is expressed as the ratio of the residual char to the initial mass of wood (db)

$$Y_{Char}\ (\%) = \frac{m_{Char}}{m_{wood_{db}}} \times 100 \quad (5)$$

2.2.3. Similarity of the experimental conditions in both reactors

A fact worth noting is that we characterised the M-TG and HTR reactors in terms of flow properties and heat transfer coefficients at



1-furnace (heating element); 2-inner tube; 3-grid sample holder; 4-mobile pyrex stick
5-quartz tubular reactor; M-mass flowmeter/controller; R-rotameter

Fig. 2. Horizontal tubular reactor experimental device.

sample surface. The global heat transfer coefficient at sample surface in the two reactors was determined following a lumped capacitance method [15], and the contributions of both convection and of radiations were estimated. Details about the procedure are given in Appendix A. The gas flow inside the two reactors was laminar. The Reynolds number was estimated to be 13.4 in the M-TG reactor and 3.7 in the HTR reactor. The results for the global heat transfer coefficients in the M-TG and in the horizontal tubular reactor are given in Table 2.

Given the similarities in the gas flow properties, in the global heat transfer coefficients and heat transfer mode (the same magnitude and radiative for more than 80%), it can be stated that the operating conditions in both reactors are similar and that it is legitimate to establish comparisons between experiments performed in the two experimental devices.

Based on the above results, we also estimated the initial heating rate of the biomass particle β_0 to be respectively 122 and 101 [K/s] in the M-TG and in the HTR reactor [16]. Details are given in Appendix B.

2.3. Characterisation of the remaining char

To determine if pyrolysing wood under a CO_2-containing atmosphere impacts on the char properties, we performed a set of characterisation tests and reactivity measurements with CO_2, H_2O and O_2 of chars obtained respectively after pyrolysis in pure nitrogen and pyrolysis in 20% CO_2 in N_2.

2.3.1. Chemical composition

The remaining char chemical composition was determined by ultimate analysis in terms of C, H, O and N contents. The ash content was determined by combustion of 100 mg of char in a muffle furnace at 550 °C.

2.3.2. Textural and structural characterisation of the remaining char

Observations of the char structure were made through a Scanning Electron Microscopy (SEM) device. The chars were also characterised for specific surface measurement. The Brunauer–Emmett–Teller (BET) surface area was determined respectively for chars pyrolysed under N_2 and 20% CO_2 in N_2 in a Micrometrics, Gemini instrument using liquid nitrogen at 77 K. Chars were outgassed under vacuum for 24 h prior to the gas adsorption experiments in order to eliminate moisture or any condensed volatiles which could prevent the adsorbate from gaining access.

Table 2
Flow properties, convective and radiative heat transfer coefficients and particle heating rate in the M-TG and HTR experimental devices.

Reactor	M-TG	HTR
h_{conv} (W/m^2 K)	26	20.3
h_{rad} (W/m^2 K)	104.7	178.7

2.3.3. Char reactivity measurement

After the pyrolysis step in the M-TG reactor, we performed gasification tests on the residual chars with steam, carbon dioxide and oxygen. The gasification experiments were made respectively with 20% CO_2 in N_2, 20% H_2O in N_2 and 5% O_2 in N_2. The chars were kept in the furnace and the atmosphere composition was switched to that of the gasification conditions.

The char conversion level is given by:

$$X_{(t)} = \frac{m_0 - m_{(t)}}{m_0 - m_{ash}} \quad (6)$$

where m_0, m_t and m_{ash} are respectively the initial mass of char, the mass at a time t and the mass of the residual ash.

The char reactivity was calculated over time following the relation:

$$R_{(t)} = \frac{1}{1 - X_{(t)}} \times \frac{dX_{(t)}}{dt} \quad (7)$$

2.3.4. Temperature programmed oxidation

The temperature-programmed oxidation (TPO) technique provides relevant information about the carbonaceous material contained in the chars. Oxidation profiles of the chars in non-isothermal conditions can inform about the type of carbon materials and their peak oxidation temperatures. For instance, it is possible to distinguish between different forms of carbons if the char oxidation profile exhibits more than one peak. Temperature-programmed oxidation (TPO) experiments were performed on the chars obtained in N_2 and in 20% CO_2 in N_2. The char samples were firstly ground gently with a mortar and pillar. A sample mass of 2–4 mg was mixed with 100 mg of silicon carbide (SiC) and introduced in an electrically-heated quartz reactor. First, a temperature-programmed desorption with 50 ml/min of helium was performed from room temperature up to 900 °C with a slope of 15 °C/min in order to clean the char surfaces of any exterior deposit. Then, after cooling and return to baseline, an oxidising gas mixture of 1% oxygen in helium (total flow of 50 ml/min) was introduced in the reactor. The temperature was increased at a rate of 15 °C/min from room temperature to 900 °C. The CO_2 emitted during the char oxidation was monitored by a Mass Spectrometer (Quadrupole Pfeifer Omnistar).

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3. Results and discussion

3.1. Pyrolysis rate

High-temperature fast pyrolysis tests show a good repeatability with the established protocol. The data presented hereafter are average values from at least two experiments. The results of pyrolysis experiments in N_2 and 20% CO_2 in N_2 are shown in Fig. 3. In the figure, a mass loss of 10% at the beginning, perhaps attributable to particle drying, has been indicated. Devolatilisation can be divided into two stages: an active phase corresponding to the major mass loss, and a passive phase within which the rate of mass loss decreases abruptly corresponding to lower emissions of gas and tars [17]. It can be seen that the pyrolysis reaction rate is almost the same for pyrolysis under N_2 and for pyrolysis under 20% CO_2 in N_2.

3.2. Final char yield

In M-TG pyrolysis experiments, an additional mass decay was observed when the CO_2 was introduced, which resulted in a lower char yield. The char yields after pyrolysis in N_2 and in 20% CO_2 in N_2 at $t = 60$ s were respectively $13.1 \pm 0.3\%$ and $11.32 \pm 0.25\%$. These results indicate that either less char was formed, or that there was a char consumption when introducing CO_2 along with nitrogen.

In HTR experiments, a decrease in the char yield from $11.7\% \pm 0.04$ down to $10.5\% \pm 0.38$ in a 20% CO_2 containing atmosphere was also observed. The char yield remained constant when increasing the CO_2 concentration further to 40%, as shown in Fig. 4.

These results confirm those obtained in pyrolysis experiments in the M-TG device, although the decrease in the final mass of the char in pyrolysis experiments with CO_2 was slightly smaller. It is also worth noting that the char mass remained constant even after the CO_2 partial pressure was increased to 40%.

The mass of the residual char is known to depend on the temperature and on the pyrolysis heating rate [2,4,18]. The final temperature was the same in the two experiments. The additional mass loss may be due to a thermal effect or to a chemical effect prompted by the CO_2.

As regards thermal effects, the higher specific heat of CO_2 in addition to its radiative properties in comparison to N_2 can modify the heating rate of particles when introduced in the pyrolysis medium. To verify this, we measured the global heat transfer coefficient h_{global} in both atmospheres, keeping the gas velocity constant. We found a slight increase when adding the CO_2, but the order of magnitude was the same: 131 and 148 [W/m^2 K] respectively. The thermal effect is thought to be negligible.

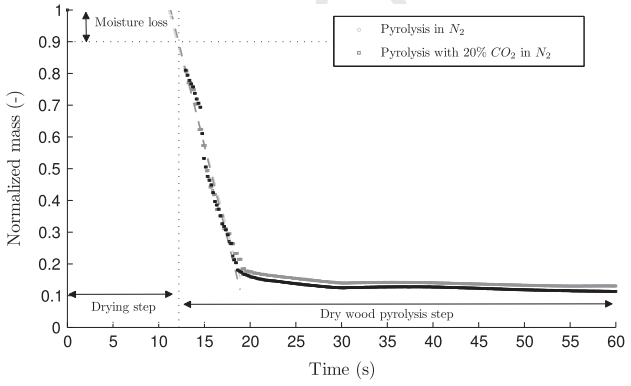

Fig. 3. High temperature flash pyrolysis of beech wood-chips in N_2 and in 20% CO_2 in N_2 (M-TG).

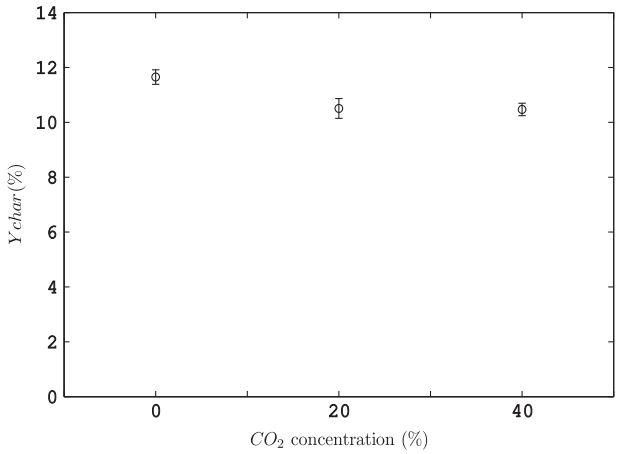

Fig. 4. Char yield as a function of the CO_2 concentration in the pyrolysis medium (HTR).

As for the potential chemical effects, there are two possibilities: (i) the CO_2 can inhibit secondary char formation by reacting with tars, and (ii) the CO_2 may react directly with the char according to the Boudouard reaction. At this level, we can not go beyond assumptions with regard to the mechanisms that may be unfolding. These assumptions will be discussed later.

3.3. Final gas yields

Fig. 5 shows the pyrolysis gas yields under 100% N_2, 20% CO_2 and 40% CO_2 in N_2. Note that the CO yields were divided by 10 to fit the figure.

We can see that the major change involved the carbon monoxide. A net increase was observed for CO, whose yield increased from 427 (g/kg wood (daf)) in pure nitrogen to 520 (g/kg wood daf) when introducing 20% CO_2, and further to 561 in a 40% CO_2-containing pyrolysis atmosphere. The CH_4 and C_2 hydrocarbons yield increased slightly in a 40% CO_2 atmosphere compared to a free CO_2 atmosphere. The H_2 yield decreased slightly from 11.8 to 11.4 (g/kg wood daf) when increasing the CO_2 concentration from 0 to 40%. In a nitrogen atmosphere, the CO_2 was produced with a yield of 168 (g/kg wood daf). It was not possible to give a reliable result on the CO_2 yield in pyrolysis experiments with CO_2 introduction due to high uncertainties: the amount of produced CO_2 is much smaller than the amount of CO_2 introduced in the atmosphere gas (ratio of 60 approximately) as the introduced

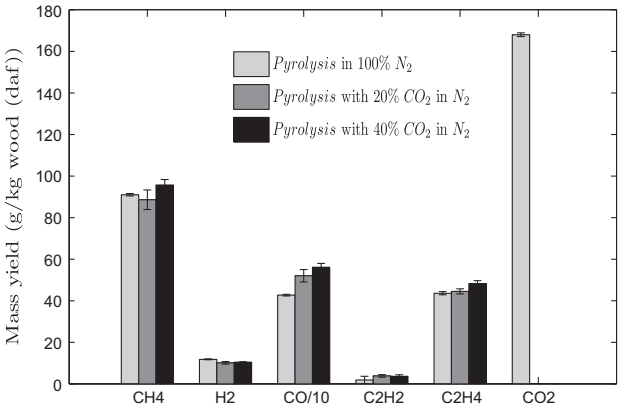

Fig. 5. Pyrolysis gas yields at 850 °C under 100% N_2, 20% CO_2 and 40% CO_2 in N_2 (HTR).

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CO_2 to biomass ratio was calculated to be 6.5 and 13 g/g wood (daf) respectively for experiments done with 20% CO_2 and 40% CO_2 in N_2.

The total permanent gas yield (excluding CO_2) increased with the increase in the CO_2 concentration in the pyrolysis medium from 576 (g/kg wood (daf)) in a free CO_2 medium to 667 (g/kg wood (daf)) with 20% CO_2 and further to 719 (g/kg wood (daf)) with 40% CO_2 in the pyrolysis medium. The energy content represented by the variable CGE increased accordingly by 13% from 0.66 (0% CO_2) to 0.75 (40% CO_2). However the H_2/CO ratio decreased with the increase in the CO_2 concentration in the pyrolysis gas medium.

3.3.1. Interpretation and discussion of results

As mentioned in the introduction section, several studies have dealt with the effects of CO_2 in biomass and coal pyrolysis. For instance, Kwon et al. [6] found that introducing CO_2 alongside nitrogen in the pyrolysis process at 550 °C in a tubular reactor decreased the generation of pyrolytic oil and enhanced pyrolytic gas production. The authors propose that hydrocarbons emitted in the pyrolysis process can be broken down in the presence of CO_2, or at least not formed. The authors also carried out steam gasification tests at higher temperatures (600–1000 °C) and noticed that the yield of C2 hydrocarbons also increased and the amount of tar was reduced by 51.2%.

In a more recent study the same authors [7] found that the CO_2 enhances cracking of C4 hydrocarbons in addition to impeding the gas phase addition reaction by which benzene derivatives are formed. The authors also made tyre pyrolysis experiments at 650 °C in a CO_2-free and in a CO_2-containing atmosphere. They found that the amount of condensable hydrocarbons decreased by 30–50% when introducing CO_2 in addition to there being a modification of the end products. The authors proposed that the CO_2 participates in the cracking reactions as well as impeding other reactions by which tars are formed.

In another study, Zhang et al. [5] investigated the effect of the pyrolysis medium composition on the biomass fast pyrolysis process in a fluidized bed gasifier at 550 °C. The pyrolysis in a CO_2 atmosphere was seen to produce less char than in the other atmospheres. The CO_2 yield decreased and the CO yield increased compared to N_2 atmosphere. Moreover, the CO_2 atmosphere led to the highest yield of acetic acid compared to the other atmospheres. Ketones yield also increased in a CO_2 atmosphere while the phenol yield decreased. The authors explained these observation by two possible mechanisms: the CO_2 reacted with the active volatiles or with the biomass char. The former assumption seems to be more plausible in view of the pyrolysis temperature.

Ahmed et al. [19] also evidenced a CO_2 consumption during the pyrolysis of cardboard and paper.

Based on these literature findings, it is clear that CO_2 influences the pyrolysis process by modifying the product yields. One of the major findings is that the CO_2 hinders condensable hydrocarbon formation and enhances the CO yield.

Primary tars can undergo polymerisation reactions and form secondary char as proposed by Gilbert et al. [20] and Zhang et al. [21]. According to the literature findings, a plausible explanation for the char mass decay may be that the CO_2 prevents tar polymerisation reactions and secondary char formation. The decrease in the final mass of char and the increase in the gas yield may be due to the enhanced tar cracking by CO_2 according to:

$$C_nH_m + nCO_2 \rightarrow 2n\ CO + \frac{m}{2}H_2 \quad (8)$$

The CO_2 may also participate in homogeneous gas reforming reactions, as reported by Sutton et al. for methane and propane reforming [22].

Methane dry reforming reaction (MDR) by CO_2 is promoted at high temperatures (thermodynamically possible above 640 °C) and leads to an enhanced CO production according to:

$$CO_2 + CH_4 \rightarrow 2H_2 + 2CO\ \Delta H = +246.9\ \text{kJ/mol} \quad (9)$$

The CO_2 can also react with hydrogen molecules according to the reverse water gas shift reaction (rWGS), which is the dominant reaction at high temperature (above 700 °C):

$$CO_2 + H_2 \rightarrow H_2O + CO\ \Delta H = +41.2\ \text{kJ/mol} \quad (10)$$

The observations of improved gas yields at low temperature found in the literature are probably related to homogeneous reactions and tar cracking by CO_2. A straightforward thermodynamic approach based on the Gibbs available energy variation shows that at temperatures below 650 °C, the Boudouard reaction does not promote CO formation (1) but on the contrary its disproportionation (2) into CO_2 and carbon deposit.

$$CO_2 + C \rightleftharpoons 2CO \quad (11)$$

At a high temperature of 850 °C, the char gasification reaction must be taken into account, especially when the pyrolysis is performed at a high heating rate. Jamil et al. [9] performed coal pyrolysis experiments in a wire-mesh reactor respectively under *He* and CO_2 with heating rates of 1 °C/s and 1000 °C/s from ambient to a prescribed peak temperature. They found that, in fast pyrolysis experiments, the char yield in CO_2 is slightly but systematically lower than that in *He* over the range of the holding time. The difference in the char yield was in the range 1–2 wt.%-daf at a peak temperature of 700 °C, but was outside the range of experimental error. Fast heating rate pyrolysis up to 800 °C showed a difference in the char yields in the range of 2–3 wt.%-daf from the very beginning of the holding time period at this peak temperature. These results confirm the observations made in the present study concerning the lower char yield in a CO_2-containing pyrolysis atmosphere. The authors went further in investigating this observation and concluded that fast pyrolysis (high heating rate) improves the thermal cracking of the char and provides high concentrations of radical species at the char surface, compared to a slow pyrolysis. These radicals constitute the active sites and are very reactive towards CO_2 molecules. The authors proposed that the rate of the gasification reaction is closely related to the rate of the thermal cracking that generates the radicals. The reactivity of the nascent char towards CO_2 during fast heating from 600 to 900°C was two or more orders of magnitude higher than reactivity data found in the literature for similar coal chars.

These observations, made by Jamil et al., can explain the additional mass decay observed in our experiments. The nascent char obtained after the fast pyrolysis may contain a high concentration of radicals at its surface, which reacted with the surrounding CO_2 and led to the char consumption.

Di Blasi reported in her review a panoply of kinetic rate constants for the CO_2-char gasification reaction of numerous biomasses [2]. A characteristic time approach shows that the rate of the Boudouard reaction is low at 850 °C. However, the mechanisms of the char gasification seems to be different for a nascent char prepared at a high heating rate [9]. The Boudouard reaction is therefore a potential cause behind CO yield increase and char mass decay:

$$CO_2 + C \rightarrow 2CO\ \Delta H = +172.5\ \text{kJ/mol} \quad (12)$$

Taking the results obtained in the present study together with the literature analysis, the improved CO yield and the final char mass decay can be the result of three combined effects of improved tar cracking by CO_2: the gas phase reactions of methane reforming

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and reverse water gas shift, and char gasification. The next sections will shed more light on the pyrolysis process unfolding in a CO_2-containing atmosphere.

3.3.2. Effect of CO_2 co-feeding on the char properties

3.3.2.1. Structural and textural properties.

- *SEM analysis*

  Fig. 6 shows SEM images of chars pyrolysed at 850 °C in N_2 and 20% CO_2 in N_2. Both chars show a similar amorphous, heterogeneous and disordered structure. No clear difference was observed between the two char structures, both of which kept the fibrous aspect of the raw wood with extensive cracks and breakages, probably due to the violent release of volatiles during the pyrolysis stage.

- *Char specific area measurement*

Fig. 7 shows the N_2 adsorption isotherms of two chars. The reported data are the average of two repeatability experiments.

The adsorbed volume of N_2 per unit mass of porous carbon (char) is more than 6 times greater for chars prepared with 20% CO_2 in the heating medium than those obtained with a pure N_2 heating medium. The respective BET specific surfaces are 68.9 ± 14.33 m^2/g and 408.3 ± 3.1 m^2/g. Former studies showed the same order of magnitude for the specific area of chars prepared with a high heating rate under nitrogen: $S_{BET} < 70$ m^2/g [4]. The specific area greatly expanded in the presence of CO_2. In a study on biomass char pyrolysis in a drop tube furnace respectively under N_2 and CO_2 [11], Borrego et al. performed textural characterisation on wood-chip chars and found similar specific areas: 277 and 331 m^2/g respectively under N_2 and CO_2. The char reactivity towards air at 550 °C in a TG device was also the same. The operating conditions were not the same (particle size of 36–75 μm, residence time of 0.3 s and reactor temperature of 550 °C), which makes the comparison rather difficult. However, in another study, Klinghoffer et al. prepared biomass chars in a fluidized bed reactor with a heating rate of 20°/min under steam and CO_2. They found that the chars were active with respect to hydrocarbon cracking. The chars exhibited similar surface areas in the range of 400–700 m^2/g depending on the operating conditions. However the char yield in a CO_2 medium is highly micro-porous. The authors imputed this micro-porosity to the CO_2, which is in accordance with our findings [23].

The physical activation of chars by CO_2 for activated carbon preparation has been extensively studied, and it is well established that the CO_2 develops the microporosity inside the char [24,25]. However, such char activation procedures for microporosity development are quite different, as they usually involve several steps of pyrolysis, carbonisation at high temperature with holding times exceeding sometimes 1 h, and finally char gasification by CO_2 for extensive microporosity development. In their review on carbon molecular sieve preparation from lignocellulosic biomass, Mohammed et al. reported on the experimental conditions and procedures for preparation of highly porous materials by CO_2 activation. The experimental procedures are usually of long duration, involving a chemical activation step, a pyrolysis/carbonisation step that may lasts from 1 to 8 h, and a CO_2 or steam activation step whose duration is in the range of 15 to 1080 min. The char burn-off is also high in the range of 34 to 80% [26]. These procedures are, in most cases, time- and energy-consuming. In the present study, the char specific area increased sixfold within a very short duration and using a quite simple one-step procedure. The high heating rate coupled to CO_2 introduction during pyrolysis are procedures worthy of consideration for the effective production of porous carbon material with a good surface area.

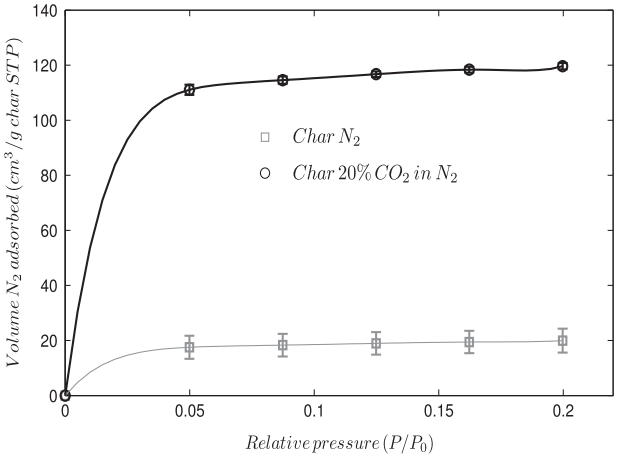

Fig. 7. N_2 adsorption isotherms of beech wood chars pyrolysed respectively under pure nitrogen and 20% CO_2 balanced with nitrogen (HTR).

- *Char chemical composition*

The proximate and ultimate analysis of the two chars are presented in Table 3.

The ultimate analysis showed a difference in the chemical composition of the two chars. Indeed, we observe that the hydrogen, oxygen and nitrogen amounts decreased in the 20%CO_2-*char*. It seems that the functional groups containing oxygen and hydrogen are removed preferentially under CO_2. The hydrogen amount decreased by 60% and that of oxygen by 18%.

The H/C and O/C ratios of the CO_2-*char* decreased in comparison with the N_2-*char*. Adding carbon dioxide into the pyrolysis atmosphere enhances hydrogen and oxygen loss and carbon enrichment of the residual char. Another fact worth noting is that the ash

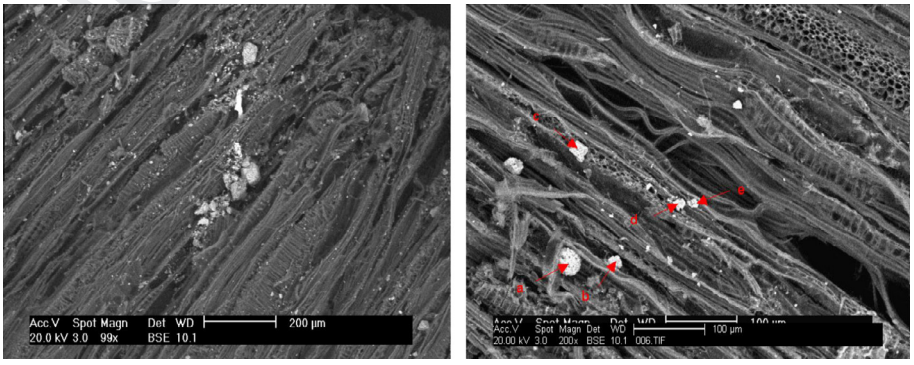

Fig. 6. SEM images of chars obtained at 850 °C respectively under N_2 and 20% CO_2 in N_2 (HTR).

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Table 3
Proximate and ultimate analysis of chars obtained under N_2 and 20% CO_2 in N_2 (% dry basis).

	Proximate analysis	Ultimate analysis			
	Ash	C	H	O	N
N_2-*char*	3.00 ± 0.24	87.91 ± 0.81	1.97 ± 0.56	6.16 ± 0.04	0.96 ± 0.28
CO_2-*char*	3.79 ± 0.15	89.82 ± 0.51	0.78 ± 0.17	5.05 ± 0.23	0.63 ± 0.09

amount increased for the 20%CO_2-*char*, which is synonymous of char conversion and confirms the char yield decrease when CO_2 is added in the pyrolysis atmosphere.

3.3.2.2. Char reactivity measurements. The reactivity tests on the two chars with alternatively 20% of steam in N_2, 20% CO_2 in N_2 and 5% O_2 in N_2 were performed after the pyrolysis step by switching the reactor atmosphere to the desired composition (CO_2, H_2O and O_2). The purpose here was to characterise the influence of the pyrolysis atmosphere composition on the char reactivity. Reactivity profiles along the char conversion are shown in Fig. 8. These reactivity results are the average of three repeatability tests. The mean reactivities (X = 0.2–0.9), as well as the standard deviations (error bars), are presented in Fig. 9.

In steam gasification experiments (Fig. 8.a), we observed that the char reactivity profiles remained the same regardless of the pyrolysis atmosphere composition, and the average reactivities (between X = 0.2 and X = 0.9) are respectively 0.0081 and 0.0083(g/g s) for chars obtained in N_2 and in 20% CO_2 in N_2 pyrolysis atmosphere. In the char gasification experiments with CO_2 (Fig. 8.b), we observed an increase in the char reactivity towards CO_2 for the chars prepared in a CO_2-containing pyrolysis atmosphere, especially in the earlier stages of the gasification reaction (up to 40% of conversion). The average reactivities are respectively 0.0028 and 0.0038 (g/g s) for chars obtained in N_2 and in 20% CO_2 in N_2 pyrolysis atmosphere, which represents an increase of 26% in the reactivity (the relative standard deviation is below 5%). This tendency may be explained by the higher surface area of chars obtained in a CO_2-containing pyrolysis atmosphere which influences the Boudouard heterogeneous gasification reaction. The CO_2 diffusion to the carbon active sites can be promoted by this developed surface area, which explains the higher reactivity in the initial stages of the gasification.In fact, total pore volume was estimated to be 0.185 cm^3/g for chars prepared with a CO_2-containing atmosphere, while it was only 0.031 cm^3/g for chars obtained under N_2. In a more recent study [8], Hanaoka et al. found that preparing chars in an $N_2/CO_2/O_2$ atmosphere leads to a more developed surface area and a higher reactivity towards pure CO_2, especially in a 18% N_2/41% CO_2/41% O_2 atmosphere. The char yield was similar to that obtained under nitrogen but there was an increase in the BET surface area from 275 m^2/g in pure nitrogen to 417 m^2/g and an increase in the char reactivity by a factor of 1.7 to 2.5 depending on the gasification temperature.

Despite the micro-porosity that developed in chars prepared in a CO_2-containing atmosphere, their reactivity towards steam was the same as that of chars prepared in N_2. Micro-porosity does not seem to influence the char-steam gasification reaction. This can be explained by the difference in char porosity development with both gases [24]. In fact, it has been demonstrated that submitting a char to activation with steam or CO_2 does not lead to the same porosity development. The CO_2 promotes the development of narrow microporosity up to about 20% burn-off, followed by a widening up to about 40% burn-off. On the other hand, steam widens the microporosity from the earlier stages of the gasification [25]. This observation can explain why a developed microporosity enhances the reactivity of the char towards CO_2 while it has no effect on its reactivity towards H_2O. The findings of Rodriguez et al. [25] can also explain the reactivity profile obtained for char prepared in a CO_2-containing pyrolysis atmosphere which exhibits a higher reactivity in the first stages of the reaction (developed microporosity) and which decreases up to 40% of conversion due to burn-off. The increase in the reactivity from 40% to 50% of conversion is due to a developed char porosity and a higher catalytic activity

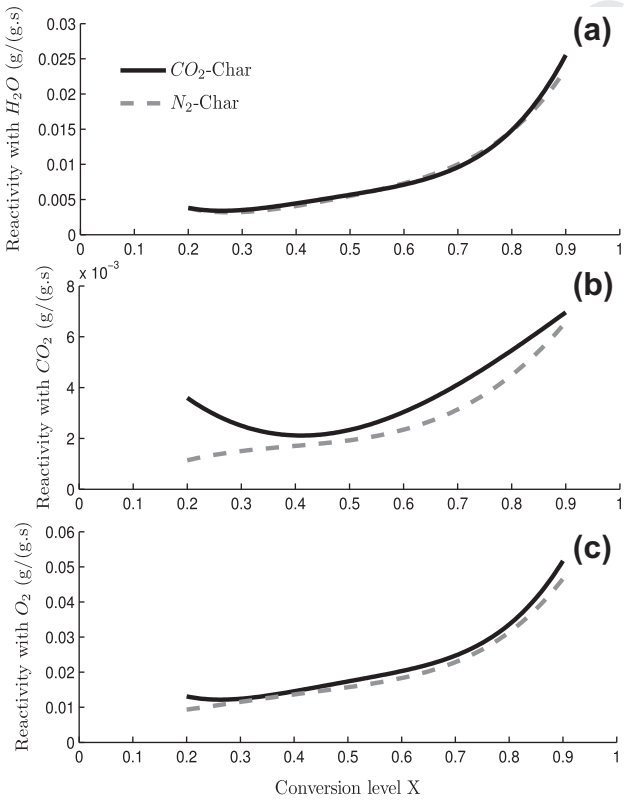

Fig. 8. Influence of the pyrolysis atmosphere on the char reactivity with (a) H_2O, (b) CO_2 and (c) O_2 at 850 °C (M-TG).

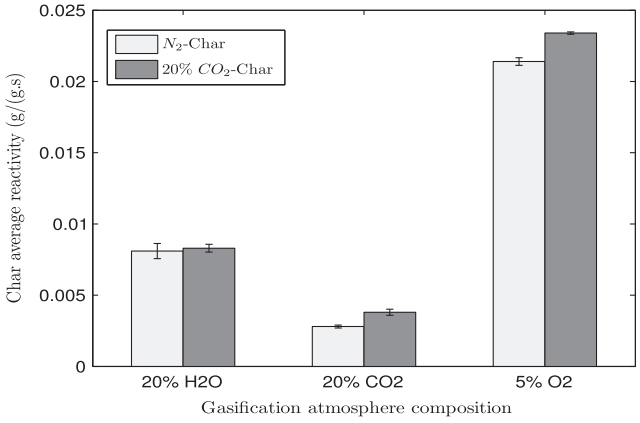

Fig. 9. Mean reactivities (X = 0.2–0.9) of N_2-char and CO_2-char towards H_2O,CO_2 and O_2 at 850 °C (M-TG).

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of the minerals. Moreover, we found in our previous study on char gasification in mixed atmospheres of H_2O and CO_2 [14], that gasifying biomass chars with CO_2 up to 30% of conversion does not affect its reactivity towards H_2O, which corroborates the current findings.

In a fluidized bed, a major part of the char will be carried in the riser and combusted with air. With this in mind, we also performed combustion tests on the two chars with an oxygen concentration of 5% to assess the impact of the CO_2 during pyrolysis on the char reactivity with oxygen (Fig. 8.c). The average N_2-char and CO_2-char reactivities were respectively 0.0214 and 0.0234 with relative standard deviations below 5%. Average char reactivity results for the different gasification atmosphere are summarised in Fig. 9.

On the basis of these results we can conclude that the presence of CO_2 during pyrolysis mainly affects the char reactivity towards CO_2 and, to a lesser extent, with O_2, but does not affect the steam gasification of the char.

3.3.2.3. Temperature programmed oxidation. Temperature programmed oxidation experiments were performed on both chars and brought relevant insights. Fig. 10 shows the outflow of CO_2 as a function of temperature. The two chars exhibited two different oxidation profiles: both signal shapes and peak temperatures are different. The peak temperatures are respectively 580 and 600 °C for the N_2-char and for the CO_2-char.For the CO_2-char TPO curve, a single peak is observed. On the contrary, the N_2-char TPO curve shows a more complex shape during signal increase and a last peak at 635 °C. We believe that the CO_2-char contains a single type of carbon material while the N_2-char may contain more.

The TPO profiles were modelled using one or several parallel reactions converting char into CO_2 and CO following:

$$\frac{dm_{char}}{dt} = -k_{(T)} \cdot m_{char} \tag{13}$$

The rate constants $k_{i(T)}$ follow an Arrhenius law that gives:

$$k_{(T)} = A \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{14}$$

A and E are the frequency factor [s^{-1}] and the activation energy [J/mol].

Fig. 11 a and b shows temperature programmed oxidation experimental profiles and models for the N_2-char and the CO_2-char. The CO_2-char oxidation is well described by a single reaction: this tends to show that it contains a single type of carbon. It was not possible to model the N_2-char oxidation with a single reaction. However, the oxidation reaction is well described – as reported in Table 4 – when assuming the presence of three types of carbons. The model reads:

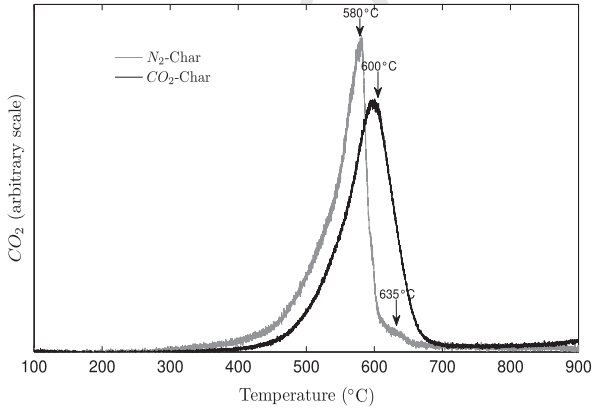

Fig. 10. TPO profiles of N_2-char and CO_2-char (HTR).

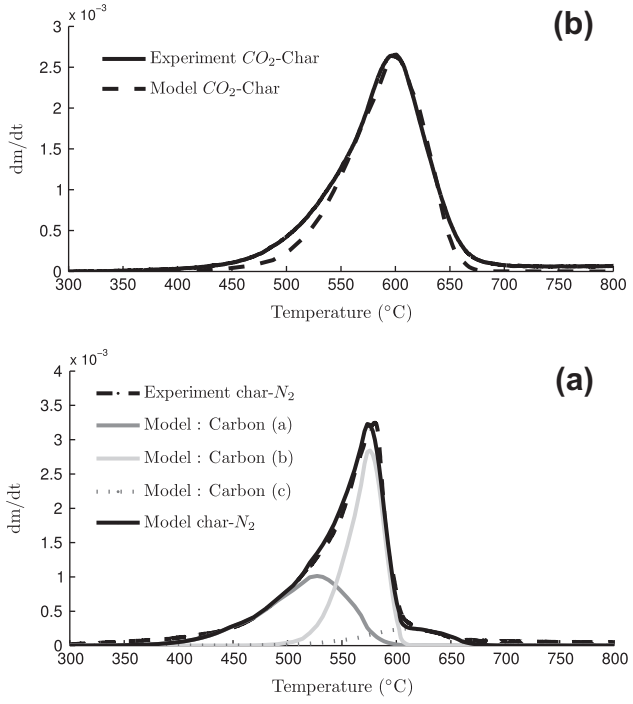

Fig. 11. TPO profiles modelling of N_2-char and CO_2-char.

Table 4
Temperature programmed oxidation kinetic parameters.

	CO_2-char	N_2-char		
		Carbon (a)	Carbon (b)	Carbon (c)
mass (g)	1	0.4	0.51	0.09
A_i (s^{-1})	12.10^7	5.10^6	6.10^{19}	3.10^8
E_i (kJ/mol)	170	135	350	190

$$\frac{dm_{char\text{-}N_2}}{dt} = -k_{1(T)} \cdot m_{carbon\text{-}a} - k_{2(T)} \cdot m_{carbon\text{-}b} - k_{3(T)} \cdot m_{carbon\text{-}c} \tag{15}$$

where $m_{carbon\text{-}a}$,$m_{carbon\text{-}b}$ and $m_{carbon\text{-}c}$ are the amount of carbon materials.

The frequency factors A_i and the activation energies E_i were identified by fitting the model to the experimental results.

The identified carbon masses, frequency factors and activation energies for the two chars are given in Table 4. The N_2-char appears to be composed of approximately 40% of a carbon with a small activation energy of 135 [kJ/mol], 51% of a high activation energy carbon 350 [kJ/mol] and 9% of a third carbon having an activation energy lying between these to values 190 [kJ/mol]. The activation energies of the first and the third carbons lie in the activation energy range for the lignocellulosic char-O_2 reaction (76–229 [kJ/mol]) given in Di Blasi's review [2]. However the second carbon has a higher activation energy in addition to a quite high pre-exponential factor. With an activation energy of 170 [kJ/mol], the oxidation reaction of the CO_2-char is typical of lignocellulosic biomass chars.

With regard to these results, the CO_2 may inhibit the last peak char formation by reacting with the tars, and therefore hinder their deposition and secondary char formation. The tars may have also been deposited on the char surface and removed afterwards by gasification. The last peak corresponds to the most stable form of carbon amongst the three identified forms. Logically, it should be the most difficult form to remove by gasification with CO_2, unless it is deposited on the char surface and is thus exposed first to this gasifying agent. A fact worth noting is that the mass of this third

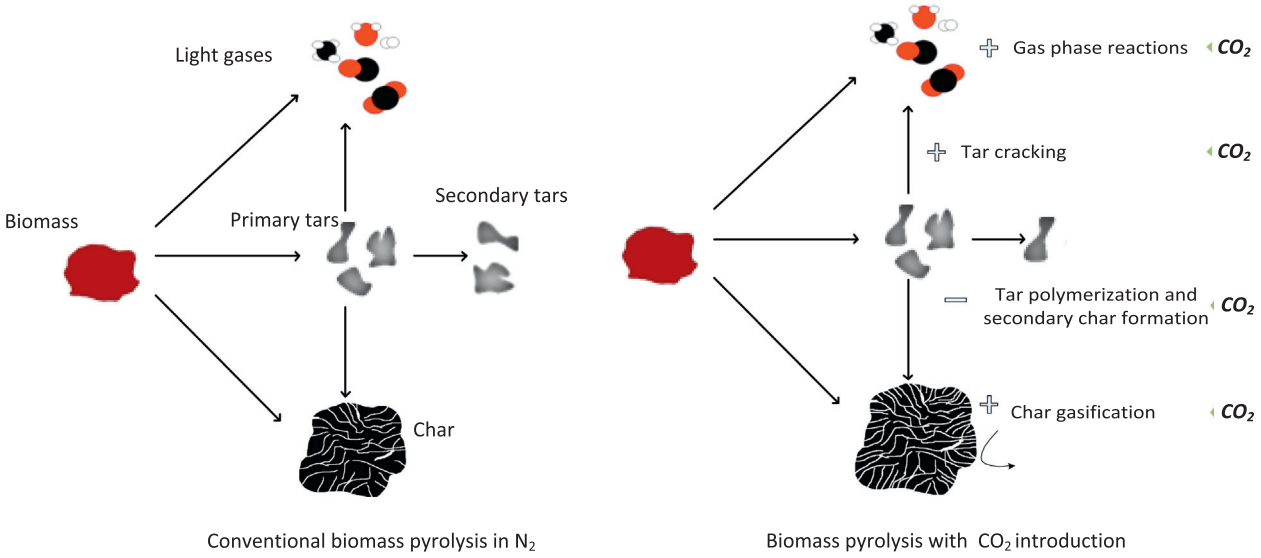

Fig. 12. The potential mechanisms in biomass pyrolysis with CO_2 introduction in the pyrolysis bath gas.

form of carbon corresponds to 10% of the total char mass, giving the TPO results. A link may be established with char mass decay observed in the MTG and HTR experiments when introducing CO_2. This char mass decay was in the range of 10–13%. Concerning the two other forms of carbon, introducing CO_2 may have changed the mechanisms of char formation and led consequently to an another type of char. It is clear that we cannot go beyond assumptions at this level. These interpretations constitute a starting point towards highlighting the effect of CO_2 on the char properties and formation mechanisms.

4. Synthesis

Introducing CO_2 in the pyrolysis process atmosphere causes additional mass decay of the residual solid by 10 to 13% compared to pyrolysis in pure N_2. This mass decay can be explained either by char gasification by CO_2, which overlapped with the biomass pyrolysis, or by the fact that CO_2 hinders polymerisation reaction and secondary char formation by reacting and breaking some tar compounds that may lead to its formation. The mass decay is associated with an increase in the final permanent gas yield. With regard to the char ultimate analysis, the CO_2 seems to have an affinity to react with hydrogenated and oxygenated groups, leading to a more carbon-rich char, as amounts of these element decreased in the CO_2-char. Finally, we observed an almost sixfold increase in char specific area. These observations are probably well correlated. In Fig. 12, we propose a representation of the potential effect of CO_2 when introduced in the pyrolysis bath gas and its interaction with the pyrolysis products.

The following scenario could be assumed as an interpretation for the different experimental observations and literature findings:

During the pyrolysis process, the CO_2 reacts with tars and enhances their cracking into light gases. This results in an increase in the gas yield and a reduction in tar polymerisation, which is behind the secondary char formation. A more homogeneous carbon-rich char with an enhanced microporosity is obtained. The TPO experiments tend to confirm this assumption: the TPO profile in the case of the CO_2-char is best described by a single reaction pathway, while the N_2-char exhibits several peaks, one of which may be imputable to the secondary char (carbon deposit). This carbon deposit is likely to contain a significant amount of hydrogenated and oxygenated groups and is probably deposited at the entry of the char pores, resulting in a lower surface area of the char.

5. Conclusion

CO_2 clearly has an influence during the biomass fast pyrolysis process. Its effects can be seen at two main levels: the pyrolysis gas yield and composition, and the char yield and properties. Introducing CO_2 induces an increase in CO concentration of the pyrolysis gas as a result of homogeneous and heterogeneous reactions of CO_2 with gases, tars and char. The char produced is also different and has high specific surface compared to a char obtained in N_2 atmosphere. TPO experiments show more than a single char oxidation peak in the N_2 char and sustain the assumption of tar polymerisation and secondary char formation. The CO_2 would appear to impede the secondary char formation and hinder tar polymerisation reactions.

Acknowledgements

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Appendix A. Determination of the heat transfer coefficients in the M-TG and HTR reactors

We drilled a steel ball of 1 cm diameter and inserted a thermocouple (K-type) at its centre. The ball was then placed in the basket that normally bears the biomass sample and introduced in the reactor the same way as in pyrolysis experiments. The temperature gradient inside the steel ball is negligible with a Biot number inferior to 0.1 and is therefore considered to be isothermal. An overall energy balance on the steel ball gives:

$$\rho_b \times V_b \times Cp_b \times \frac{dT}{dt} = h_{global} \times S_b \times (T_b(t) - T_\infty) \quad \text{(A.1)}$$

The ball's temperature evolution with time is given by:

$$\frac{T_b(t) - T_\infty}{T_b(0) - T_\infty} = exp\left(\frac{h_{global} \times S_b}{\rho_b \times V_b \times Cp_b} \times t\right) \quad \text{(A.2)}$$

The thermal time constant τ or characteristic time, representing the required time for the ball to reach 63% of the environment temperature is defined by:

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$$\tau = \frac{\rho_b \times V_b \times Cp_b}{h_{global} \times S_b} \quad (A.3)$$

τ is determined experimentally. Knowing the physical characteristics of the steel ball, we can calculate the global heat transfer coefficient h_{global} according to the previous formula. The validity of this method can be verified by calculating the Biot number which represents the ratio of the internal thermal resistance to the boundary layer thermal resistance and must be inferior to 0.1:

$$Bi = \frac{h_{global} \times d_b}{\lambda_b} \quad (A.4)$$

The Biot numbers are respectively 0.06 and 0.09.

The heat transfer inside the two reactor occurs by convection and radiation. The global heat transfer coefficient is the sum of a convective and a radiative heat transfer coefficient:

$$h_{global} = h_{conv} + h_{rad} \quad (A.5)$$

To determine the contribution of each mode to the global heat transfer, we calculated the convective heat coefficient and determined the radiative coefficient by difference. The convective heat transfer coefficient is given by:

$$h_{conv} = \frac{Nu \times \lambda_{N_2}}{d_b} \quad (A.6)$$

where $\lambda_{N_2}[W/m\,K]$ and d_b[m] are respectively the thermal conductivity of nitrogen at the reactor temperature and the steel ball diameter. The Nusselt number can be determined by the Whitaker correlation for flow over a spherical body [15]:

$$Nu = 2 + 0.4 \times (Re^{0.5} + 0.06 \times Re^{2/3}) \times Pr^{0.4} \quad (A.7)$$

where Re and Pr are respectively the Reynolds and the Prandlt numbers given by:

$$Re = \frac{\rho_{N_2} \times u_\infty \times d_b}{\mu_{N_2}} \quad (A.8)$$

$$Pr = \frac{\mu_{N_2} \times Cp_{N_2}}{\lambda_{N_2}} \quad (A.9)$$

where u_∞[m/s] is the average gas velocity, $\mu_{N_2}[Pa\,s]$ the nitrogen dynamic viscosity and $Cp_{N_2}[J/kg\,K]$ the nitrogen specific heat capacity.

Appendix B. Determination of the particle heating rate in the M-TG and HTR reactors

For a biomass particle introduced in the reactor hot zone,its surface heating rate at $t = 0$ can be calculated following the next relation [16]:

$$\beta_0 = \frac{\partial T}{\partial t}|_{t=0} = (T_\infty - T_{w,0}) \times \frac{h_{global}}{L_0 \times \rho_w \times Cp_w} \quad (B.1)$$

where L_0 [m] is the characteristic size, $\rho_w = 710$ [kg/m^3], $Cp_w = 1500$ [J/kg K] and $\lambda_w = 0.18$[W/m K] are respectively the wood density, specific heat value and conductivity. These physical properties are estimated from the literature [3].

References

[1] Basu Prabir. Biomass gasification and pyrolysis, practical design and theory. Elsevier; 2010.
[2] Di Blasi Colomba. Combustion and gasification rates of lignocellulosic chars. Progr Energy Combust Sci 2009;35(2):121–40.
[3] LI CHEN. Fast Pyrolysis of millimetric wood particles between 800 °C and 1000 °C. PhD thesis, Université Claude Bernard - Lyon 1, 2009.
[4] Mermoud F, Salvador S, Van de Steene L, Golfier F. Influence of the pyrolysis heating rate on the steam gasification rate of large wood char particles. Fuel 2006;85:1473–82.
[5] Zhang Huiyan, Xiao Rui, Wang Denghui, He Guangying, Shao Shanshan, Zhang Jubing, et al. Biomass fast pyrolysis in a fluidized bed reactor under N^2, CO^2, CO, CH^4 and H^2 atmospheres. Bioresour Technol 2011;102(5):4258–64.
[6] Kwon Eilhann E, Jeon Young Jae, Yi Haakrho. New candidate for biofuel feedstock beyond terrestrial biomass for thermo-chemical process (pyrolysis/gasification) enhanced by carbon dioxide (CO^2). Bioresour Technol 2012;123:673–7.
[7] Kwon Eilhann E, Yi Haakrho, Castaldi Marco J. Utilizing carbon dioxide as a reaction medium to mitigate production of polycyclic aromatic hydrocarbons from the thermal decomposition of styrene butadiene rubber. Environ Sci Technol 2012;46(19):10752–7.
[8] Hanaoka Toshiaki, Sakanishi Kinya, Okumura Yukihiko. The effect of N^2/CO^2/O^2 content and pressure on characteristics and CO^2 gasification behavior of biomass-derived char. Fuel Process Technol 2012;104(0):287–94.
[9] Jamil Kawser, Hayashi Jun-ichiro, Li Chun-Zhu. Pyrolysis of a Victorian brown coal and gasification of nascent char in CO^2 atmosphere in a wire-mesh reactor. Fuel 2004;83(7-8):833–43.
[10] Gao Song-ping, Zhao Jian-tao, Wang Zhi-qing, Wang Jian-fei, Fang Yi-tian, Huang Jie-jie. Effect of CO^2 on pyrolysis behaviors of lignite. J Fuel Chem Technol 2013;41(3):257–64.
[11] Borrego AG, Garavaglia L, Kalkreuth WD. Characteristics of high heating rate biomass chars prepared under N^2 and CO^2 atmospheres. Int J Coal Geol 2009;77:409–15.
[12] Gil MV, Riaza J, Ivarez L, Pevida C, Pis JJ, Rubiera F. Oxy-fuel combustion kinetics and morphology of coal chars obtained in N^2 and CO^2 atmospheres in an entrained flow reactor. Appl Energy 2012;91(1):67–74.
[13] Rathnam Renu Kumar, Elliott Liza K, Wall Terry F, Liu Yinghui, Moghtaderi Behdad. Differences in reactivity of pulverised coal in air (O^2/N^2) and oxy-fuel (O^2/CO^2) conditions. Fuel Process Technol 2009;90(6):797–802.
[14] Guizani C, Escudero Sanz FJ, Salvador S. The gasification reactivity of high-heating-rate chars in single and mixed atmospheres of H^2O and CO^2. Fuel 2013.
[15] Fundamental of heat and mass transfer. DON Fowley; 2011.
[16] Lede Jacques. Biomass pyrolysis: comments on some sources of confusions in the definitions of temperatures and heating rates. Energies 2010.
[17] Jeguirim Mejdi, Trouve Gwenaelle. Pyrolysis characteristics and kinetics of arundo donax using thermogravimetric analysis. Bioresour Technol 2009;100(17):4026–31.
[18] Guerrero M, Ruiz MP, Alzueta MU, Bilbao R, Millera A. Pyrolysis of eucalyptus at different heating rates: studies of char characterization and oxidative reactivity. J Anal Appl Pyrol 2005;74:307–14.
[19] Ahmed I, Gupta AK. Characteristics of cardboard and paper gasification with CO^2. Appl Energy 2009;86(12):2626–34.
[20] Gilbert P, Ryu C, Sharifi V, Swithenbank J. Tar reduction in pyrolysis vapours from biomass over a hot char bed. Bioresour Technol 2009;100(23):6045–51.
[21] Zhang Li xin, Matsuhara Toru, Kudo Shinji, Hayashi Jun ichiro, Norinaga Koyo. Rapid pyrolysis of brown coal in a drop-tube reactor with co-feeding of char as a promoter of in situ tar reforming. Fuel 2011(0).
[22] Sutton D, M Parle S, H Ross JR. The CO^2 reforming of the hydrocarbons present in a model gas stream over selected catalysts. Fuel Process Technol 2002;75(1):45–53.
[23] Klinghoffer Naomi B, Castaldi Marco J, Nzihou Ange. Catalyst properties and catalytic performance of char from biomass gasification. Indus Eng Chem Res 2012;51(40):13113–22.
[24] Marsh Harry, Rodriguez-Reinoso Francisco. Activation processes (thermal or physical). Oxford: Elsevier Science Ltd.; 2006 [Chapter 5].
[25] Rodringuez-Reinoso F, Molina-Sabio M, Gonzalez MT. The use of steam and CO^2 as activating agents in the preparation of activated carbons. Carbon 1995;33(1):15–23.
[26] Mohamed Abdul Rahman, Mohammadi Maedeh, Darzi Ghasem Najafpour. Preparation of carbon molecular sieve from lignocellulosic biomass: a review. Renew Sust Energy Rev 2010;14(6):1591–9.

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