

BIOMASS GASIFICATION IN A FLUIDIZED BED REACTOR: EFFECT OF TEMPERATURE ON PROPERTIES AND OXIDATIVE REACTIVITY OF CHARs

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Introduction:

Biomass gasification is a promising alternative to fossil fuels for the synthesis of highly energetic products via Fischer-Tropsch or methanation processes. It is a thermochemical conversion occurring at high temperatures with many simultaneous reactions. For temperatures above 350°C, biomass undergoes a thermal decomposition called pyrolysis which leads to the formation of volatile products either condensable (steam and tars) or incondensable (H_2 , CO, CO_2 , CH_4 and C_2H_x) and a solid residue called char [1]. Then, the char reacts with steam and carbon dioxide at temperatures greater than 700°C to produce syngas.

These transformations are endothermic. Therefore, a contribution of energy is required to maintain the temperature and the different reactions. One of the most encouraging and advanced technology is dual fluidized beds [2]. Its principle relies on the circulation of a media (sand, olivine or catalyst particles) which acts as a heat carrier between an endothermic reactor, where biomass gasification produces syngas, and an exothermic reactor where combustion of a part of the char from the gasification of biomass produces heat. Therefore, it is of importance to carefully understand the effect of operating conditions on char structure and composition which are directly related to its reactivity in combustion and steam gasification.

During pyrolysis of biomass, many changes occur in the solid structure including (1) the loss of functional groups on the carbon surface, (2) ordering of the carbon microstructure to tend to a graphitic crystalline form, (3) the formation of pores which directly influence the surface area, (4) the modification in ash content and its distribution that affect the catalytic activity of chars. Together, these changes are responsible for the steam gasification and combustion reactivity of the chars.

A number of studies are reported in the literature concerning the effect of pyrolysis conditions (temperature, pressure, nature of biomass) on the physical and chemical characteristic of chars [3-6]. In these works, most of pyrolysis processes are carried out in a fixed bed reactor at temperature below 600°C. By using characterization techniques such as FTIR, Raman and NMR spectroscopy, the authors have concluded that char has a higher hydrogen and oxygen content at low pyrolysis temperature (below 400°C) and becomes more and more aromatic by increasing pyrolysis conditions.

The intrinsic reactivity of char is primarily determined by the concentration of carbon edge and defects as well as oxygen and hydrogen contents [7]. Hence, raising pyrolysis temperature decreases the reactivity of char both in combustion and steam gasification processes. Many authors have studied the effect of pyrolysis conditions on coal char structure and reactivity, either in fluidized bed reactor [8-9] or in fixed bed reactor [10-13]. Only a few studies discussed the evolution of char structure and reactivity from pyrolysis of biomass or biomass derived-materials [14-15].

Therefore, the aim of the study is to thoroughly understand the physicochemical changes in the char structure and properties during pyrolysis process of two types of biomass. The pyrolysis is carried out in a fluidized bed reactor at different temperatures ranging from 450 to 850°C. The combustion of chars in TGA is also studied in order to observe the influence of structure and chemical properties of the solid on its oxidative reactivity. The char was characterized in terms of its elemental composition and by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), Raman spectroscopy and X-Ray diffraction (XRD). Finally, the reactivity of char toward the combustion is measured by isothermal TGA analysis.

Experimental Section:

Char production Protocol:

The biomass used in this work was cylindrical pellets of oak bark (D=6 mm, L=13 mm) called "Pellet" obtained by mechanical compaction of sawdust, and beech stick (D=5 mm, L=10 mm) called "Stick". Fast pyrolysis of the two types of biomass was carried out in a batch fluidized bed reactor containing particles of sands (sauter mean diameter: 264 μ m) in an inert atmosphere. The reactor is fluidized by nitrogen with a velocity corresponding to 7

times the minimum velocity fluidization of sand particles at bed temperature. The runs were made at atmospheric pressure and for different bed temperatures: 450, 650 and 850°C. The insertion of the biomass is carried out inside the fluidized bed to avoid any degradation in the freeboard zone. The run duration was two hours and about 20 grams of biomass was introduced inside the fluidized bed every 15 minutes to make sure that the temperature was completely isotherm. The produced char was then cooled under nitrogen flow before being recovered by sieving inside the reactor. It was stored inside a pill-box until it was analyzed. Prior to characterization tests, the different chars were grounded and homogenized to ensure that all samples have the same properties.

Characterization methods

The chars collected from the pyrolysis procedure were analyzed in order to determine their physicochemical properties. The true density of the chars was determined by helium pycnometer.

Determination of C, H and O contents of the chars was performed at “the Institute of Analytical Science” in Lyon (France).

Structure morphology of char was determined through Scanning Electron Microscopy analysis using a SEM FEG JSM 7100FTTLS by JEOL at the “Laboratoire de Génie Chimique”. The analyses were performed on the samples previously coated with gold 10 nanometer Au/Pd film.

Infrared spectra were recorded in absorbance mode on Tensor 27 instrument connected to a Digitec™ DLATGS detector high sensibility. Typically 2 mg of grounded char sample were blended into 200 mg of KBr to form standard pellets for FTIR analysis. A spectrum resolution of 4 cm⁻¹ was used and the spectra were recorded from 400 to 4000 cm⁻¹.

XRD analysis was carried out with a Bruker instrument to examine the carbon structure of the different chars. The wavelength of the X-ray diffraction is 1.5418 Å.

Raman analyses were performed in air at room temperature using an Horiba Jobin Yvon Labram HR 800 spectrometer equipped with an He/Ne laser at 633 nm at the “Centre Inter-universitaire de Recherche et d’Ingénierie des Matériaux”. A laser power of 7 MW was selected. The spectrum of each sample was acquired through a grating of 600tr / mm with a spectral resolution of 2 cm⁻¹. As char can be heated up easily in the laser beam, a filter was used to avoid any degradation of the sample. The final method selected to perform Raman analysis uses two filters, microscope lens x100, 60s of exposition time and 2 accumulations.

The char reactivity in combustion was determined using isothermal TGA tests. About 10 mg of char was introduced inside an alumina crucible for each test. The experimental protocol is divided into two stages. The first one, carried out under high-purity nitrogen flow (100 NmL/min), consists of:

- an initial period (ca. 15 min) at ambient temperature used to initialize the system,
- a linear heating rate of 10°C/min from ambient temperature to the run temperature,
- a period (ca. 15 min) of constant temperature at 850°C to stabilize the system.

The second stage is the isothermal combustion carried out by switching the nitrogen to air with the same flow rate.

The carbon conversion rate is calculated via the following equation:

$$X = \frac{w_i - w(t)}{w_i - w_{ash}}$$

Where w_i , w_{ash} and $w(t)$ are the values of the initial, final, and temporal mass of the sample, respectively.

The oxidative char rate is given by:

$$r_c = \left. \frac{dX}{dt} \right|_{X=0.5}$$

Results and discussions

Ultimate analysis:

Characterization of char showed important structural, physical and chemical changes with pyrolysis conditions. Table 1 presents the C, H and O contents and true density of the chars obtained for different pyrolysis temperatures in fluidized bed. It shows that a higher pyrolysis temperature results in higher carbon content and lower hydrogen and oxygen level. Thus the char cannot be considered as pure carbon and should be expressed in the form of CH_xO_y. The oxygen and hydrogen contents in the char can be related to the availability of active sites and are believed to influence the overall reactivity in combustion [7,16].

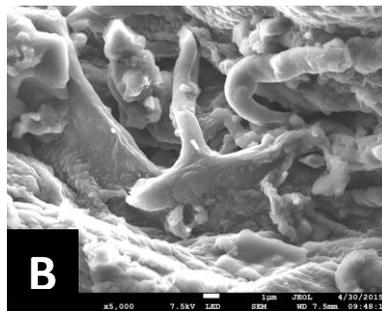
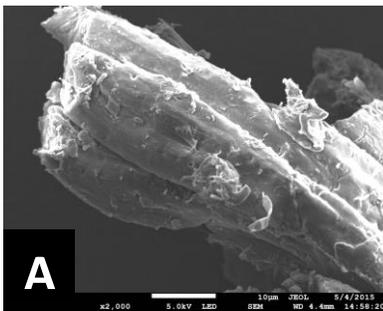
The true density of the chars rises with increasing pyrolysis temperature to approach true density of graphite ($\rho_{t,graphite} = 2000\text{-}2200 \text{ kg/m}^3$).

Table 1 : Ultimate analysis and properties of the different chars

Materials	Pyrolysis conditions			Density	Ultimate analysis				Chemical Formula
	Biomass type	Solid form	Pyrolysis Temp. [°C]	(kg/m ³)	(db, wt%)				
				He	C	H	O	Ash	
Oak		Pellet	-		44.79	6.09	47.29	1.83	CH _{1.63} O _{0.79}
PEL 450	Oak	Pellet	450	1504.2	74.47	2.99	12.88	9.66	CH _{0.48} O _{0.13}
PEL 650	Oak	Pellet	650	1722.8	75.62	2.03	8.98	13.37	CH _{0.32} O _{0.09}
PEL 850	Oak	Pellet	850	1832.5	70.47	0.43	6.06	23.04	CH _{0.07} O _{0.06}
Beech		Stick	-		44.63	6.37	45.24	3.76	CH _{1.71} O _{0.76}
STI 450	Beech	Stick	450	1394.3	74.10	4.17	18.96	2.77	CH _{0.68} O _{0.19}
STI 650	Beech	Stick	650	1589.4	84.47	2.75	7.39	5.39	CH _{0.39} O _{0.07}
STI 850	Beech	Stick	850	1924.4	87.17	1.57	6.95	4.31	CH _{0.22} O _{0.06}

SEM analysis:

Figure 1 illustrates SEM analysis of the cylindrical pellets of oak and its chars obtained under different pyrolysis temperatures. The parent biomass exhibits a structure of numerous typical wood fibers aligned in the longitudinal direction having an approximately diameter of 10 μm. Biomass chars consist of different morphologies according to pyrolysis conditions. For pyrolysis temperatures in the range of 450 to 650°C, the particles have melted as it is revealed by smooth regions which correspond to carbonized wood fibers. The structure also exhibits some disorder such as surface etchings (Figure 1(B and C)). Raising the pyrolysis temperature causes significant transformation to the surface morphology of the char. The emission of volatile products led to the formation of vesicles (bubbles), open and close pores Figure 1(C and D). When pyrolysis temperature increased, structure seemed more breakable. Some researchers [15] have concluded that a loss of the original morphology can lead micropores to collapse and decrease the surface area of the char.



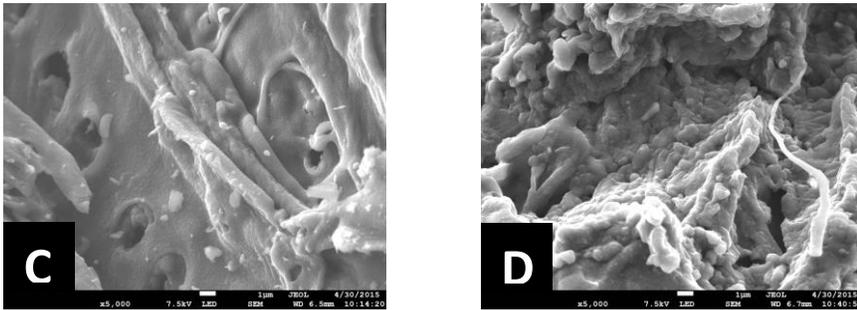


Figure 1 : SEM images of (A) pellet oak, and char from fast pyrolysis of pellet oak in a fluidized bed reactor at (B) 450°C, (C) 650°C, (D) 850°C.

Figure 2 shows SEM pictures of stick beech and its chars produced from different pyrolysis temperatures. It can be seen that stick beech is compact and consists of irregular particles with slit-shaped surfaces that provide an internal porous structure. At low pyrolysis temperature, no significant morphological variations are present compared to the raw material. The char is made of open pores which seem to continue inside the particles and illustrate the result of the volatile components being released (Figure 2 (B)). As the temperature is increased from 450 to 850°C, open bubbles in the surface of the bounded cells show a breakable char with more open structure. Similar findings for biomass chars prepared at high heating rates have been observed by other researchers [17].

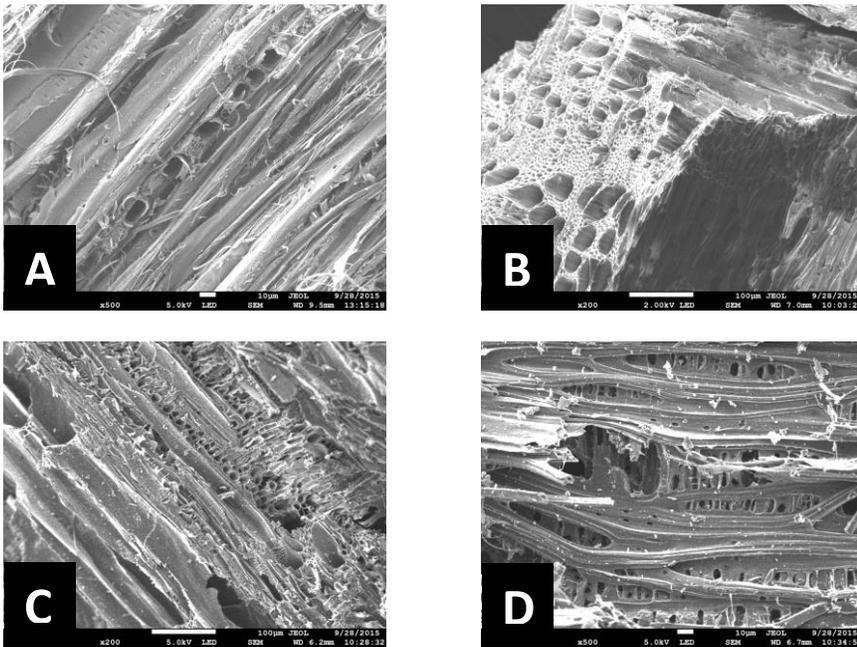


Figure 2 : SEM images of (A) stick beech, and char from fast pyrolysis of stick beech in a fluidized bed reactor at (B) 450°C, (C) 650°C, (D) 850°C.

FTIR analysis:

Figure 3 compares the FTIR spectra of the raw materials and their associated chars from pyrolysis at 450, 650 and 850°C. The spectra have been corrected for atmospheric CO₂ and water vapor contributions. Various bands are identified such as stretch due to OH (at wavenumbers of 3114-3679 cm⁻¹), aliphatic CH₃ (2881-2983 cm⁻¹), aliphatic CH₂ (2821-2879 cm⁻¹), C=O (1667-1701 cm⁻¹), aromatic ring C=C (1505-1667 cm⁻¹). Other bands in the region of 1323-1484, 1010-1068 and 723-862 cm⁻¹ are attributed to the deformation vibration of CH₃-CH₂, C-O and aromatic C-H, respectively. An increase in the pyrolysis temperature leads to a less complex spectrum with a continuous decrease in intensity for many bands. The absence of most bands suggested that the char is completely carbonized. An obvious decrease is observed for stretches due to C=O, aliphatic CH₃/CH₂ and aromatic CH. The latter is attributed to the loss of peripheral hydrogen and suggested that the char is mainly composed of carbon above 650°C. Intensity of the phenolic hydroxyl groups (-OH) is variable with pyrolysis temperature and is associated with the present of H₂O adsorbed in the char structure. Besides, the results in

Figure 3 show an increasingly upward drift in baseline at high wavenumbers. This is believed to be due to an increase in the aromatic carbon content of the chars [3]. These conclusions are in good agreement with many previous literature studies on biomass, biomass derived materials or biomass components [4,8].

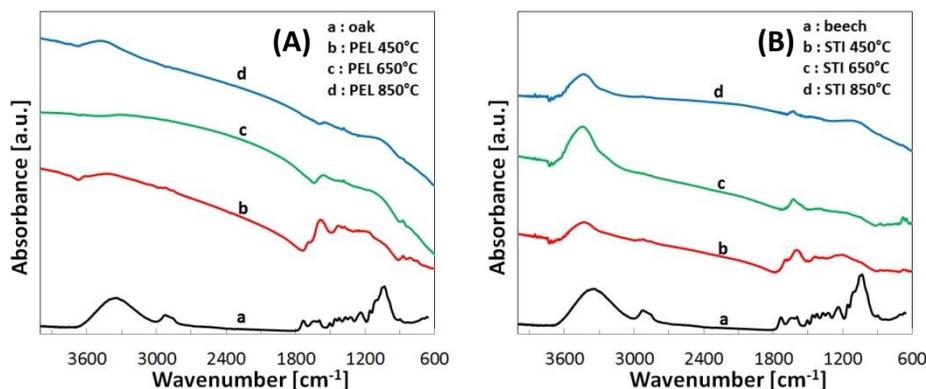


Figure 3 : FTIR spectra of (A) pellet oak and its associated chars, (B) stick beech and its chars produced at different pyrolysis temperatures.

X-Ray diffraction:

Char has a graphite-like structure as well as some amorphous carbon. The structural properties of the different chars were examined by X-ray diffraction. XRD analysis is a useful tool to provide information regarding the crystallinity and the presence of aromatic layers. Char microcrystalline structure directly influence its combustion and gasification reactivity.

Figure 4 presents the diffraction curves of chars prepared for different pyrolysis temperatures. Two broad bands are observed over the examined 2θ : the (002) peak is located at 2θ approximately equal to 24° and is attributed to the stacking of the graphitic basal plans of char crystallites [17,18], the (100) centered at about 44° is associated to hexagonal ring structure in char crystallite [18]. These two broad bands also indicate a highly disordered structure caused by both the presence of amorphous carbon and aliphatic side chains. Some authors have assigned the background intensity to amorphous carbon [15]. The (002) and (100) bands seem to sharpen by increasing pyrolysis temperature indicating a more ordered carbon structure, especially for stick chars. In addition to these bands of carbons, sharp peaks are also visible in the spectra which are associated to the crystal structure of ash. This last result is in good agreement with ultimate analysis (Table 1) which shows a higher amount of ash in pellet chars.

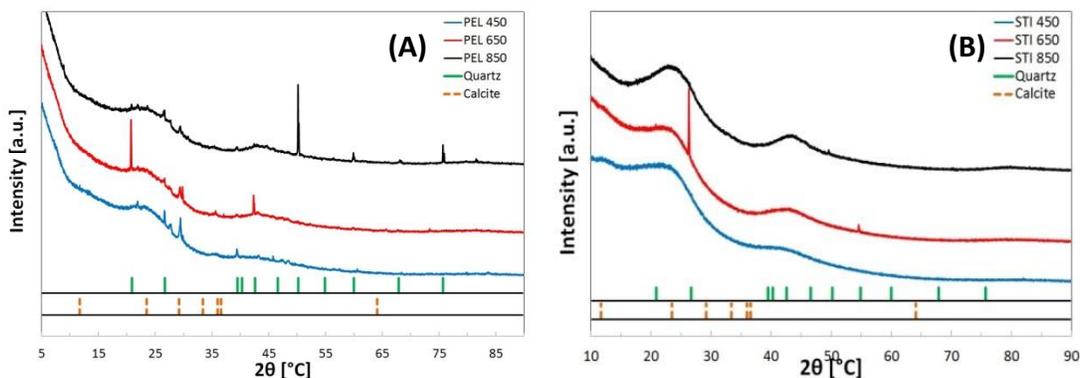


Figure 4 : XRD spectra of chars generated under different temperatures (A) from pyrolysis of pellet oak, (B) from pyrolysis of stick beech.

Raman spectroscopy:

Raman spectroscopy is widely used in literature to investigate the structure feature of carbonaceous materials and coal derived products [14,19,20]. The Raman spectra of single crystals of graphite show one single, strong band at 1575 cm^{-1} designated as the G band due to the E_{2g} vibrational modes [21]. For disordered carbon such as activated carbon or chars, an additional band appears at 1380 cm^{-1} denoted as the D band. The origin of the D band is not well understood and might be due to the increase of the amount of unorganized carbon in the sample [15]. It is expected that the D band will disappear for compounds having an infinite sized aromatic

cluster such as the graphitic structure.

Two procedures are carried out in the literature to interpret Raman spectra. In the works of Li and co-workers [22], the coal char did not show any signs of graphitic structures (XRD curves not shown in the papers). The authors have curved-fitted the spectra into 10 Gaussian bands by assuming that the G modes is associated to the aromatic quadrant ring breathing and the D modes is assigned to the aromatic ring with a ring size of no less than 6 fused benzene rings. These 10 bands are briefly summarized in Table 2. The second point of view is to consider a graphitic structure in the char. Therefore, the Raman spectra are curved-fitted into 4 Lorentzian and 1 Gaussian peaks following the method of Sadezki and co-workers [23].

In the present paper, Raman spectra are analyzed following the method proposed by Li and co-workers [22]. Figure 5 (A) shows an example of Raman spectra of char from pyrolysis of pellet oak at 450°C and the curve-fitting into 10 Gaussian peaks to obtain quantitative parameters. Two broad Raman bands can be discerned at approximately 1350 and 1600 cm^{-1} attributed to the D and G band respectively.

Figure 5 (B) and (C) illustrated the I_D/I_G ratio and the ratio between the D band and the ($G_R+V_L+V_R$) in term of pyrolysis temperature. The increase in the I_D/I_G ratio with pyrolysis temperature indicates the increase in the concentrations of aromatic rings having at least six fused benzene rings. This is due to the dehydrogenation of hydroaromatics and the rise of aromatic rings in the char. The three bands G_R , V_L and V_R stand for the typical structures found in amorphous carbon materials, especially the small aromatic ring systems having 3-5 fused benzene rings. Hence, the increase in the ratio observed in Figure 5 (C) is taken as a rise in the presence of large aromatic ring systems.

Table 2 : Summary of peak/band assignment [22]

Band name	Band position, cm^{-1}	Description	Bond type
G_L	1700	Carbonyl group C=O	sp^2
G	1590	Graphite E_{2g}^{2g} ; aromatic ring quadrant breathing ; alkene C=C	sp^2
G_R	1540	Aromatic with 3-5 rings ; amorphous carbon structures	sp^2
V_L	1465	Methylene or methyl ; semi-circle breathing of aromatic rings ; amorphous carbon structures	sp^2, sp^3
V_R	1380	Methyl group; semi-circle breathing of aromatic rings; amorphous carbon structures	sp^2, sp^3
D	1300	D band on highly ordered carbonaceous materials; C-C between aromatic rings and aromatics with not less than 6 rings	sp^2
S_L	1230	Aryl-alkyl ether; para-aromatics	sp^2, sp^3
S	1185	$C_{aromatic}-C_{alkyl}$; aromatic (aliphatic) ethers; C-C on hydroaromatic rings; hexagonal diamond carbon sp^3 ; C-H on aromatic rings	sp^2, sp^3
S_R	1060	C-H on aromatic rings; benzene (ortho-di-substituted) ring	sp^2
R	960-800	C-C on alkanes and cyclic alkanes; C-H on aromatic rings	sp^2, sp^3

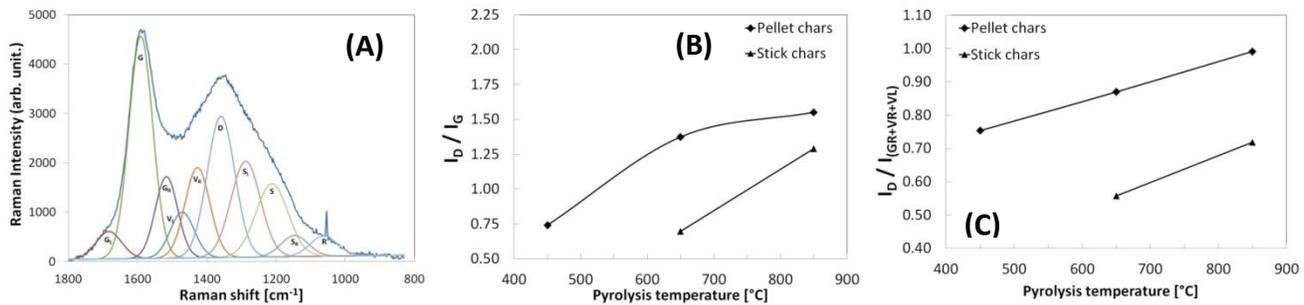


Figure 5 : (A) Curve-fitting of a Raman spectrum of the char obtained by pyrolysis of pellet oak at 450°C, (B) and (C) Band ratio as a function of pyrolysis temperature for pellet and stick chars.

Combustion reactivity:

Combustion tests were carried out under different temperatures: 330, 350, 380, 400, 450, 500 and 850°C.

Figure 6 (A) presents the logarithm of the oxidative rate versus $1/T$ for the chars PEL 850 and STI 850 under a constant partial pressure of oxygen and a given carbon conversion ($X = 0.5$). According to the evident difference in slope, each curve can be divided into two sections representing a low temperature region (330-450°C) and a high temperature region (500-850°C). In low temperature region, char oxidative rate is highly dependent of combustion temperature and is mainly subject to chemical kinetic control. Besides, we noticed a strong influence of the type of biomass (pellet oak bark or stick beech). PEL 850 is more reactive than STI 850. For instance, at a given combustion temperature of 673K, oxidative reaction rate is equal to 0.043 min^{-1} for PEL 850 and 0.009 min^{-1} for STI 850. This is due to the difference in structure between pellet and stick biomass. Pellet chars are composed of agglomeration of fine particles which present a higher external surface available for oxygen. Pellet chars also present a higher ash content which is known to catalyze the oxidative reaction. In the high temperature region, the reaction rate is less affected by temperature. This can be explained by the control of the reaction by the external heat and mass transfer.

Figure 6 (B) illustrates the char oxidation rate of the stick chars at 330°C. It shows that the char reactivity obviously increases by decreasing the pyrolysis temperature. This is the result of a higher content of hydrogen and oxygen groups that increase the amount of active sites. In other words, the high pyrolysis temperatures promote an extensive aromaticity nature of the char which is known to lower the char reactivity. Similar result is obtained for pellet chars.

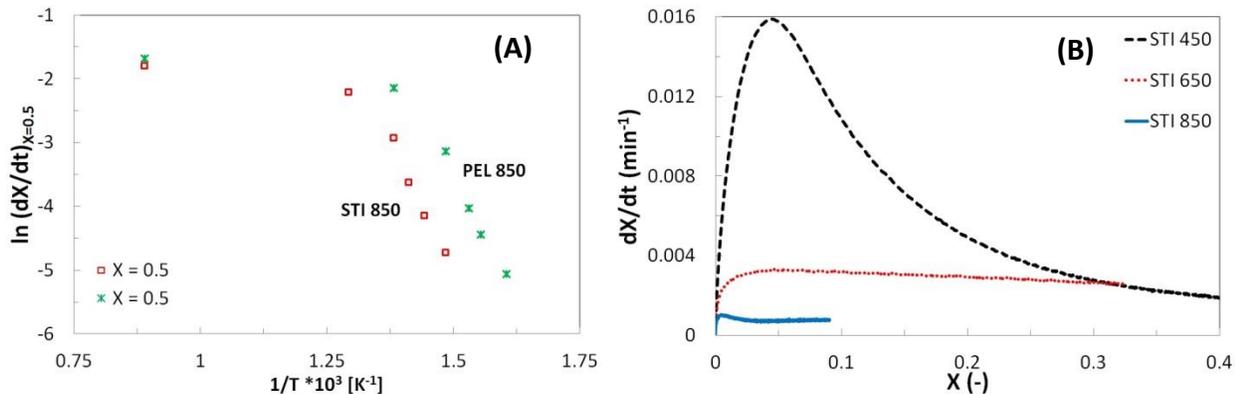


Figure 6 : (A) Char oxidative rate versus $1/T$ for two types of chars, STI 850 and PEL 850, (B) Oxidative reactivity of stick chars at 330°C for different pyrolysis temperatures.

Conclusion:

This work concerns the characterization of the chars obtained by fast pyrolysis of biomass in a fluidized bed at 450°C, 650°C and 850°C. Two types of biomass were employed: pellet oak and stick beech. The char properties were highly dependent of pyrolysis temperature and nature of biomass. By increasing pyrolysis temperature, the main conclusions are:

- (1) Chars developed a more disordered structure.

- (2) Hydrogen and oxygen contents as well as hydroxyl and carbonyl groups of char decreased indicating an increase in the aromaticity and carbonaceous nature of the char.
 - (3) The ratio of large to small aromatic ring system strongly increased to tend to a graphitic structure but still away from graphite.
 - (4) The loss of these functionalities strongly affected the oxidation reactivity of char which decreased with pyrolysis temperature.
- Oxidative reactivity of chars is highly dependent of combustion temperature, especially between 330 and 450°C. Above 500 ° C the effect of temperature is less important on the combustion kinetics.
- The nature of biomass has a significant effect on the oxidative reactivity of chars at low combustion temperatures (330-450°C).

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