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CO_2 gasification of woody biomass chars: The influence of K and Si on char reactivity

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ABSTRACT

Although the influence of metallic and alkaline elements on biomass char reactivity is well known, a quantitative assessment of this catalytic effect is hard to obtain because of the chemical and textural complexity of biomass. The effect of K and Si on the CO_2 gasification reactivity of a biomass char was studied using thermogravimetric analysis. A beech sample was pyrolyzed at 800 °C and then impregnated with known amounts of silicon or potassium allowing to obtain a wide range of K/Si ratios. The reactivity of the impregnated samples was studied under a CO_2 (20% vol.) atmosphere. The results show that at low conversion ratios, the char reactivity depends on its textural properties, with strong diffusional limitations. When conversion reaches 60%, the presence of a catalyst (K) and an inhibitor (Si) becomes the major parameter influencing reactivity. From these experiments, a general trend was obtained between K/Si ratio and reactivity as a function of conversion.

RÉSUMÉ

Mots-clés:
Gazéification au CO_2
Catalyseurs
Bois
Réactivité
Résidu carboné
Potassium
Silicium

L'influence des métaux et des éléments alcalins sur la réactivité des carbones issus de biomasse est connue, mais une analyse quantitative de ces effets catalytiques est difficile à cause de la complexité texturale et chimique de la biomasse. L'effet du potassium et du silicium sur la gazéification au CO_2 d'un carbone obtenu par pyrolyse de bois de hêtre a été étudié par thermogravimétrie. Pour cela, le carbone a été imprégné avec des quantités connues des deux éléments de façon à obtenir des rapports K/Si variés. Les résultats montrent qu'à faible conversion, la vitesse de réaction est principalement liée à la texture, et que des limitations diffusionnelles importantes empêchent l'accès à la surface microporeuse. Pour des taux de conversion supérieurs à 60 %, la réactivité dépend de la présence des catalyseurs et des inhibiteurs. Une corrélation générale entre réactivité et rapport K/Si a pu être démontrée en fonction du taux de conversion.

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1. Introduction:

In recent years, research in the field of renewable energy has become more important. The global energy demand has multiplied by 2.4 within the last 40 years. If this trend continues for the next 40 years, and considering the significant demand of new affluent countries (China and India), the energy consumption could double by the year 2050 [1]. Currently, fossil fuels provide 80% of the energy supply showing the world's dependence on these resources and explaining the growing interest in renewable energy. Among various renewable energies, biomass is considered as a truly renewable source of energy. Biomass refers to all organic materials from living organisms in various ecosystems and products derived therefrom, such as wood, straw, waste wood, etc [2].

Energy can be obtained from biomass through various biochemical and thermochemical processes. There are three main types of thermochemical biomass conversion processes [3]. Combustion is well-established and is widely applied on an industrial scale. Two other thermochemical conversion processes, namely pyrolysis and gasification, are still under development. Biomass gasification is a technology for the production of chemicals and energy from various resources. Gasification, which is still at the demonstration stage, is a flexible process that generates a synthesis gas mainly constituted by H_2 and CO and that could be used in gas engines, turbines, and for the synthesis of liquid or gaseous fuels [4,5]. This process is based on two successive steps. 1) Biomass pyrolysis or devolatilization is the decomposition under the pure effect of heat of biomass and leads to the formation of a solid containing mainly carbon and usually called char and of volatiles containing several compounds such as CH_4, CO_2, CO, water and tars. 2) The gasification reaction of char is a heterogeneous reaction of char with gasifying agents, such as CO_2, H_2O and O_2 and leads to the formation of CO and H_2. This latter reaction is known to be the limiting step under the typical operational conditions of gasifiers like fluidized beds [6]. It is therefore important to know the kinetics of char gasification in order to provide useful data for the gasification reactor design.

Several studies have focused on coal and biomass char reactivity toward CO_2, and some reviews have summarized these results [7,8]. It is known that the reaction of char with the gasifying agent (here CO_2) is accelerated by alkaline and alkaline earth metals (AAEM) and by metals like Ni or Fe [9,10]. There are some publications on the mechanisms of the reaction of carbon with CO_2 catalyzed by AAEM [11,12], but these mechanisms are far from being fully understood. During these investigations, AAEM may be present inherently or added by impregnation to increase the reaction rate. More recently, the growing interest in biomass gasification has led to several studies on this topic. Several investigations have examined the effects of AAEM on the first step of the biomass gasification process. These studies reported that the variability of reactivity observed is due to the inorganic elements present in biomass. In particular, it was shown that potassium, calcium or magnesium has a catalytic effect [13–16]. The problem is nevertheless complex since many parameters may vary from one biomass to another, and even for one biomass depending on its preparation process [17].

In contrast with catalytic effects, some other elements have shown an inhibiting influence on gasification such as silicon [15–20] and phosphorus [21]. It has been proposed that the inhibition mechanism occurs through silicate formation [15]. The results obtained by Dupont et al. have shown the catalytic role of potassium and the inhibiting behavior of silicon and phosphorus in char steam gasification. Authors have shown that the gasification kinetics for high conversions rate seemed to be correlated with the ratio $K/(Si + P)$ which influences strongly the char reactivity profile [21,22].

Very few studies have addressed the influence of potential inhibitors like silicon on the CO_2 gasification process. In a recent investigation, the influence of textural, structural and chemical properties of biomass chars on the CO_2 gasification rate was examined. During this study, various lignocellulosic biomass chars were prepared and their reactivities were evaluated in a thermogravimetric setup under 20% CO_2 in nitrogen at 800 °C. Different behaviors of gasification rate profiles versus conversion were obtained [23]. In particular, it was observed that at high conversion, the alkali index and the average gasification rate seemed to be correlated.

Based on this background, this study focuses on the role of the catalyzed CO_2 gasification of biomass char. The main objectives of the study were: (1) to investigate the catalytic effect of K and Si on char gasification reactivity using non-isothermal thermogravimetric analysis (TGA), (2) to investigate the impact of metal catalysts on the char structure using scanning electronic microscopy (SEM) and (3) to determine the kinetics of metal-catalyzed CO_2 gasification of biomass chars. To reach this goal, samples of beech wood were impregnated with K and Si at various concentrations. The resulting samples were characterized and their reactivities were evaluated.

2. Experimental

2.1. Raw materials

The biomass used in this study was beech wood. The chips used were provided by the company Mallo wood (Reguisheim, France). Beech is a hardwood species, which is widespread in Europe. The wood was obtained as saw dust and it was used without any further grinding for pyrolysis, the particle size ranged between 0.1 and 1 mm with a mean size close to 0.3 mm. Beech wood char was obtained by heating the different samples in a tubular furnace from room temperature to 800 °C at 10 °C/min under argon at a flow rate of 25 NL/h. The sample was kept at this temperature for 1 h before cooling down to the room temperature. The final char particles were similar in size to the pristine wood.

2.2. Preparation and characterization of metal-impregnated biomass and blank samples

The metallic precursors used for impregnation were potassium nitrate (KNO_3) and silicon dioxide (SiO_2). The sample was impregnated with potassium to obtain 0.5 wt%, 1 wt% and 2 wt% K-impregnated samples and with silicon to obtain 0.5 wt%, 1 wt% and 2 wt% Si-impregnated samples. These impregnated chars were called K0.5, K1.0, K2.0 and Si0.5, Si1.0, Si2.0, respectively.

The choice of potassium nitrate for the impregnation is explained by the fact that it provides no additional carbon atoms and therefore no change in the carbon balance at the end of conversion. Also, nitrate can be easily decomposed by a simple increase of temperature. On the other hand, the impregnation with Si was carried out with colloidal silica Ludox 40% wt. This is a suspension of silicon in water. The choice of this precursor was made to prevent any further intrusion of inorganic elements in the composition of biomass. Indeed, by using sodium, calcium or potassium silicate, there would have been inorganic intrusion in the sample of biomass studied and the effect of silicon could not be investigated correctly.

The impregnation with inorganics was inspired by the methodology used in the study by Hwang et al. [24]. However, no acidic treatment was performed in order to avoid any damage of the structure of the char which could influence char reactivity. The impregnation was carried out on the char obtained after heat treatment of the beech sample. A mixture containing 8 mL of anhydrous absolute ethanol and 2 mL of distilled water was prepared and a defined amount of the precursor was added. 500 mg of the char was immersed in the mixture. Each mixture was then placed on a magnetic stirrer at room temperature until evaporation of the solvents. After stirring, the sample was neither filtered nor dried in an oven. The impregnated char was recovered to be characterized. A witness sample was prepared by following the same protocol in an impregnating solution containing no precursor.

2.3. X-ray fluorescence

The amounts of inorganic elements in raw and impregnated samples were measured by using an X-ray fluorescence spectrometer in order to investigate the content in inorganic elements in chars and to verify if they had been correctly impregnated on chars. The spectrometer was of type PHILIPS MAGIX series with a ferryman PW2540 sample changer.

2.4. Textural characterization of raw and impregnated chars

Surface areas were determined from nitrogen adsorption manometry at 77K and isotherms were obtained using an ASAP 2420 apparatus (Micromeritics). Each adsorption measurement was out-gassed overnight at 300 °C prior to analysis. The BET model was applied to the N_2 adsorption data at relative pressures of 0.01–0.05. The sample pore volume was obtained from the amount of N_2 adsorbed at $P/P^0 = 0.95$.

2.5. SEM analyses

Scanning electron microscopy (SEM) was used to investigate the sample morphology. SEM was coupled with EDX (energy dispersive X-ray spectroscopy). The microscope was of type SEM XL30 FEG. The software used for EDX analysis was Oxford INCA Energy with a detector Si (Li). The analyses were done in low vacuum mode without gold coating of the samples.

2.6. Char reactivity measurements

Char samples reactivity was investigated by thermogravimetric analysis (TGA) using a thermoanalyzer SENSYS evo TG-DSC (SETARAM). About 8 mg of char was placed in an alumina crucible of 0.1 mL and the temperature was measured by using a thermocouple placed near the sample. The sample was heated from 25 °C to 800 °C with a heating rate of 24 °C/min under N_2 and then, after stabilization of temperature and mass, the gas was switched to a mixture of 80% N_2 and 20% CO_2 at a 12 NL/h flow rate. Due to the particle size, no diffusion limitation was observed inside the bed.

From TGA measurements, the conversion level at a given time t was obtained according to the equation:

$$X_t = \frac{m_0 - m_t}{m_\mathrm{i} - m_\mathrm{f}}$$

where m_0 is the mass at the beginning of the reaction with CO_2, m_f the final mass and m_t is the mass at time t. The gasification rate r_t was obtained by the derivation $r_t = \mathrm{d}X_t/\mathrm{d}t$.

3. Results and discussion

3.1. Composition and texture of impregnated samples

Fig. 1 presents the results obtained after X-ray fluorescence analysis of the raw char and the impregnated samples with K and Si. As expected for wood (see for instance Vassilev, 2010 [25] and Dupont, 2010 [26]), Fe, Al, P and Mn were found in low quantities in the pristine and impregnated samples while Mg and Ca were found in significant concentration. The concentrations of these six elements were not significantly modified by the different impregnation processes. The data showed that the saturation in the sample impregnated with potassium was reached. Indeed, the K content of the impregnated sample at K1.0 and K2.0 was substantially equal to a concentration of 0.4 wt%. This may be due to the saturation of the surface of the char because it has been covered by a monolayer of catalysts [14]. Saturation could also be explained by the microporous texture of the pristine char sample. The nitrogen adsorption isotherm of beech char was of type 1 (Fig. 2), and showed that the samples exhibit very narrow micropores below 1 nm. It is shown in Table 1 that for K1.0 and K2.0 samples, the major fraction of the pores is plugged, and the surface area decreases from 262 to 30 m^2/g.

For samples impregnated with silicon, a clear difference was observed between the contents of Si at different levels of impregnation indicating that saturation was not reached for this element. The textural properties presented in Table 1 clearly show that the porosity of chars was only slightly affected by the impregnation process. This allows us to make the amount of silicon added to the pristine beech

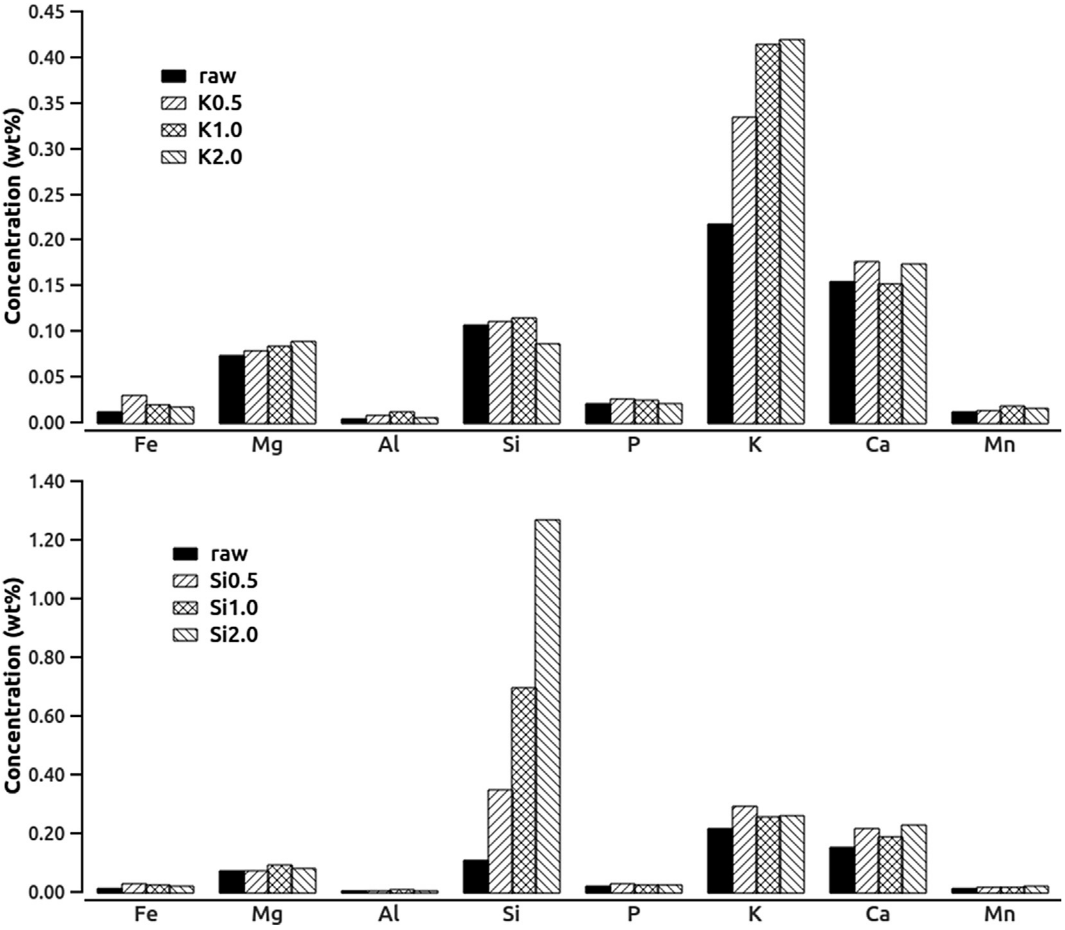

Fig. 1. Fractions of main inorganic elements in char samples. Top: impregnated with K, bottom: impregnated with Si.

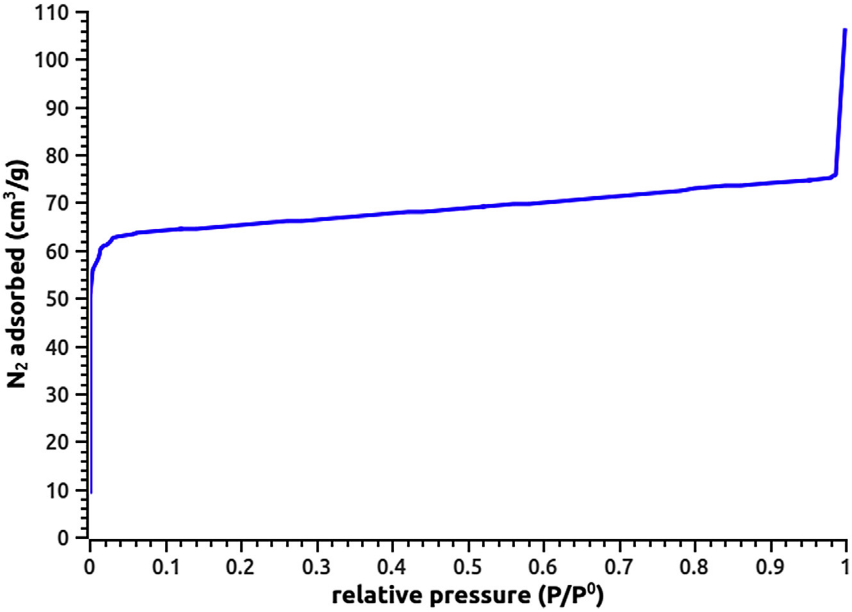

Fig. 2. Nitrogen adsorption isotherm of raw beech wood.

Table 1
Textural and chemical properties of pristine and impregnated char samples.

K samples	K (wt%)	Si (wt%)	K/Si (mass)	S_{BET} (m^2/g)	V_p (cm^3/g)
Beech char	0.22	0.11	2.0	262	0.12
K0.5	0.33	0.11	3.0	219	0.13
K1.0	0.41	0.11	3.7	32	0.02
K2.0	0.42	0.08	5.2	31	0.02
Si0.5	0.25	0.35	0.7	226	0.12
Si1.0	0.29	0.70	0.4	160	0.10
Si2.0	0.26	1.28	0.2	196	0.12

char vary in significant proportions. Then it could be assumed that the silicon content was the only property modified in these chars compared with the pristine beech char.

3.2. Dispersion of elements in the char structure

As shown in Fig. 3, as expected for wood char (reference), macropores are clearly visible. The surface area of the char is 263 m^2/g, which means that the walls of these macropores exhibit some microporosity. EDX mapping of raw char confirms that potassium is well dispersed on the entire matrix. This is not the case for silicon which is concentrated in small micrometer-sized inclusions. Calcium was another catalytic element present in high amounts in the pristine char. The EDX map showed that, as for silicon, calcium was located in micrometer-sized particles, probably as calcium carbonate or as calcium hydroxide. It must be noticed that oxygen mapping showed higher concentrations on the locations of calcium and silicon particles (data not shown). This confirms that calcium and silicon elements are in oxidized form in the pristine char.

After impregnation with potassium, the macrostructure of char was not significantly modified (Fig. 4). Potassium is still well dispersed in char although its concentration has increased from 0.22 to 0.33 wt%. From this EDX analysis and the evaluation of textural parameters after impregnation by KNO_3, we can conclude that potassium forms a layer on the external surface of the char which plugs the micropores of the carbon material.

A similar analysis was done on the char impregnated with silicon Si-1 (Fig. 5). The silicon is also well dispersed on the external surface of the char, but micrometer-sized particles can be detected. These particles should be related to the pristine silicon content of the char (see Table 1). The SEM image in Fig. 5 shows a major difference between K-chars and Si-chars: in the latter case silicon is under the form of very small particles which are dispersed in the macropores of the char. These particles have a size of a few micrometers and do not plug the micropores of the carbon material. This fact explains that the surface area does not significantly decrease after impregnation. As for the pristine char, the analysis of oxygen showed that silicon was present as silica.

A comparison of the pristine char (Fig. 3) and the impregnated ones (Figs. 4 and 5) shows that we are able to obtain a dispersion of K and Si which is very similar to the natural one with our impregnation process. It has been observed nevertheless that beside dispersion, the mobility of added catalysts may be lower than that of naturally occurring catalysts [27]. This may lead to differences between pristine and impregnated chars since the mobility of potassium is a key point for its catalytic activity and for its release at high temperatures.

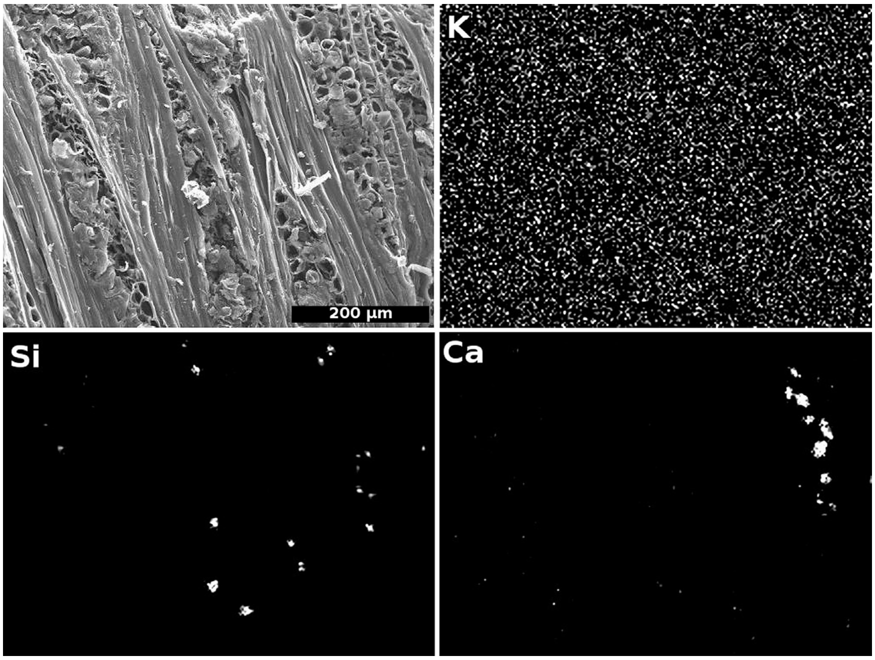

Fig. 3. Scanning electron microscopy image of pristine char, and the corresponding EDX maps of silicon, potassium and calcium.

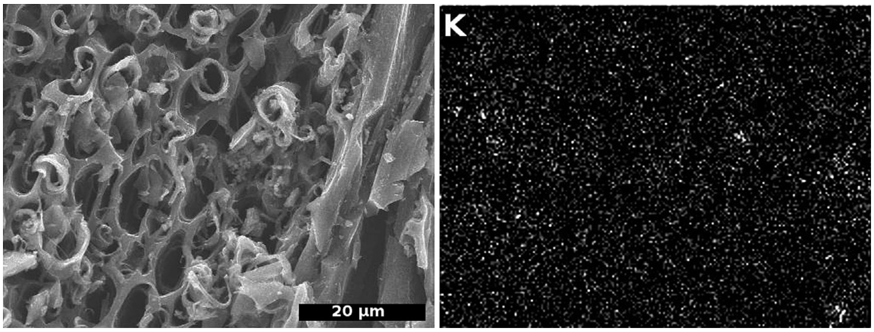

Fig. 4. Scanning electron microscopy images of impregnated sample K0.5 and corresponding EDX mapping for K.

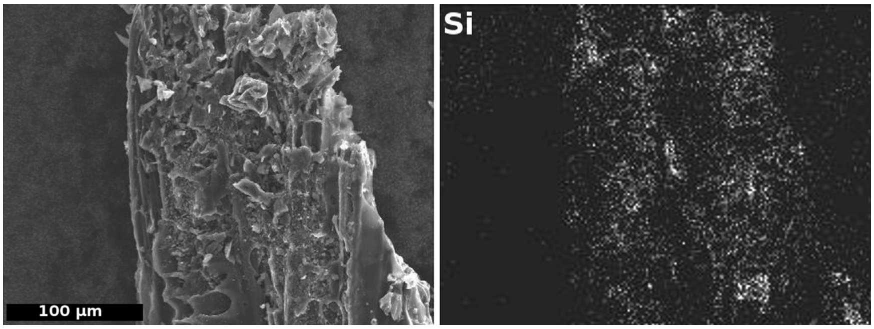

Fig. 5. Scanning electron microscopy images of impregnated sample Si1.0 and corresponding EDX mapping for Si.

3.3. *Catalytic effects of metal on char CO_2 gasification*

For the pristine beech char, the profile of reaction rate as a function of conversion exhibits a shape which was already observed in previous studies on CO_2 gasification under isothermal conditions [14]. The reactivity increases up to 50% of conversion due to an increase of accessible surface area, while the subsequent decrease can be attributed to the collapse of pores or the deactivation of potential catalysts. K and Si are present in the pristine char, and the K/Si ratio is 2.0, as shown in Table 1. Hognon et al. [22] found that for K/Si values higher than 1.0, an activation occurred at high conversion ratios during steam gasification of biomass chars. This shows that the quantitative influences of catalysts and inhibitors on gasification reactions with CO_2 and H_2O are different.

The curves of gasification rate r_t versus conversion for samples impregnated with K and Si are shown in Figs. 6 and 7, respectively. As shown in Fig. 6, for samples impregnated with potassium two successive behaviors were observed:

At low conversion ($X_t < 60\%$), no influence of the potassium concentration could be observed on the rate of the reaction in the range of potassium concentrations tested. Indeed, the difference of reactivity between samples with high K content and those with lower content is not significant. As in many similar experiments, an increase of the reaction rate is observed when the conversion increases up to 50%, which is related to the development of open porosity inside the char structure. Then, the increase of external surface area leads to an increase of reaction rate. The values of r_t are similar for all samples although the BET surface areas are far lower for samples K1.0 and K2.0 compared to the two other chars (raw and K0.5). This behavior shows that the internal surface is not accessible for CO_2, the nitrogen adsorption isotherms were of type 1 and they showed indeed that the micropore size is mainly below 1 nm. Then, we can assume that diffusion limitations would occur for raw and K0.5 samples and only the external surface area is used for gasification. The plugging of micropores for chars K1.0 and K2.0 has then no influence on the gasification rate. This diffusion limitation for CO_2 gasification of biomass chars was already observed for some particle sizes and gasification conditions [28]. In our case, it is strongly related to the very small size of the micropores, which are mainly ultra-micropores (i.e. below 0.8 nm).

At high conversion ($X_t > 60\%$), reaction rates of the samples are significantly different depending on the potassium content of the sample. For the two samples with the lowest potassium content (raw and K0.5), the reaction rate decreases with conversion. This behavior was observed in many cases and may be related to the collapse of pores for $X_t > 50\%$ which would result in a decrease of the external surface area. For the two samples with the highest potassium content (K1.0 and K2.0), the catalytic effect would lead to a continuous increase of reaction rate until the conversion ratio reaches 95%. Several publications have related the reactivity of a set of different biomass to an alkali index, but the correlations are complex since many elements found in the samples may have activating or

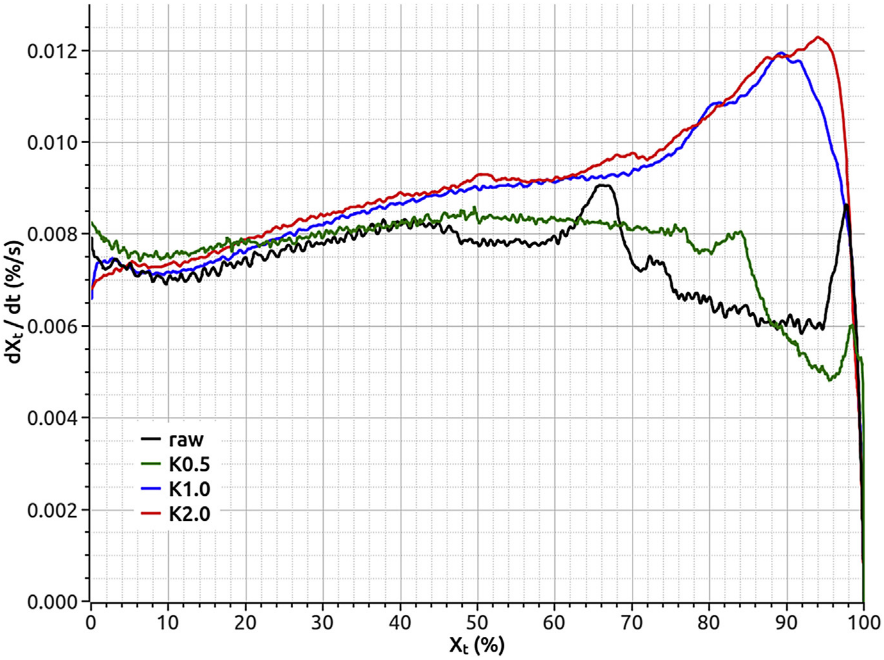

Fig. 6. Gasification rate of samples impregnated with K.

inhibiting influences [15,16,18]. In our case, only the potassium content was modified in the chemical analysis of the different chars tested, and a correlation was observed between the potassium content and the char reactivity.

The effect of Si content on the rate of the gasification reaction was also examined in Fig. 7. It could be seen that whatever the silicon content, the global shape of the gasification profile was similar to the one of pristine beech char. Two different behaviors could be observed for low and high conversion ratios:

- For $X_t < 60\%$, the influence of Si concentration on char reactivity is low. This may be related to the fact that the dispersion of silicon inside the char structure is different

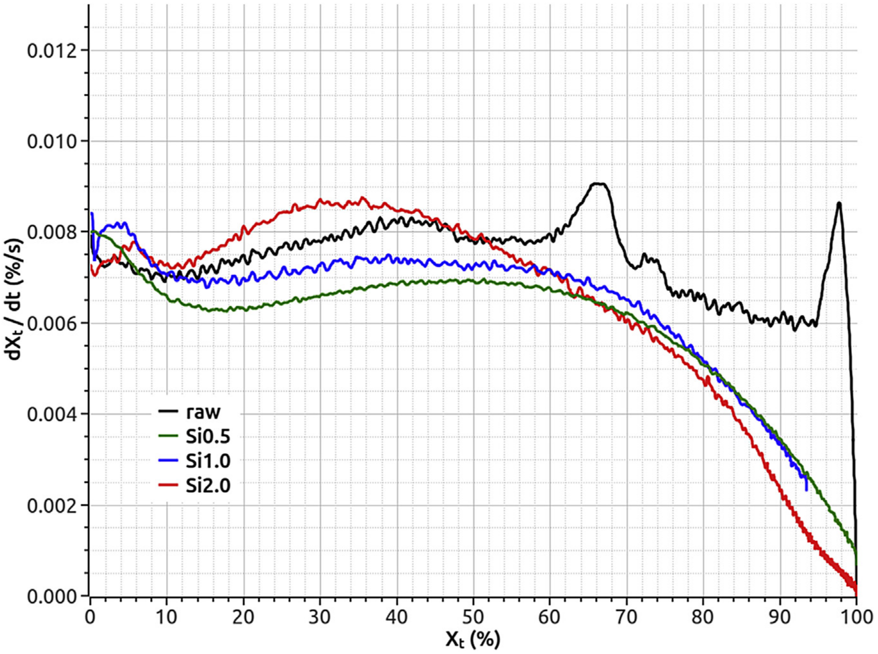

Fig. 7. Gasification rate of samples impregnated with Si.

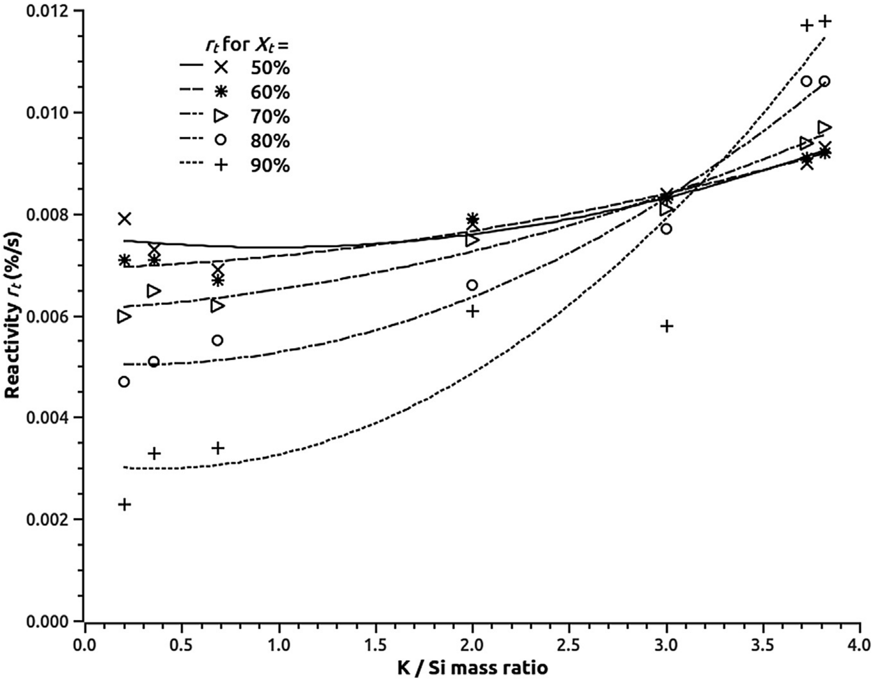

Fig. 8. Reactivity at selected conversion levels as a function of K/Si ratio (curves are just shown to highlight the tendencies).

from the one of catalysts like potassium and calcium. Therefore, reactions between these elements would not be favored.

- For $X_t > 60\%$, the major inhibiting influence of Si could be observed, even for the Si0.5 sample. It must be noticed that even for this char, the K/Si mass ratio is far lower (0.7) than that for the beech char (2.0). As pointed out in previous studies, this kind of catalyst/inhibitor parameter leads to good correlations with biomass char reactivity [21,23]. The observed results on the effect of Si on the reactivity of chars under CO_2 are in line with what has been mentioned in the literature in a recent study on the reactivity of chars under H_2O by Hognon et al. [22]. The authors explained this effect by assuming the encapsulation of K by Si.

The theory of encapsulation of alkaline catalysts by Si during the combustion phase was also discussed in the study of Sippula et al. [29]. The mechanism of this phenomenon can be the formation of alkali metal silicates by chemisorption of alkali by silicates. The addition of potassium to form silicate is one of the mechanisms which lead to slagging in biomass fired boilers [27]. This phenomenon is strongly related to the high mobility of potassium which allows it to come in contact and react with less mobile silica.

It must also be noticed that char reactivity also depends on its calcium content, and it was also observed that this element also tends to bind to silicon to form silicate [30]. The influence of this element on char reactivity may be complex: it could also participate in the decrease of char reactivity with increasing Si content through the capture of calcium. Calcium can also limit the silica available for potassium capture, thus limiting this decrease of reactivity [31].

By combining all the samples used in this study, a general tendency for the gasification rate as a function of X_t and K/Si ratio can be obtained. Fig. 8 shows the reactivity for conversion higher than or equal to 50%. The values below 50% were not shown since only small variations were observed. A more general correlation should include the variation of textural parameters from one sample to another. However, we have shown, in our case, that diffusion limitations occurring in narrow micropores hid this influence. Therefore, a direct comparison of reactivities is meaningful. Although the reactivities for $X_t = 90\%$ exhibit a larger spreading, it could be seen that for K/Si below 3 (in mass), reactivity strongly decreased with increasing conversion, while a significant increase could be observed for K/Si > 3.

4. Conclusions

In this work, the effects of K and Si elements on woody biomass char gasification by CO_2 were studied at 800 °C. A beech char obtained by pyrolysis at 800 °C was impregnated with controlled amounts of potassium and silicon, with variations of the K/Si mass ratio from 0.2 to 3.8. The dispersion of the two elements was studied by SEM – EDX, and it was observed that potassium is very well dispersed while silicon tends to form larger particles inside the char structure.

The reactivity toward CO_2 was then studied by thermogravimetric analysis at 800 °C. The results showed that char reactivity was almost the same at the beginning of the gasification process (at low conversion yield) for all samples. A correlation of this behavior with the textural properties of the chars shows that diffusional limitations occur in very small micropores and therefore only the external surface area is accessible for the reaction. When conversion is above 60%, the catalytic influence of potassium becomes obvious, provided that its concentration is at least close to 0.4 wt%. For high conversion, it was also observed that char reactivity decreases when the silicon becomes the main mineral compound. The general trend is that when the K/Si mass ratio is higher than 3, an acceleration of the gasification reaction is observed up to 90% of conversion. Below this value, the reaction rate begin to decrease continuously when the conversion is above 60%. These experiments tend to show that the measurement of the K/Si ratio is an important parameter to predict CO_2 gasification reactivity for high conversion, while at low conversion reactivity would be mainly related to textural parameters.

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