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The gasification reactivity of high-heating-rate chars in single and mixed atmospheres of H_2O and CO_2

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A B S T R A C T

Gasification reactivity of high heating rate chars (HHR chars) in steam, carbon dioxide and their mixtures was investigated in a new macro TG experimental device. The higher reactivity of the HHR chars was highlighted by a comparison with reference chars prepared at a low heating rate (LHR chars). It was found that the char reactivity in a mixed atmosphere of steam and carbon dioxide can be expressed as the sum of the individual reactivities obtained in single atmosphere gasification experiments. This result was not dependent on the pyrolysis heating rate. In addition, gas alternation gasification experiments for both HHR chars and LHR chars showed that gasifying the char with CO_2 up to 30% of conversion does not affect its reactivity to H_2O. Altogether, the results tend to indicate that the two reactant gases H_2O and CO_2 react on separate active sites when mixed atmospheres are used, and that CO_2 does not affect the char structure to favor or inhibit the char H_2O gasification reaction.

1. Introduction

Both industrialized and developing countries are today intensifying their work on the development of renewable energies. This increasing interest is a response to the unavoidable depletion of fossil fuels and to continuous and alarming environmental problems, especially global warming. Global warming is a direct consequence of the increasing concentration of greenhouse gases in the atmosphere, particularly CO_2, whose concentration has risen drastically since the industrial revolution [1].

The conversion of biomass to energy is considered to be a pathway towards clean and renewable energy production, because of the availability of the resource and the carbon neutral feature of the thermochemical processes [2].

Among these thermochemical processes, biomass gasification is gaining further interest as it allows the production of clean fuel gases (e.g. H_2, CO, CH_4) that can be used either to produce electricity and heat or as an input stream to produce chemicals or transportation biofuels [3].

Biomass gasification can be processed with various gasifying reagents like air, steam or carbon dioxide [4]. Using carbon dioxide in such a process would provide a long term solution to mitigate its increasing concentration in the atmosphere. The CO_2 will be then incorporated in a valorisation cycle for the production of marketable fuels, rather than simply being captured and stored.

The biomass gasification reaction includes three main steps: pyrolysis, volatile matter reforming and char gasification. The char gasification reaction is considered to be the limiting step of the process because it is kinetically slow compared to the two other steps.

A huge amount of studies can be found in the literature, as well as very good reviews on char gasification in steam or carbon dioxide containing atmospheres [4–6]. Still, the majority of these studies do not tackle the issue of char gasification in mixed atmospheres; only a few do so, and these are performed mainly on coal char gasification.

Their conclusions differ from one study to another; some authors concluded that adding the carbon dioxide alongside the

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steam slows down the gasification reaction: (i) by ***inhibition*** and competition for the same carbon active sites [7 9]. For instance, in their work on coal char gasification, Robert and Harris measured the gasification reaction rate in single and mixed atmosphere of H_2O and CO_2 in a thermogravimetric apparatus and concluded that the presence of CO_2 reduces the rate of the C H_2O reaction [7].

Others think that the two gases operate on separate active sites: (ii) by ***passive cooperation*** [10 12]. The work of Everson et al. describes this assertion well [11]. The authors studied the gasification reactions of coal chars in a TG apparatus with different atmosphere compositions and concluded that the char gasification reaction with mixtures of CO_2 and H_2O is best described by the sum of the single reaction rates. The same observation was made in the work of Chen et al. on sewage sludge char gasification in a fluidized bed [13]. The authors again found that the reaction rate in a mixture of CO_2 + H_2O is well represented by the sum of the individual reaction rates.

Other researchers think that there is a kind of (iii) ***synergy or active cooperation*** between the two gases that leads to an enhanced char reactivity [14,15]. For instance, Tagutchou [14] found that adding CO_2 alongside steam leads to enhanced char reactivity which is superior to the sum of the individual reactivities obtained respectively with steam and carbon dioxide. A more detailed literature review and discussion is presented later in this paper as an approach for an extended experimental plan.

The different findings and conclusions in the literature make it difficult to draw a clear conclusion on the unfolding of the gasification reaction in a mixed atmosphere of H_2O and CO_2. The present work was thus performed with the aim to further understand the reaction mechanisms of biomass gasification in mixed atmospheres of steam and carbon dioxide.

2. Materials and methods

2.1. Macro TG experimental device

The new Macro TG experimental device (Fig. 1) consists of three major parts:

- The heating system, including a liquid H_2O evaporator, a gas preheater and an electrically heated alumina reactor.
- The gas flow control system consisting of 3 mass flow meters/controllers.
- The weighing system that comprises an electronic scale, a stand and a platinum basket.

The 2 m long, 75 mm i.d. alumina reactor is electrically heated. The temperatures of the three reactor zones (high, medium and low) are independently controlled to ensure good temperature homogeneity throughout the furnace.

Gas flow rates are controlled by means of mass flow meters/controllers. Before entering the reaction zone, the reactant gases (N_2, CO_2 and H_2O) are preheated up to the reactor temperature. When H_2O is added in the gasification medium, the H_2O + gas mixture passes first through an electrically heated evaporator maintained at 180 °C to vaporize the water. The reacting gas flow inside the reactor is laminar and flowing at an average velocity of 0.2 m/s.

The weighing system comprises a set of electronic scales with an accuracy of ±0.1 mg, a metallic stand placed over the balance, on which are fixed three ceramic hollow tubes with a length of 1 m and a 2.4 mm external diameter. These ceramic tubes hold up a platinum basket with a 50 mm diameter, a solid bottom and a side wall made from a 500 μm grid to allow the gas to pass through it. The biomass samples are placed into it and are then pyrolysed and gasified in the hot furnace.

The weighing system can be moved in the vertical direction using a crank handle. The platinum basket can hence be introduced into the hot furnace within less than 15 s.

Altogether, the macro TG experimental device has the advantage of being of a far greater experimental scale than conventional TG devices. This makes sample representativity better because an average result for several woodchips is obtained for each run. The wood chips or char particles are not ground as they use to be when the gasification was performed in a classic TG device. This is important because the size reduction process leads to modifications in the structural and chemical composition, loss of fibrous texture and heterogeneous dispersion of catalytic minerals, which vary according to the biomass particle size range [16]. This would affect the biomass reactivity data, which may not be representative of the raw biomass. Moreover, the biomass particles are submitted to a thermal shock similar to that endured when they are introduced in a fluidized bed.

Finally, to our best knowledge, it is not possible to perform isothermal gasification experiments in a classic TG device without preheating the char sample to the desired temperature over a considerable time. This thermal treatment has an impact on the char reactivity. In fact, It has been widely demonstrated for several biomasses such as maize stalk, rice straw, cotton straw, rice husk, Brazil Nut shells and eucalyptus that the char reactivity decreases with thermal treatment as a result of morphological modifications encompassing the evolution of the level and type of porosity and the average pore size [17 21]. The char structure becomes increasingly condensed and ordered when increasing the heat treatment temperature and duration. This thermal annealing phenomenon would surely distort the real char reactivity data. On the contrary, in our case, the biomass sample is introduced into the reactor within 15 s. The pyrolysis takes less than 1 min to be fulfilled.

2.2. Biomass feedstock and char preparation

2.2.1. Biomass feedstock

The biomass feedstock (beech wood chips) was provided by a company called SPPS (France). The woodchips were firs sieved to select particles with a size ranging between 4 and 5 mm and a thickness of 1 2 mm.

The size and thickness of biomass particles may greatly influence the rate of the gasification reaction if they impact on the heat and mass transfer inside the particle [6,22]. In a recent study [23,14], the authors demonstrated that the gasification rate was not influenced when varying the char particle size in the range of 10.5 15 mm. The influencing characteristic dimension was rather the particle thickness, as it slowed down the reaction rate by 1.6 times when it was increased from 1.5 to 6 mm for a constant size of 10.5 mm. No differences were observed between thicknesses of 2.5 and 1.5 mm, which suggests that the reaction is chemically controlled below a 2.5 mm particle thickness. On the basis of these observations and of the similarities between the raw biomasses used (beech wood chips) and between the experimental devices (Macro TG), we performed the gasification reactions with biomass and char particles having a size in the range of 4 5 mm and a thickness of about 1 2 mm.

2.2.2. Experimental procedure for char preparation and gasification

A mass of wood chips of 0.8 1 g is introduced in the platinum basket; the biomass particles are spaced widely enough to avoid chemical and thermal interactions. After heating the reactor to the desired temperature, the weighing system is lifted up using the crank handle; the platinum basket containing the wood chips is introduced into the hot furnace in less than 15 s. The biomass

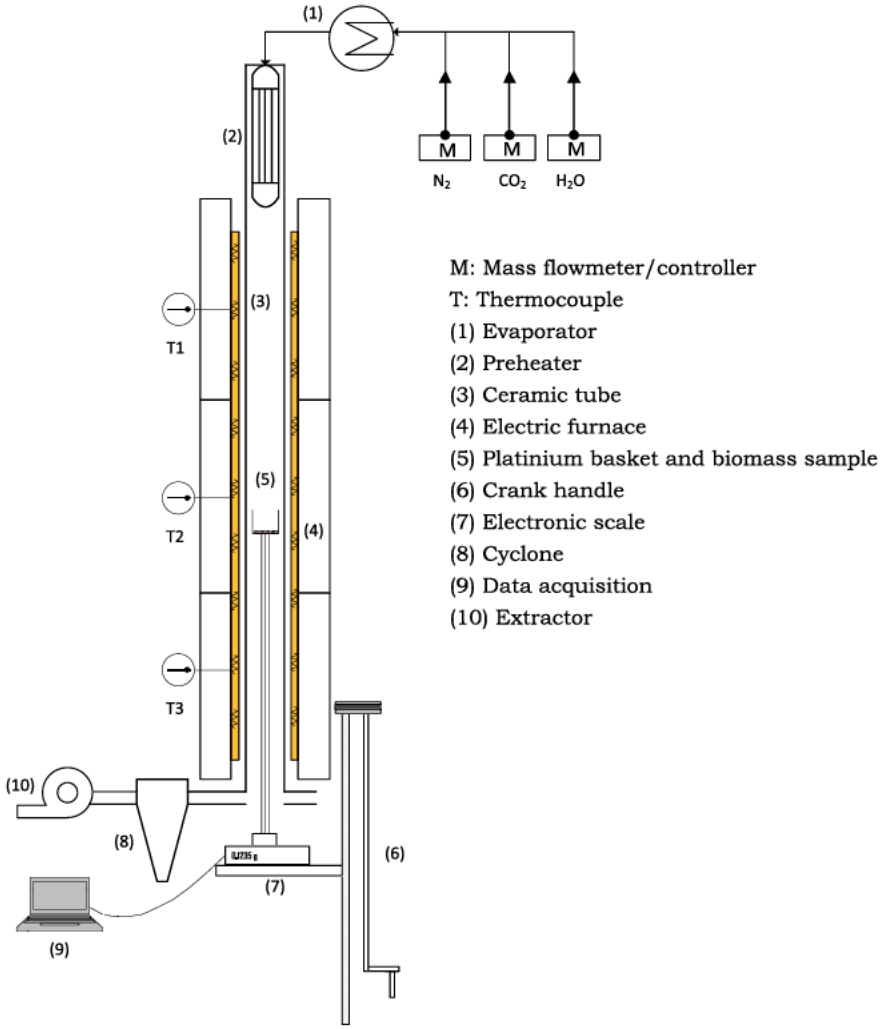

Fig. 1. Macro-TG experimental device scheme.

is firstly pyrolysed in a flow of nitrogen until reaching a constant mass, corresponding to the char. This procedure produces special chars prepared at a high heating rate which was estimated to be around 100 K/s [24]. When the mass of char is stabilized, the displayed weight on the electronic scales is reinitialized to zero and the reactant gas flow is established, marking the beginning of the char gasification stage. When introducing the reacting gas (CO_2 or H_2O) alongside the nitrogen, we observe a flow deceleration effect (gas pressure on the platinum basket) on the force registered by the scales. This effect is corrected afterwards in the data processing phase. The mass of char begins to decrease progressively until it reaches a plateau corresponding to the end of the experiment. The weighing system is then moved downwards using the crank handle and the residual ashes are weighed after cooling. Following this procedure, we can obtain an accurate value for the mass of char that was converted during the gasification reaction.

The study focuses mainly on the gasification of biomass chars prepared at a high heating rate in the Macro TG device, as described in the previous paragraph. However, in order to highlight the higher reactivity of these "HHR chars" (in terms of reactivity towards H_2O and CO_2), we also conducted gasification experiments with chars prepared at a low heating rate "LHR chars".

These LHR chars were obtained after a slow pyrolysis in a retort furnace with a heating rate of 5 °C/min up to 550 °C and a residence time at the final temperature of 30 min. The slow pyrolysis was performed under a nitrogen flow of 2 Nl/min. The LHR char samples were then cooled to room temperature and stocked in a sealed recipient for gasification tests in the M TG device. With a low heating rate, the char yield was about 24.8%, whereas it was much lower with a high heating rate. It decreased slightly when increasing the reaction temperature, from 9.89% at 850 °C to 7.87% at 950 °C. These results were expected in view of previous studies on biomass pyrolysis [25,19,4].

Table 1 lists the results of the proximate and ultimate analysis of the raw biomass wood chips, the LHR chars and the HHR chars obtained at three temperatures. The results are reported on a dry basis.

The ash content rose with an increase in the pyrolysis heating rate, due to lower char yields and little devolatilisation of the mineral species. One can note that the fuel nitrogen remained in the char. The concentrations of hydrogen and oxygen decreased with an increase in the temperature.

2.2.3. Experimental conditions and data analysis method

The gasification experiments were performed at atmospheric pressure with operating conditions similar to those encountered in fluidized bed gasifiers. The reactor temperature was in the range of 800 950 °C and the gasifying medium partial pressure in the

Table 1
Proximate and ultimate analysis of the biomass samples (dry basis).

	Proximate analysis (%)			Ultimate analysis (%)			
	VM	Ash	FC	C	H	O	N
Wood chips	88.1	0.4	11.6	46.1	5.5	48.1	0.10
LHR-Char	20.03	1.88	78.09	82.06	2.85	12.88	0.30
HHR-char 850 °C	–	3.75	–	83.51	0.86	11.60	0.28
HHR-char 900 °C	–	4.14	–	85.56	0.80	8.42	1.04
HHR-char 950 °C	–	4.15	–	85.83	0.91	8.07	1.05

range of 0.1 0.3 atm. Table 2 gives the operating conditions for the different gasification experiments.

2.2.4. Method of data analysis

The normalized mass or conversion ratio 'X' during the gasification reaction is calculated according to:

$$X_{(t)} \quad \frac{m_{(0)} \quad m_{(t)}}{m_{(0)} \quad m_{(\mathrm{ash})}} \tag{1}$$

where m_0, $m_{(t)}$ and m_{ash} are respectively the initial mass of char, the mass at any time "t" and the mass of the residual ash.

The gasification experiments were reproduced 2 5 times and showed a good repeatability with deviation less than 12%, which is considered acceptable regarding the heterogeneity of the wood material. Mass loss data curves were firstly smoothed using a polynomial least square function covering a fixed time period before and after each point. Precautions were taken for restoring smoothed data, with high fidelity to the experimental results. These data were then used to calculate the instantaneous reactivity of the char throughout the gasification.

Reactivity data were obtained following the next equation:

$$R_{(X)} \quad \frac{1}{m_{(t)}} \frac{dm_{(t)}}{dt} \quad \frac{1}{1 \quad X_{(t)}} \frac{dX_{(t)}}{dt} \tag{2}$$

The char undergoes structural modifications throughout the gasification reaction due to phenomena such as pore enlargement, coalescence or blocking. This leads to variations in the number of carbon active sites $C_t(X)$ available for the gasifying agents. The reactivity, which is a function of temperature, gas partial pressure and available reactive surface, is therefore continuously changing during the gasification. It is consequently expressed by means of a chemical kinetic term accounting for temperature and partial pressure effects $R(X)_{(}T, P_i)$, and a reactivity profile $F(X)$ that aims to describe the effects of available reactive surface.

The reactivity must therefore refer to a specific conversion level. Reactivities at 10% or 50% of char conversion are often used for the determination of the kinetic parameters; the latter is actually the most commonly selected parameter in several similar investigations [26,27,7]. In our study, reactivity at 50% conversion level is taken as a reference. Assuming that the structural function does not depend on the temperature and pressure ranges of the gasification experiments, the reactivity can be expressed as follows:

$$R_{(T,P_i,X)} \quad R(50)_{(T,P_i)} \times F(X) \tag{3}$$

An nth order kinetic model following the Arrhenius law for the reactivity temperature dependence and a power law for the reactivity gas partial pressure dependence is considered for the determination of the kinetic parameters of the steam and carbon dioxide gasification reactions. The reactivity at 50% conversion level is given by:

$$R(50)_{(T,P_i)} \quad k_{(T)} \times P_i^n \tag{4}$$

$$k_{(T)} \quad A \exp\left(\frac{E}{RT}\right) \tag{5}$$

The reactivity profile expression can be developed from general structural models such as uniform conversion models, shrinking core models, grain models or random pore models that may contain one or more parameters to adjust so as to match the parameters of the experimental data [6]. It is however worth noting that the structural modifications are not solely responsible for the reactivity change throughout the gasification. Other factors intervene, such as the char inner mineral species concentration and types [28 30,25,31], the thermal annealing phenomena occurring in parallel with the gasification reaction [32], and also the type of gasifying media, as it has been demonstrated that the char contact with the steam drastically changes its structure into a more ordered one [33 35]. Owing to these observations and to the difficulties in determining the individual contribution of each of these parameters on the gasification reactivity, we opted for a determination of an empirical formulation for the structural term $F(X)$ which is assumed to encompass all the influencing parameters that cause the reactivity change along the gasification reaction.

The structural function $F(X)$, which is a normalized reactivity, can be calculated at any conversion level as follows:

$$F(X) \quad \frac{R(X)}{R(50)} \tag{6}$$

In the literature, the ratio $\frac{R(X)}{R(ref)}$ is calculated within a conversion level range where experimental errors are, in the author's appreciation, acceptable. For instance, some authors referred to a (0.2 0.8) conversion range with a reference at X 0.2 [36], others chose ranges between (0.2 0.8) and (0.15 0.9) with a reference reactivity at X 0.5 [26,23]. In our study, $F(X)$ is determined in the conversion level range of 0.2 0.9. This range was selected to minimize weight measurement uncertainties at the small mass loss in the early stages of the reaction (X 0 0.2), and to avoid high reactivity values as the mass goes to zero in the final stages of the gasification reaction (X 0.9 1). A 5th order polynomial regression is applied to the experimental X and $F(X)$ data to determine the reactivity profile.

Table 2
Operating conditions of the gasification experiments.

Reacting medium	Reacting gas partial pressure (atm)	Temperature (°C)
H_2O	0.1, 0.2, 0.3	800, 850, 900, 950
CO_2	0.1, 0.2, 0.3	850, 900, 950
H_2O/CO_2	0.1/0.1;0.1/0.2; 0.2/0.1	900

3. Results and discussion

In this section we shall first present results of HHR char gasification in single atmospheres containing H_2O or CO_2 and then determine the intrinsic kinetic parameters and the reactivity profiles for each case. The high reactivity of the HHR chars will be also highlighted through a comparison with LHR chars. Finally we shall take a comprehensive, experiment based approach to the understanding of the mechanisms involved in char gasification in mixed atmospheres of steam and carbon dioxide.

3.1. HHR char gasification in single atmospheres of steam and carbon dioxide

To determine the kinetic parameters and the reactivity profiles for the H_2O and CO_2 char gasification reactions, we performed experiments in which we varied the gas partial pressure at constant temperatures and vice versa. Although all the possible combinations of temperature and gas partial pressure were tested, in the following sections we present only some results of reference experiments.

3.1.1. Char H_2O gasification experiments

3.1.1.1. Influence of the temperature and H_2O partial pressure on the char H_2O gasification reaction. Fig. 2a and b illustrate respectively the effect of the temperature and steam partial pressure on the H_2O char gasification rate.

The influence of temperature was evaluated in the range of 800 950 °C. Fig. 2a shows the char conversion versus time in gasification experiments with 20% H2O in the gasifying medium at 800, 850, 900, and 950 °C. Increasing the temperature from 800 to 950 °C reduced the time required for 90% conversion by a ratio of more than fivefold.

A temperature of 900 °C was taken as a reference to evaluate the role of H_2O partial pressure in the char H_2O gasification reaction. A conversion level of 90% was reached respectively after 220, 330, and 580 s with H_2O concentrations of 30%, 20%, and 10% in the gasifying medium. That is to say, increasing the H_2O concentration from 10% to 30% results in 2.5 times higher char reactivity.

3.1.1.2. Determination of kinetic parameters for the H_2O char gasification reaction. Adopting an *n*th order model and a reference reactivity at 50% of conversion provides a set of linear equations when taking the logarithm of both sides of Eq. (4) for the different temperatures and H_2O partial pressures.

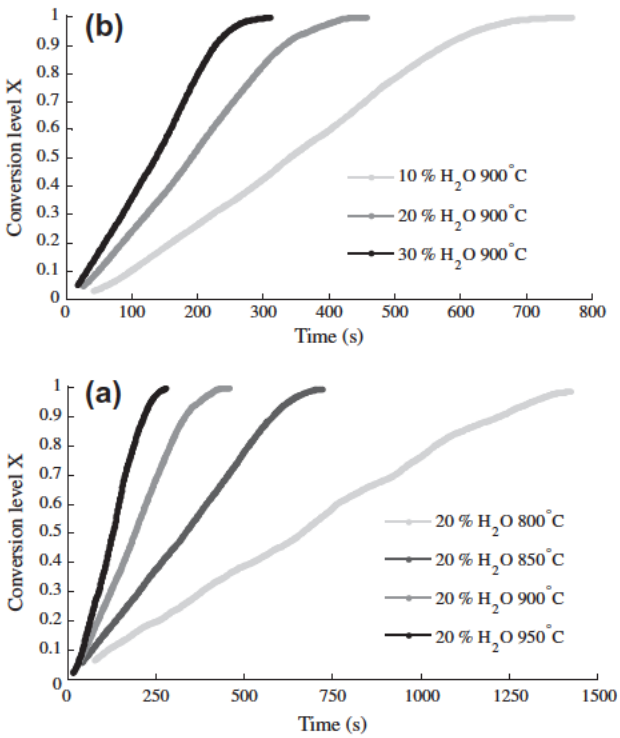

Fig. 2. Influence of the temperature (a) and steam partial pressure (b) on the char gasification rate.

$$Ln(R_{50}) \quad ln(A) \quad \frac{E}{R}\frac{1}{T} + nln(P_{H_2O}) \tag{7}$$

The set of equations was put in a matrix form to determine *A*, *E* and *n* with a minimization of the error according to the least squares method. The logarithm of R_{50} is plotted versus the inverse of the temperature in Fig. 3 to illustrate the temperature dependence of the reactivity following an Arrhenius law for the different steam partial pressures.

The linear dependence of the logarithm of R_{50} on the inverse of the temperature was verified with a good correlation. Similarly, the dependence of the logarithm of R_{50} on the steam partial pressure for the different gasification temperatures was also verified. The correlation coefficient is superior to 0.99, thus validating the proposed model. The derived kinetic parameters are respectively: E 139 kJ/mol, A 26.30×10^3 s ^{1} bar ^{n} and n 0.64. A comparison of the char reactivity with literature data is shown in Fig. 4 for a steam partial pressure of 0.2 atm. The conversion level at which the reactivity is calculated is indicated on the figure with the references.

The derived kinetic parameters are in accordance with recent studies on steam beech char gasification. Moreover, the activation energy and the reaction order are in the range of the values reported in Di Blasi's review for biomass char steam gasification reactions, i.e. 40 240 kJ mol ^{1} for '*E*' and 0.4 1 for '*n*' [4].

3.1.1.3. Determination of the reactivity profile F(X) H_2O. Reactivity profiles for the different H_2O char gasification experiments are plotted in Fig. 5. Except for a few irregularities, probably due to the measurement uncertainties, all reactivity profiles are monotonically increasing functions and almost superposed.

The temperature and H_2O partial pressure would not therefore seem to affect the reactivity evolution tendency in the studied range of parameters. The average of the functions obtained for the different gasification experiments can be expressed through:

$$F^{H_2O}_{(X)} \quad 0.008230X^5 + 0.02038X^4 + 0.11367X^3 + 0.23074X^2 + 0.56013X + 1.12488 \tag{8}$$

The weak influence of the temperature and H_2O partial pressure on the shape of the reactivity profile was also observed by [23] whereas in Barrio's study there was a clear influence of the temperature on the reactivity profile, especially in the final stages of conversion, as the function decreased with an increase in the temperature. This can be imputable to mineral species loss or accentuated thermal annealing of the char which exhibited a lower reactivity [37].

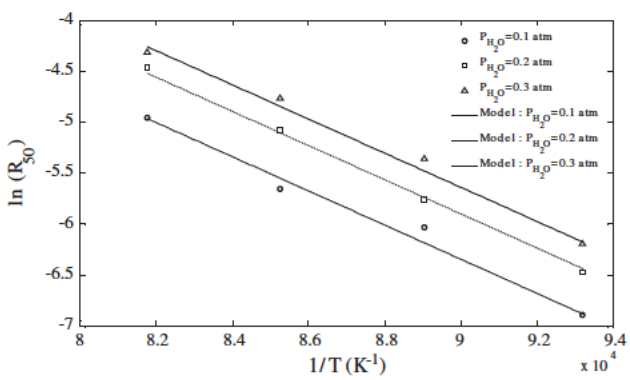

Fig. 3. Arrhenius plots for H_2O gasification of HHR-chars.

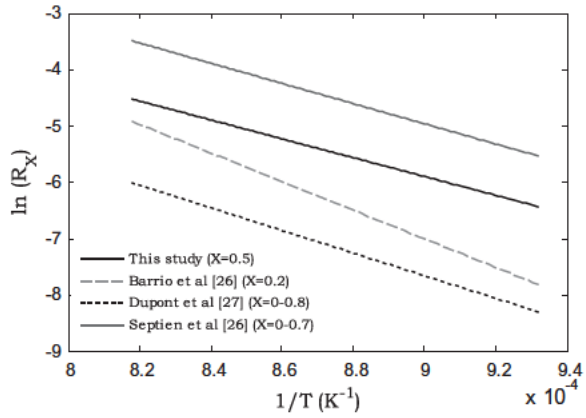

Fig. 4. Literature review on the reaction kinetics of the gasification of beech chars with steam (P_{H2O} = 0.2 atm).

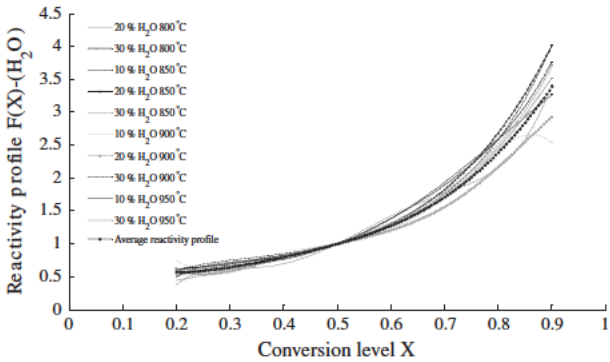

Fig. 5. Reactivity profile $F(X)$ in the H_2O–char gasification experiments.

3.1.2. Char CO_2 gasification experiments

3.1.2.1. Influence of the temperature and CO_2 partial pressure on the char CO_2 gasification reaction. Fig. 6a and b illustrate respectively the effect of the temperature and CO_2 partial pressure on the CO_2 char gasification rate. Experiments with CO2 partial pressure of 0.2 atm were taken as references to evaluate the role of the tem perature. As shown in Fig. 6a, increasing the temperature by 100 °C reduced the time required for a 90% conversion by more than 3.5 times.

The results of the char gasification experiments at a reference temperature of 900 °C with CO_2 partial pressure ranging from 0.1 to 0.3 atm illustrate the effect of the CO_2 partial pressure on the gasification rate. Increasing the CO_2 concentration in the gasifying medium from 10% to 30% allows 50% of char conversion to be reached in almost half the time. 90% conversion times are respec tively 800, 590, and 460 s in gasifying atmospheres containing 10%, 20%, and 30% of CO_2. Similar trends were found at 850 °C and 950 °C.

3.1.2.2. Determination of kinetic parameters for the CO_2 char gasifi cation reaction. The same procedure as for steam gasification was followed to determine the kinetic parameters for the char CO_2 gas ification reaction. Fig. 7 shows the Arrhenius dependence of the char reactivity on the temperature for the different CO_2 partial pressures. The linear dependence between the logarithm of R_{50} and the reciprocal temperature is verified with a good correlation. The solid lines in the Arrhenius represent the calculated reactivity in the temperature range of the study.

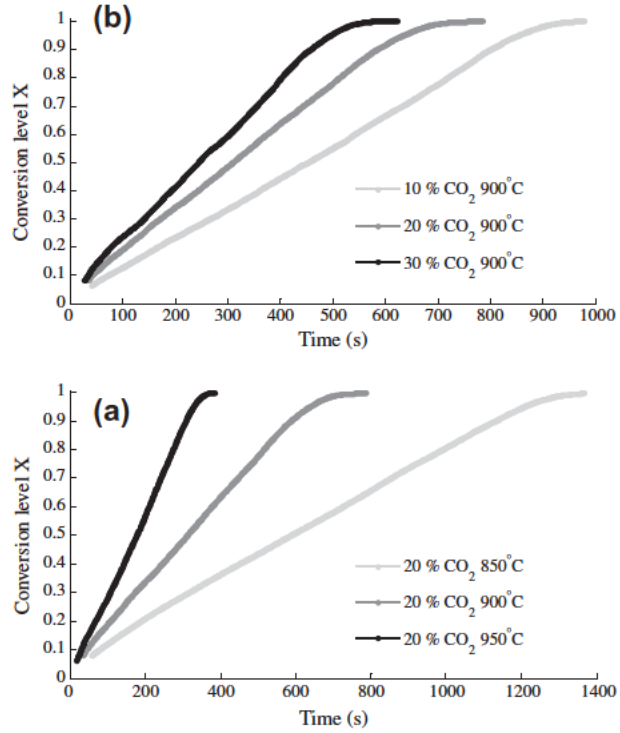

Fig. 6. Influence of the temperature (a) and CO_2 partial pressure (b) on the char gasification rate.

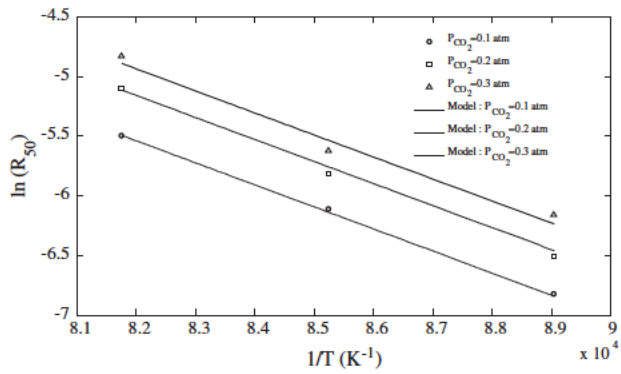

Fig. 7. Arrhenius plots for CO_2 gasification of HHR-chars.

Likewise, we obtained a linear dependence of the logarithms of R_{50} and CO_2 partial pressure at the different gasification tempera tures. The results are not plotted here.

The model is also verified for CO_2 gasification experiments with a very good determination coefficient R^2 0.996. The derived ki netic parameters are: E 154 kJ/mol, A 55.18 × 10^3 s^{-1} bar^{n} and n 0.55, which are in the respective value ranges reported in Di Blasi's review for biomass char CO_2 gasification reactions [4].

3.1.2.3. Determination of the reactivity profile $F(X)$ CO_2. Fig. 8 shows the reactivity profiles obtained for the CO_2 char gasification exper iments at different temperatures and CO_2 partial pressure. The char reactivity increases with the gasification; this reactivity tendency is typical of the majority of biomass chars in contrast with that of coal chars, which decreases as the conversion level increases [38].

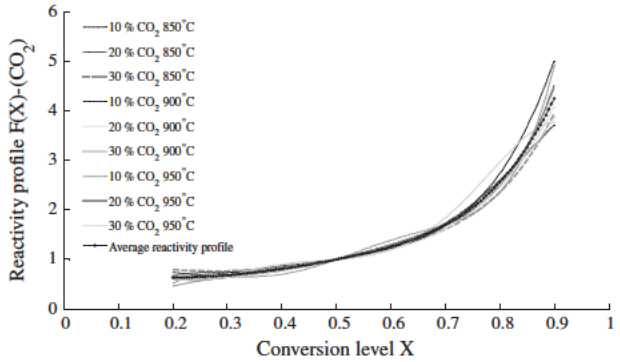

Fig. 8. Reactivity profile $F(X)$ in the CO_2–char gasification experiments.

Apart from small discrepancies, all the reactivity profiles are superposed. Neither the temperature nor the CO_2 concentration affects the reactivity profile. The reactivity profile is clearly related to other phenomena such as the structural modifications and the increasing concentration of minerals in the biomass char, as suggested in many similar studies. Weak effects of the temperature and CO_2 partial pressure on the reactivity profile were observed in the work of Vandesteene et al. [23], while the temperature clearly affected the reactivity profile for birch char gasification experiments, as presented elsewhere [36].

The average of the obtained functions in the different gasification experiments has the following expression:

$$F^{CO2}_{(X)} \quad 0.014422X^5 + 0.081024X^4 + 0.1379X^3 + 0.2142X^2 + 0.5254X + 1.1175 \qquad (9)$$

3.1.3. HHR chars high reactivity

In order to highlight the higher reactivity of the HHR chars, we performed gasification experiments under respectively 20% of steam and 20% of CO_2 at 900 °C with the beech char particles prepared with a low heating rate (5 °C/min). The results are plotted in Fig. 9 in terms of average reactivity calculated in the conversion range of 20–90%. The effect of the heating rate is clear, as the HHR char reactivity was more than 3.5 times higher in 20% of steam than for the LHR char in the same operating conditions. Similarly, the LHR char reactivity in an atmosphere containing 20% CO_2 was estimated at 0.001 g/(g s) while it was 4.3 times higher for the HHR char in the same operating conditions.

These results are in accordance with the literature [25,19,39], although the effect of the heating rate on the char reactivity is much more pronounced in the present study than in that of Guerrero et al. [19] for eucalyptus char gasification, and comes close to the observations made by Mermoud et al. [25].

In the work of Guerrero et al. [19], the increase in the char reactivity with the HR was not as marked as in the present work or in that of Mermoud et al. [25]. Mermoud et al. found that the char yields under low and high heating rates were respectively 24.3% and 14.2% with an increase in the ash amount when increasing the heating rate. The effect of the heating rate on the char reactivity with steam was as significant as it is in the present work, since the HHR char reactivity was 2.6 times higher than that of the LHR char. The authors concluded that besides the more porous structure obtained in HHR chars, the mineral species seems to play a crucial role.

In the present work, the HHR chars exhibited high gasification rates which may be imputable to two main factors: the small particle thickness and the high pyrolysis heating rate. The former factor minimizes the mass transfer limitations while the second leads to a highly porous char having a mineral content more than twice as high as that of LHR char. These combined parameters are known to greatly enhance the char reactivity.

3.2. Char gasification in mixture of $H_2O + CO_2$

In order to study the effect of introducing the CO_2 as a co-reactant alongside steam, we performed gasification experiments at 900 °C with a steam concentration of 10% and a CO_2 concentration increasing from 0% to 30%. Conversion levels versus time plots are shown in Fig. 10.

The CO_2 introduction clearly enhances the reaction rate. 90% conversion time was about 580 s with 10% H_2O and no CO_2 in the gasifying medium but decreased with the increase in the CO_2 concentration in the input gas to 215 s with a CO_2 molar fraction of 30%. The evolution of the char average reactivity calculated in the conversion range of 20–90% with the increasing CO_2 concentration is illustrated in Fig. 11. The average reaction rate with 20% of CO_2 introduced alongside steam was twice that of free CO_2 gasification experiments with only 10% steam in the gasifying medium.

It is clear that the introduction of the CO_2 would not inhibit the gasification reaction, as proposed elsewhere [7]. This assumption is not valid for the present gasification experiments.

To gain greater understanding of the gasification reaction in the CO_2/H_2O mixture, we compared the char reactivity obtained in mixed atmospheres with the sum of the reactivities obtained in single atmosphere experiments for the same steam and carbon dioxide partial pressures.

Reactivity curves in the conversion range of 20–90% are plotted in Fig. 12. Apart from small discrepancies probably due to experi

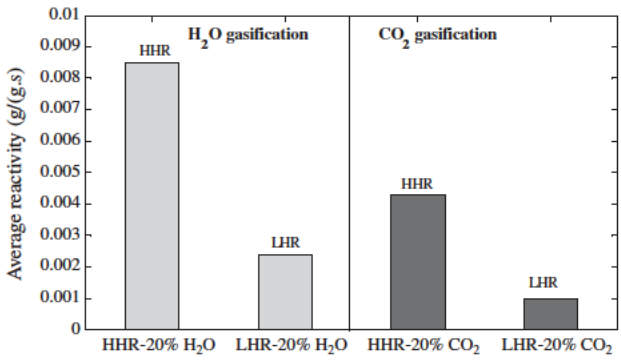

Fig. 9. HHR and LHR char average reactivity at 900 °C.

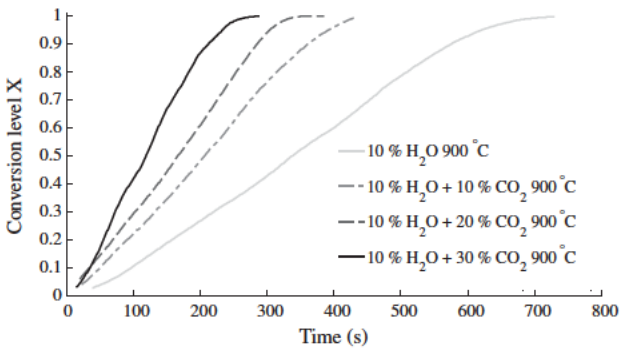

Fig. 10. Effect of the CO_2 co-feeding next to steam on the gasification reaction rate.

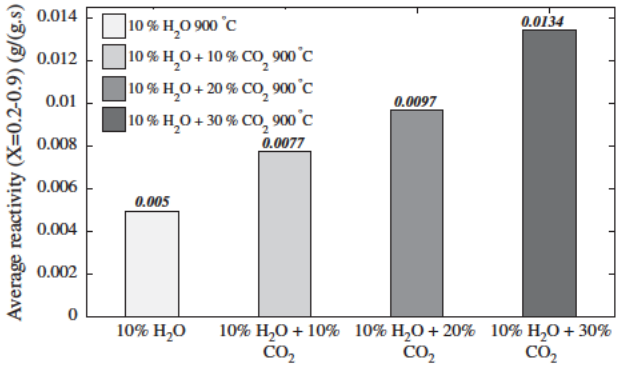

Fig. 11. Char average reactivity evolution with the increasing amount of CO_2 introduced next to 10% steam.

mental errors, an additive law is valid to describe char gasification under mixed atmospheres.

A first *a priori* conclusion would be that H_2O and CO_2 are operating on separate active sites (Passive cooperation). Nevertheless, this observation may be due to two opposed actions resulting in an "apparent additive law". To further interpret this result, we propose in the next section a detailed reflexion based on a literature review and on additional gasification experiments.

3.2.1. On the understanding of the char gasification reaction in mixed atmospheres of $CO_2 + H_2O$

3.2.1.1. Literature review and discussion. Concerning the mechanisms involved in the char gasification reaction in mixed atmospheres, three main assumptions are held in the literature:

CO_2 and H_2O gasification reactions occurring on common active sites (Inhibition): In a previous study on coal char gasification, the authors observed that the char reactivity decreased when adding CO_2 alongside steam and concluded that there was a competition between the two gases for the access to the carbon active sites [7]. Although the chars are different (coal and biomass chars) which may lead to different results, the authors limit their observations to the first 10% of char conversion, which is not representative of the overall gasification reaction. The coal char may exhibit a different behavior beyond 10% of conversion, mainly when pores open more widely and gasification spreads homogeneously through the particle. In a more recent study, the authors found the char H_2O gasification reaction was independent of the char CO_2 reaction, while the latter is inhibited by the former [9]. Others proposed a model based on a partial sharing of active sites. The two gases are competing in part of the active sites, while reacting separately in their own ones [8].

This assumption is clearly not valid regarding the result of the present study. Other studies on coal char gasification showed that there was no inhibition between the gasifying agents, but rather a passive cooperation on separate active sites [11,10,34]. This will be discussed in the next paragraph.

CO_2 and H_2O gasification reactions on separate active sites (Passive cooperation): The model of passive cooperation assumes that the two gases react on separate active sites without influencing each other. In their study on coal char gasification, Bliek et al. [12] found that the overall carbon conversion rate in the presence of CO_2 and H_2O is the sum of the single char reactivities. This assumption was also held by Tay et al. [34] for coal char gasification. The authors found that the gasification rate in mixed atmospheres of $O_2 + H_2O + CO_2$ was approximately equal to the sum of the gasification rates in the respective single atmospheres. They suggest that the additivity in

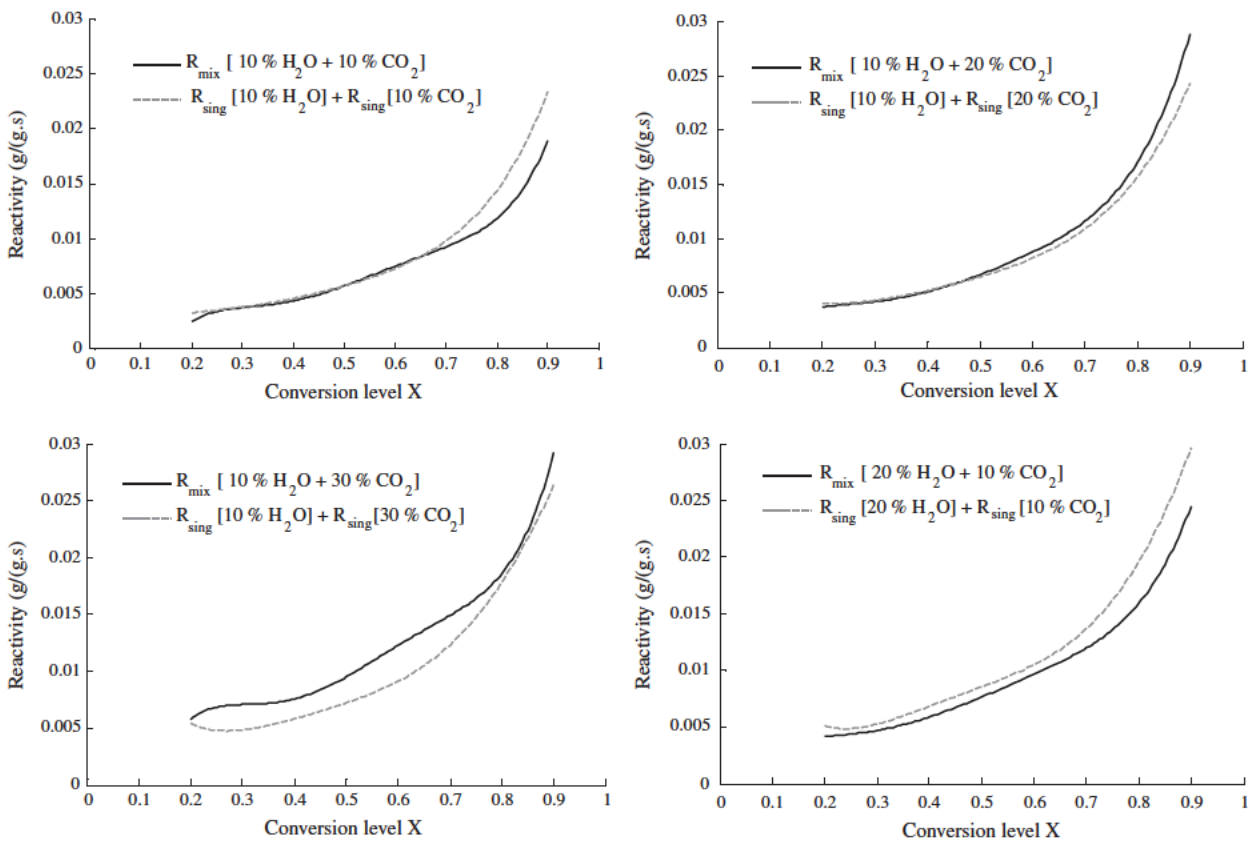

Fig. 12. Comparison of the HHR-char reactivity in mixed atmosphere with the sum of the single reactivities for different gasifying medium composition at 900 °C.

char conversion rates means that O_2, H_2O and CO_2 do not compete for the same active sites on the coal char but are rather operating on separate active sites. Similar conclusions can be found elsewhere for the coal char gasification reaction in mixed atmospheres containing CO_2 and H_2O [11,10]. In both of these studies, 2 models based on the assumptions of char CO_2 and char H_2O reactions occurring on common and separate active sites were tested. The model assuming reactions on separate active sites fitted the experimental results well, whereas the model assuming competition for the same carbon active sites under predicted the experimental results.

Minkova et al. [40] also performed gasification experiments of birch wood, straw and miscanthus pellets in non isothermal conditions (HR 10 °C/min) up to a temperature of 750 °C with a residence time of 2 h, and found that the yield of solid product is lower in a mixed atmosphere of $CO_2 + H_2O$ than with steam only, which means that the CO_2 is also participating in the global gasification reaction. They also observed that the $CO_2 + H_2O$ gasification environment leads to a more developed pore structure and surface area, which is merely the result of an advanced stage of the biomass gasification reaction.

In a more recent study on sewage sludge gasification in a fluidized bed, the authors found that the reaction rate in a mixture of $CO_2 + H_2O$ is well represented by the sum of the individual reaction rates obtained with CO_2 and H_2O individually [13].

Synergy between CO_2 and H_2O (Active cooperation): This model assumes that besides reaction on separate active sites, there is an active cooperation between the gases for the accessibility to the carbon active sites. At least one of the reactants is supposed to act in a certain way as to enhance the char reactivity towards the second gas. Such an action can be, for example, the creation of additional porosity, as proposed by Butterman and Castaldi [15], or the retention of catalytic mineral species inside the char, as mentioned elsewhere [34].

Recently, in their study on pine char gasification, Tagutchou et al. [14] proposed a model where the CO_2 and H_2O cooperate together for accessibility to the carbon active sites. The authors found that the char reactivity in a mixed atmosphere was higher than the sum of the reactivities obtained in single atmospheres of CO_2 and H_2O. They concluded that a cooperative effect of the two reactants with char gasification reactions occurred on separate active sites, but they did not go further into the understanding of the mechanisms involved.

Butterman and Castaldi [15] also think that CO_2 alongside steam may lead to an enhanced reactivity, as it could further develop the porosity inside the char particle and provide a greater reactive surface. The authors performed gasification experiments on several biomasses in a TG apparatus with a heating rate of 10 °C/min and observed that the total number of pores during CO_2 thermal treatment was an order of magnitude greater than that observed during H_2O/N_2 processing. Even the range in pore sizes was much more extended with CO_2 (2 50 μm) than with steam (10 20 μm). They also observed that the gasification was completed when introducing 30% of CO_2 with the steam, while a black char residue remained when using only steam as a gasification medium.

As regards the results obtained in the present study, the most plausible assumption would be that the two reactants are operating in separate active sites without any kind of synergy. Still, we cannot draw a definitive conclusion without taking into consideration the observations of Tagutchou et al. [14] and Butterman and Castaldi [15]. For this reason, we performed two other types of char gasification experiments: (i) with LHR chars, so as to come closer to Tagutchou's experimental conditions in terms of HR, (ii) char gasification experiments with gas transition, wherein the char is firstly operated with CO_2 up to a defined conversion level and then gasified with steam to see if the CO_2 influences the char

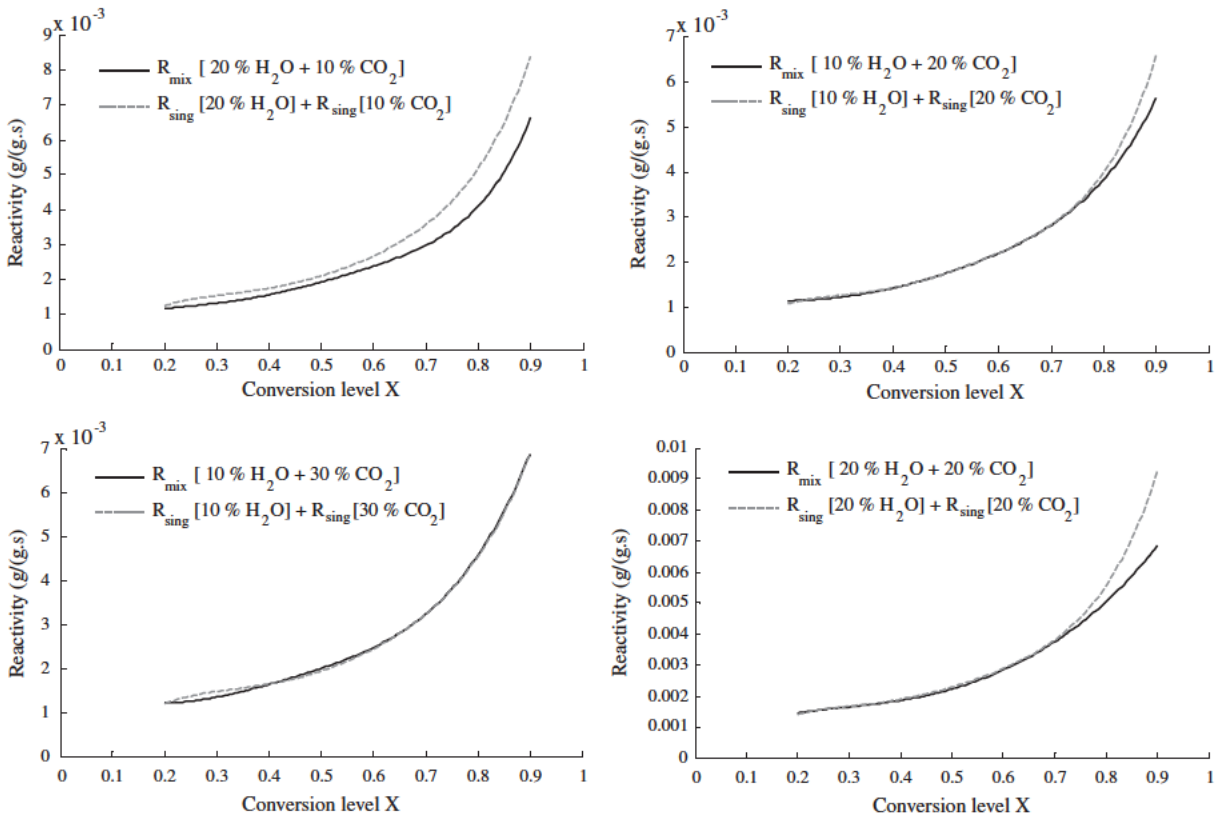

Fig. 13. Comparison of the LHR-char reactivity in mixed atmosphere with the sum of the single reactivities for different gasifying medium composition at 900 °C.

physical properties and consequently impacts its reactivity toward steam.

3.2.2. Reactivity of LHR chars in mixed atmospheres of $H_2O + CO_2$

Unlike in our experiments, Tagutchou et al. used char particles with a greater thickness (5 mm) and prepared with a relatively low heating rate (60 °C/min) in a screw pyrolysis reactor. Unsurpris ingly, the differences in operating conditions for the char prepara tion led to chars with different reactivities and morphological features (available reactive surface and pore opening). Chars pre pared at a high heating rate already have their pores open and present a high surface area, whereas those prepared at a low heat ing rate have a less developed reactive surface and a narrower por ous network [39,19,25].

We performed additional gasification experiments with LHR char in mixed atmospheres of steam and carbon dioxide to see if the additivity of single reactivities is valid for LHR chars. The re sults are plotted in Fig. 13.

The reactivity curves obtained in mixed atmospheres match very well with those of the added single reactivities, except for a small deviation observed for the gasifying atmosphere composed of 10% CO_2 + 20% H_2O. Additivity of reactivities is again a valid assumption for the LHR char. The heating rate would therefore only impact the reaction rate but not on the reaction mechanisms in a mixed atmosphere. Other authors found that the contributions of the char H_2O reaction and char CO_2 reaction in the global mixed atmosphere reaction rate remained the same indepen dently of the pyrolysis heating rate [9]. This is in accordance with our findings.

If we assume that there is no influence from the type of biomass (pine and beech wood), we believe that in Tagutchou's work, it is more likely that it is the char particle thickness that influences the global reaction rate and the mixed atmosphere gasification mechanisms. Because of internal diffusion limitations for the CO_2 molecules, due to a greater particle thickness (5 mm) in compari son with the present case, the enhancement of the gasification reaction observed by Tagutchou in mixed atmosphere conditions may be due to the fact that the steam gasification reaction further developed the char's internal porosity and ameliorated the access of the CO_2 molecules to the heart of the char particle, which re sulted in an apparent reactivity that was greater than the sum of the respective single reactivities.

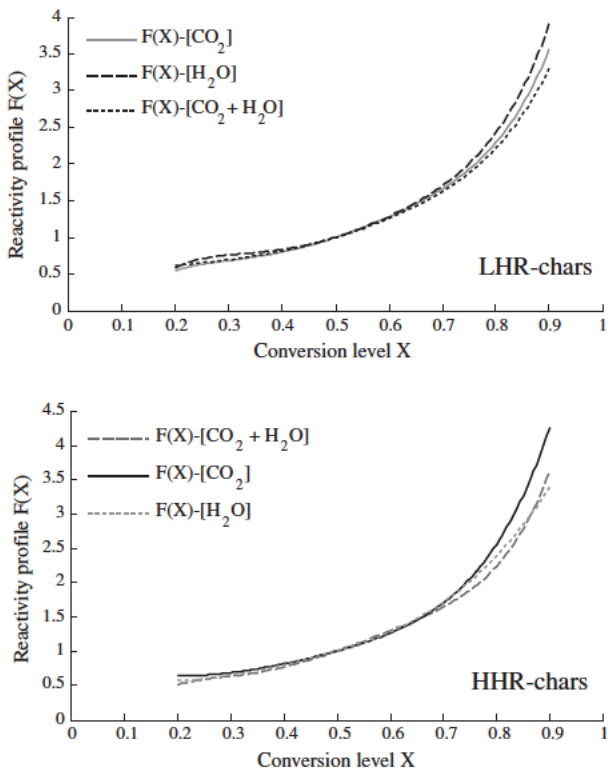

Fig. 14. Comparison of the average reactivity profiles for steam and carbon dioxide gasification experiments.

The additive law would therefore be valid as long as the char particle is thin enough to prevent internal diffusion limitations to ward the CO_2 molecules. This possible explanation must be further investigated by comparing the effect of the particle thickness respectively on the H_2O and CO_2 gasification reaction rates.

Another fact worth noting is that the average reactivity profiles for H_2O, CO_2 and mixed atmosphere gasification experiments for HHR and LHR chars are practically the same, except for some devi ations for higher conversion levels that can be attributed to mea surement uncertainties, as depicted in Fig. 14.

This tendency was not observed, for example, by Tagutchou et al. [14,23] who found different reactivity profiles for CO_2 and H_2O gasification experiments. The authors observed that the H_2O reactivity profile showed a continuous increase throughout the conversion while the CO_2 reactivity profile did not go beyond the value of 1 until a conversion level of 80%, from which it began to increase. In other words the char reactivity did not increase in the range of 50 80% of conversion. This may be due to the limited access of the CO_2 molecules to the heart of the char particle, de spite the advanced gasification stage. In the present study, the sim ilarity of the reactivity profiles may be imputed to the absence of internal diffusion limitations due to the particle's lower thickness. Once again, this assumption needs to be investigated further.

3.2.3. Gas alternation gasification experiments

The aim of such experiments is to verify whether or not there is a kind of synergy, as claimed by Butterman et al. [14,15], that leads in the present case to an apparent additive law. The CO_2 is first introduced as a gasifying reagent to establish whether or not it cre ates additional porosity and further develops the reactive surface for H_2O. The unfolding of this type of experiment comprises three stages:

- Char gasification with CO_2 up to a certain conversion level.
- Stopping the CO_2 flow, stabilization of the mass and purge of the reactor under N_2.
- Introduction of steam and pursuance of the gasification reaction up to total conversion.

The first experiment was performed on a HHR char that was gasified with 20% CO_2 up to a conversion level of 28% and subse quently operated with 10% of steam. The second one, on a LHR char, was performed with 20% of CO_2 up to a conversion level of 35% followed by steam gasification with a steam concentration of 20% in the gas flow. Fig. 15a and b illustrate the unfolding of these experiments. On these figures are plotted reference char reactivi ties obtained in single atmospheres of steam and carbon dioxide (gray and black solid lines) and the char reactivity in the gas alter nation experiment (black dashed line).

For the HHR and LHR chars, in the first stage of the gas alterna tion experiment, the char reactivity curve naturally follows the ref erence curve obtained under a CO_2 containing atmosphere. No results are reported during the gas transition zone. We can clearly see on the two figures that the char reactivity curve in the H_2O gasification stage re joins the reference curve obtained with the reference steam containing atmosphere. If the CO_2 had changed the char's properties, we would have seen an enhancement or a de crease in the char's reactivity towards H_2O; it is not the case here.

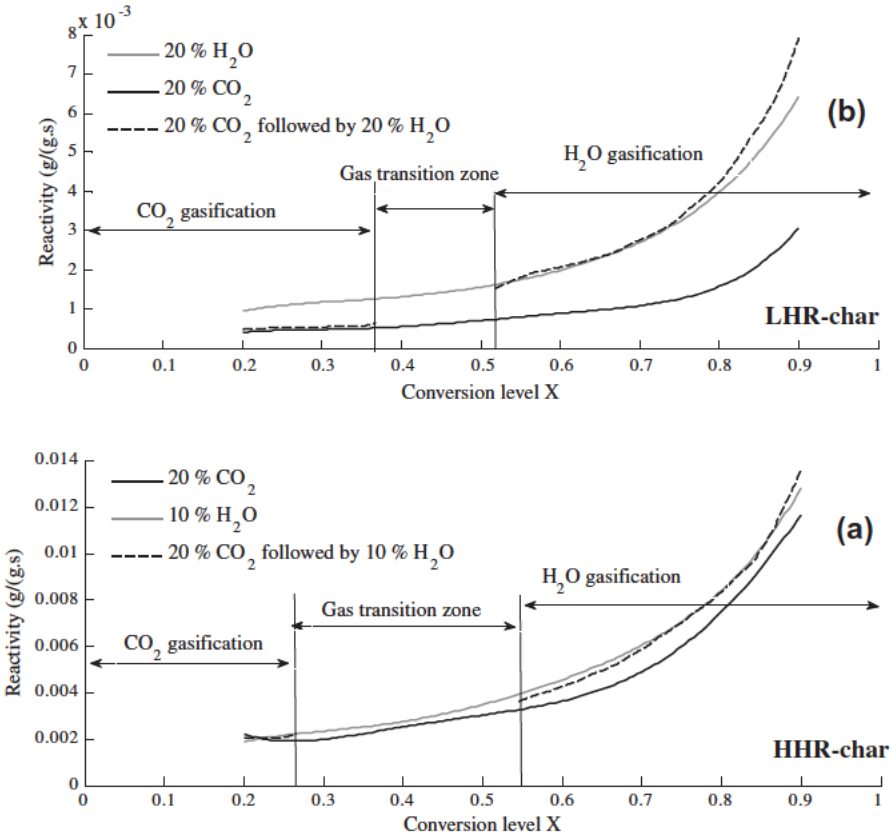

Fig. 15. HHR-char (a) and LHR-char (b) gasification experiments with alternance of CO_2 and H_2O at 900 °C.

On the basis of these observations, the most likely explanation for the observed additive law would be that the CO_2 and H_2O are operating on separate active sites without any kind of synergy. This conclusion is to be taken with precaution, as there can be other phenomena when the two gases are reacting simultaneously. Nonetheless it constitutes a step forward in the understanding of the mechanisms involved in char gasification in mixed atmospheres.

Finally, the observation of Butterman and Castaldi [15] concerning the incomplete char burnout with only steam as reactant may be a consequence of an ordering of the carbon structure due to the thermal annealing that is promoted by the contact with steam, as proposed elsewhere for coal and biomass char gasification [33,34]. Introducing 30% of CO_2 would have overcome the structural ordering of the carbon matrix as the rate of the gasification reaction would then be higher than that of the carbon ordering and result in complete char burnout.

For our study, in view of the results obtained and the literature review and discussion, the char reactivity in a mixed atmosphere of $CO_2 + H_2O$ can be written as the sum of the single reactivities:

$$R_{H_2O+CO_2} \quad R_{H_2O} + R_{CO_2} \tag{10}$$

4. Conclusion

The new macro TG experimental device allowed us to perform gasification experiments on beech chars prepared at high heating rates. These experimental conditions are of interest as they come close to those encountered in fluidized beds. The fast pyrolysis was followed directly by gasification experiments without additional heating of the char particle to the gasification temperature, as is usually done in conventional TG devices. Reliable kinetic data were obtained for HHR char gasification reactions with H_2O and CO_2 and can be used for the design and optimization of fluidized bed gasifiers.

The heating rate greatly affects the char reactivity to H_2O as well as to CO_2. The HHR char reactivity was 3.5 times higher in H_2O gasification and greater than fourfold with CO_2 in comparison with LHR chars.

Introducing CO_2 alongside steam resulted in a higher reactivity of the beech char, regardless of the pyrolysis conditions (low or high heating rate). For a HHR char, increasing the CO_2 concentration from 0% to 30% in a 10% steam containing atmosphere resulted in a 2.7 times higher char reactivity.

A comprehensive approach was established in order to clarify further the mechanisms involved in mixed atmosphere gasification reactions. The present work demonstrates the validity of an additive law reflecting a passive cooperation of steam and carbon dioxide in the gasification reaction. Specific experiments carried out in this work showed that converting a char under CO_2 to approximately X 30% did not affect its reactivity during further conversion under H_2O.

The additive law would appear to be valid as long as the particle is thin enough to prevent diffusional limitation phenomena toward the CO_2 molecules. We believe that the steam gasification reaction would facilitate the access of CO_2 molecules to the heart of the char particle in the case of thick particles, resulting in an apparent enhanced reactivity.

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