

# Contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors

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## A B S T R A C T

In this study, contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and activated carbons from various lignocellulosic materials were studied. A predictive calculation was established using the experimental results obtained for the three components separately to evaluate the carbonization and activation yields and their respective contributions to the chars and to the subsequent activated carbons of various precursors in term of weight fraction. These equations were validated. The results showed that lignin can be considering as being the major contributor of all chars and activated carbons. Besides, the evolution of the mean pore size versus the specific porous volume showed that each component contributes to the porosity of chars and activated carbons whatever is its weight contribution.

**Keywords:** Activated carbon Activation Hemicellulose Cellulose Lignin

## 1. Introduction

Significant researches have been devoted to the production of activated carbons from waste materials of agricultural origin and based on lignocellulosic materials. The main studied precursors are wood (Amaya et al., 2007; Benaddi et al., 1998; Byrne and Nagle, 1997), almond shells (Marcilla et al., 2000; Rodriguez-Reinoso et al., 1982, 1984), olive stones (Caballero et al., 1997; Gonzalez et al., 1997; Zabaniotou et al., 2008), coconut shells (Cagnon et al., 2003; Daud and Ali, 2004; Mortley et al., 1988), peach (Molina-Sabio et al., 1995; Rodriguez-Reinoso et al., 1985), apricot stones (Gergova et al., 1993), and apple pulp (Fernandez et al., 2001; Suarez-Garcia et al., 2002). It has been already extensively demonstrated that the microporous properties of activated carbons depend not only on the experimental conditions of the carbonization and activation steps but also preponderantly on the original nature and structure of the involved precursor. In term of weight, the main constitutive fractions of these lignocellulosic materials are the hemicellulose, the cellulose and the lignin, the thermal

decomposition of which form the carbonaceous structure of the char precursor and the subsequent activated carbon.

During the carbonization of the lignocellulosic precursors, hemicellulose, cellulose and lignin decompose at different rates and within distinct temperature ranges. Due to the differences in reactivity between those three basic components during the pyrolysis step, as well as the competition of the reactions involved during their decompositions, the study of their carbonization is rather complex. Moreover, the thermal transformation of each component is highly dependent upon the experimental conditions of carbonization (Brunner and Roberts, 1980). Their respective proportions at the end of the carbonization stage and the structural rearrangement in the chars can also play an important part in the adsorption properties of the final activated carbon (Mackay and Roberts, 1982a).

Furthermore, it is rather difficult to compare the results of the various studies devoted to the physical activation of a given precursor, since the experimental conditions vary considerably from an author to another (i.e. precursor amount, heating rate, nature of the inert gas flow during the carbonization step, final temperature of carbonization and partial pressure of oxidizing gas during the activation step). Relevant comparisons would be possible only

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if the same experimental protocols were used for all materials in term of elaboration and characterization.

The present study is focused on the thermal decomposition and steam activation, under the same experimental conditions, of several lignocellulosic materials in order to compare their ability to form activated carbons. According to the open literature, the present paper is an attempt to extend Mackay and Roberts approach to this problem (Mackay and Roberts, 1982b). In a first part, the three major lignocellulosic components (hemicellulose, cellulose and lignin) are studied separately in order to predict their respective contributions to the chars and to the subsequent activated carbons in term of weight fraction and contributions to the different porous domains (microporosity, mesoporosity, macroporosity).

In a second part, these results are compared to those obtained with various raw natural precursors (coconut shell, apple pulp, plum pulp and stones, olive stones and a soft wood), using the same experimental conditions, and for a synthetic mixture of the three laboratory-grade basic components in the same proportions than those of a natural coconut shell.

## 2. Experimental

Series of chars and steam activated carbons have been prepared using different lignocellulosic materials: coconut shells (CS), apple pulp (AP) which is a solid apple residue from the manufacture of cider and apple juice, plum pulp (PP), plum stones (PS), olive stones (OS) of the variety called "manzanilla", the same olive stones after treatment with sulphuric acid (TOS) and a soft wood (SW).

Isolated lignocellulosic fractions supplied by *Sigma Aldrich Co.*, were also used in this study, namely xylan (ref:36-355-3) corresponding to hemicellulose (H.), cellulose (ref:9004-34-6) (C.) and lignin (ref:8072-93-3) (L.). A synthetic mixture (MIX.) of those fractions, corresponding to the composition of a typical coconut shell (35 wt% of H., 15 wt% of C., 50 wt% of L.), was thoroughly homogenized by grinding in a mortar.

All raw materials have been crushed and sieved to a particle size of some 200  $\mu\text{m}$ .

Prior to any pyrolysis and activation treatments, thermogravimetric experiments were carried out to determine the decomposition rate and temperature range of pure hemicellulose, cellulose, lignin and the artificial mixture during the carbonization step. This has been achieved using a thermobalance coupled with a calorimeter (TG-DSC 111 Setaram) in which 0.040 g of sample was treated under nitrogen flow at 0.5 L  $\text{min}^{-1}$ . A blank experiment was carried out, under the same conditions, in order to determine the correction required for the base-line. The samples were not dried before carbonization in order to avoid any modification of their initial composition and structure which could change their thermal decomposition process within the low temperature range from the ambient temperature to 200 °C.

The pyrolysis treatment (carbonization) was carried out in a horizontal electric furnace under nitrogen flow at a volumetric rate of 0.5 L  $\text{min}^{-1}$ . It was composed of an initial heating from room temperature to 800 °C at a heating rate of 5 °C  $\text{min}^{-1}$ , followed by an isothermal plateau of 1 h at this temperature. The sample was then allowed to cool down to room temperature at a rate of 10 °C  $\text{min}^{-1}$ . Each sample was held in a stainless steel basket with an initial loading of some 10 g, in order to allow significant sampling amount for analysis.

The subsequent activation was carried out in the same furnace at 800 °C (initial heating ramp at 5 °C  $\text{min}^{-1}$ ) for 2 h under a  $\text{N}_2/\text{H}_2\text{O}$  flow of 1 L  $\text{min}^{-1}$ . The steam was produced from water at 70 °C following a procedure already published in a previous paper (Cagnon et al., 2003).

The porous textures of those samples were characterized using the conventional nitrogen adsorption isotherms at -196 °C (77 K) measured on a *Micromeritics ASAP 2000M* apparatus. The samples were first treated at 250 °C for 24 h under a residual vacuum of less than  $10^{-4}$  Pa.

These nitrogen isotherms were analyzed on the basis of Dubinin's approach (Bansal et al., 1988; Stoeckli, 1995). Both the specific microporous volume ( $W_0$  in  $\text{cm}^3 \text{g}^{-1}$ ) and the mean pore size ( $L_0$  in nm) were estimated from the linear part of the so-called Dubinin-Radushkevich plot (Guillot et al., 2000; Stoeckli, 1995). It has been shown that in the case where the DR equation applies, the mean pore size  $L_0$  is related to the characteristic energy of adsorption ( $E_0$  in  $\text{kJ mol}^{-1}$ ) by :

$$L_0 = \frac{10.8}{E_0 - 11.4} \quad (1)$$

As the experimented solids have low specific external surface areas ( $S_e < 20\text{--}25 \text{ m}^2 \text{g}^{-1}$ ), the specific total pore volume ( $W_t$  in  $\text{cm}^3 \text{g}^{-1}$ ) has been estimated directly from the gas amount adsorbed at relative pressure of  $p/p_s = 0.95$ .

Following a procedure described in detail in a previous work (Guillot et al., 2000),  $\text{CO}_2$  isotherms at high pressure were also measured at 0 °C, in order to determine the pore size distributions (PSD) of the activated materials built using a method based on model isotherms resulting from molecular simulations already described in previous publications (Stoeckli et al., 1999, 2000, 2002).

## 3. Results and discussion

### 3.1. Raw materials compositions

The compositions of the different experimented raw lignocellulosic materials are given in Table 1 (courtesy of *Service Central d'Analyse du C.N.R.S.*). Compared to cellulose and hemicellulose, the lignin presents initially the highest carbon content and the lowest oxygen content. Both the water and hydrogen contents of the three basic compounds are similar and close to 6%wt. Moreover, both hemicellulose and lignin present important ash amount (respectively 6.7 wt% and 3.9 wt%) compared to cellulose (<0.3 wt%).

The various experimented natural lignocellulosic precursors present carbon contents ranging between 41.6 and 50.7 wt%, hydrogen contents between 5.8 and 6.5 wt% and oxygen contents between 41.1 and 47.2 wt%. This elemental analysis also indicates calcium content between 300 ppm and 0.4%wt and an ash amount ranging from 0.9 to 4.4 wt%.

The hemicellulose, cellulose and lignin weight fractions present within those natural lignocellulosic materials have been also determined following a procedure described in detail elsewhere (Saeman et al., 1954; Sarwardeker et al., 1965). As shown in Fig. 1, the raw materials present very different compositions. Large amounts of residues (composed of ashes, salts, tannins and pigments) were found in apple pulp, plum pulp, raw olive stones and soft wood unlike in coconut shells, plum stones and olive stones after treatment with sulphuric acid. This amount of residues was significantly reduced (from 29 to 9 wt%) after  $\text{H}_2\text{SO}_4$  treatment of olive stones.

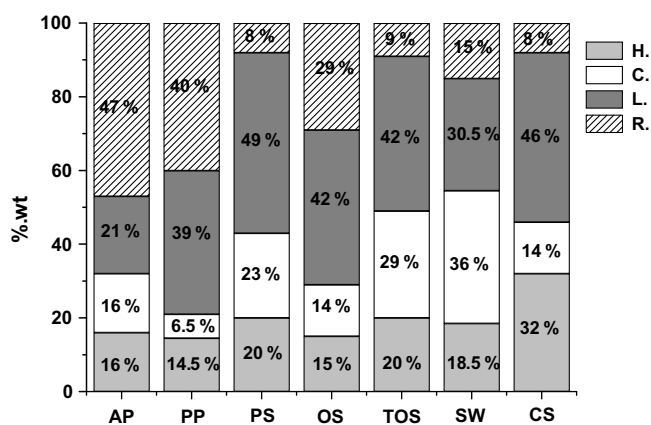
### 3.2. Thermogravimetric analysis

In Fig. 2 are gathered the TG-DTG curves (realized at 10 °C  $\text{min}^{-1}$  under nitrogen) for hemicellulose, cellulose and lignin.

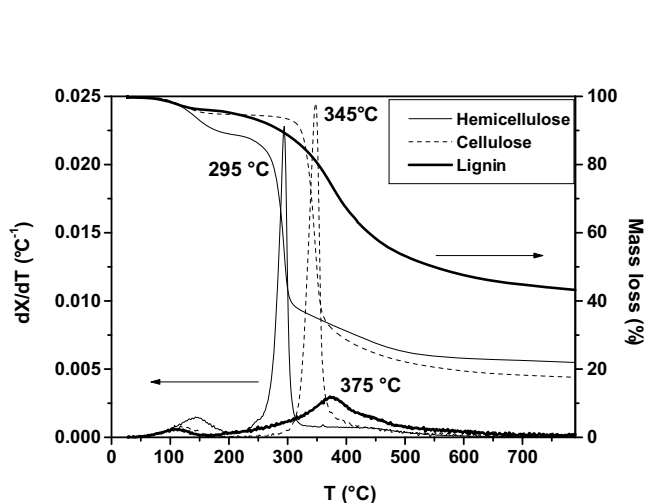
The solid fraction conversion  $X$  is expressed using the following equation:

**Table 1**  
Compositions of the experimented raw lignocellulosic materials

	C (%)	H (%)	O (%)	N (%)	S (%)	Ca (%)	H <sub>2</sub> O (%)	Ash (%)
Hemicellulose	38.1	6.0	48.5	<0.1	<0.3	–	6.4	6.7
Cellulose	41.8	6.4	51.2	<0.1	<0.3	–	6.2	<0.3
Lignin	58.6	5.7	30.8	0.7	<0.3	–	5.9	3.9
MIX.	50.1	5.9	38.3	0.5	<0.3	–	6.5	4.9
CS	48.7	5.8	42.5	<0.3	<0.3	380 ppm	5.0	2.7
AP	41.6	6.2	47.2	<0.3	<0.3	800 ppm	6.3	0.9
PP	48.1	6.5	41.8	2.1	<0.3	0.4 %	3.6	4.3
PS	50.7	6.3	41.1	0.9	<0.3	0.3 %	3.8	0.9
OS	46.0	5.9	42.3	1.0	<0.3	0.4 %	4.9	4.4
TOS	48.3	6.1	43.1	<0.3	<0.3	300 ppm	4.6	0.4
SW	46.1	6.0	45.5	<0.3	<0.3	0.1 %	7.5	0.3



**Fig. 1.** Composition of the raw lignocellulosic materials: H. (hemicellulose), C. (cellulose), L. (lignin) and R. (residues).



**Fig. 2.** Hemicellulose, cellulose and lignin TG-DTG experimental curves at 10 °C min<sup>-1</sup> under nitrogen.

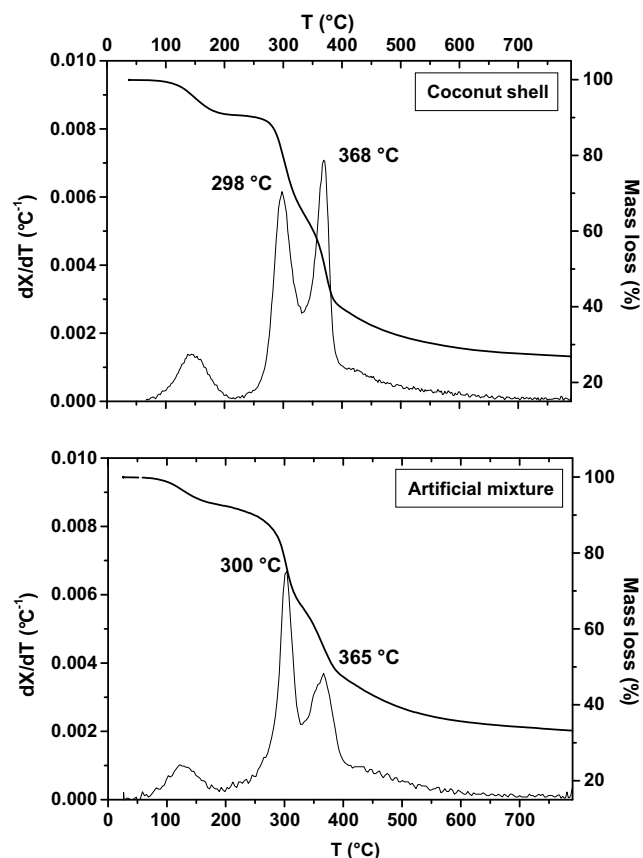
$$X = \frac{Z_0 - Z}{Z} \quad (2)$$

where  $Z_0$  (in%) and  $Z$  (in%) are respectively the initial mass fraction and the mass fraction.

In terms of temperature range of decomposition and maximum weight-loss rate, the TG–DTG curves of Fig. 2 obtained for the H., C. and L. fractions are very similar to those already reported by other authors (Font et al., 1991; Orfao et al., 1999), but different than those of Kifani-Sahban et al. (1996) who presented DTG curves with two peaks for lignin.

Some authors have tried to separate the decompositions of the different fractions by preliminary elimination of the hemicellulose and cellulose compounds by H<sub>2</sub>SO<sub>4</sub> treatments (Caballero et al., 1997) or thermal treatments (Marcilla et al., 2000) of a lignocellulosic precursor. If this approach is possible for the H. and C. fractions, it is not easy to apply to the lignin compound without any significant modification of its structure and consequently of its kinetic behaviour. Comparatively, such treatment modify also certainly the hemicellulose and cellulose molecules, but this approach leads to easier kinetics studies, the results of which can be confronted to various experimental validations.

In Fig. 3 are gathered the TG–DTG curves (realized at 10 °C min<sup>-1</sup> under nitrogen) for the coconut shell and a synthetic mixture. This one has a similar composition to the coconut shell (35 wt% of H., 15 wt% of C. and 50 wt% of L.) without taking into account ashes which do not contribute to the carbonization yield. According to



**Fig. 3.** The coconut shell and the artificial mixture (corresponding to the coconut shell composition) TG-DTG experimental curves at 10 °C min<sup>-1</sup> under nitrogen.

the results illustrated in Figs. 2 and 3, the temperature range decomposition of the three basic fractions and the shape of the DTG curves are the same within a synthetic mixture or in coconut shell. The obtained DTG curve of the synthetic mixture is in very good agreement with that of the natural precursor. Nevertheless, the rates of conversion of hemicellulose and cellulose are different. This can be attributed to the thermal effect and char produced by the decomposition of a fraction influencing the thermal degradation of the others.

Therefore, the study of the three separated basic compounds has been considered to be relevant to estimate their respective contribution to the production of chars and microporous fractions in the natural lignocellulosic precursor.

In term of weight of char obtained after carbonization, the TG curves of Fig. 2 show that H. and C. present a weight loss much more important than L. (76.5%, 81% and 55%, respectively). This difference in behavior is probably due to the proportions of oxygen (50% for H. and C. and 30% for L., in Table 1) and carbon in the starting material and the chemical composition of each fraction. In agreement with the literature (Mackay and Roberts, 1982b; Shafizadeh and Chin, 1977), the lignin is found to be the main contributor to the final char weight. Nevertheless, as opposed to authors who neglected the hemicellulose contribution to the chars (Ouen-sanga et al., 2003), this fraction appears to lead to a significant yield of some 23%.

### 3.3. Properties of chars and activated carbons

In order to identify the respective contributions of hemicellulose, cellulose and lignin to the weight and microporosity of the chars and subsequent activated carbons, the isolated components have been carbonized and steam activated following the above procedures. Moreover, those treatments were also applied to the coconut shell and to the corresponding synthetic mixture of similar H.C.L. composition. The corresponding results have been gathered in Table 2 for comparison.

#### 3.3.1. Chars properties

Under carbonization, H. and C. present similar yields while L. leads to a char amount twice: respectively, 23.5%, 19% and 45%. Those results are in perfect agreement with those obtained by thermogravimetry (as seen in Section 3.2) and the trends observed by Mackay and Roberts (1982b) that have shown that the char amount generally increases with both the number of aromatic cycles and the molecular weight of the precursor. Nevertheless, some authors have found rather different results (Brunner and Roberts, 1980; Kifani-Sahban et al., 1996; Orfao et al., 1999). The microporous properties of the corresponding chars (Table 2) are different.

Nevertheless, each char presents a same value in total ( $W_t$  in  $\text{cm}^3 \text{g}^{-1}$ ) and microporous ( $W_0$  in  $\text{cm}^3 \text{g}^{-1}$ ) volumes indicating a pure microporous structure without meso- and macro-porosity. The chars obtained from C. and from L. present microporous volumes of  $0.19 \text{ cm}^3 \text{g}^{-1}$  and  $0.15 \text{ cm}^3 \text{g}^{-1}$  respectively. Those values are close to those of the chars obtained from coconut shell which is  $0.18 \text{ cm}^3 \text{g}^{-1}$ . On the other hand, hemicellulose presents very low porous volumes close to  $0.09 \text{ cm}^3 \text{g}^{-1}$ . The char obtained by carbonization of the synthetic mixture presents porous volumes of  $0.10 \text{ cm}^3 \text{g}^{-1}$ , 45% lower than those of the coconut shells char.

The mean pore sizes ( $L_0$ ) of the chars obtained from the three isolated compounds and the coconut char are similar and close to 0.5 nm. Moreover, all the adsorption and desorption isotherms lead to different  $L_0$  values except for the cellulosic char. The mean pore sizes calculated from the adsorption isotherms are larger than those estimated by desorption. This result reflects incomplete micropore filling under adsorption due to gate effects at the pore entrance, leading to activated diffusion of nitrogen at  $-196^\circ\text{C}$  (77 K) (Cagnon et al., 2003). The char elaborated from the synthetic mixture presents the highest value of  $L_0$  by adsorption and the lowest by desorption.

#### 3.3.2. Activated carbons properties

As illustrated in Table 2, H., L., the coconut shell and the artificial mixture present similar yield under steam activation in the range of 71.5–77.8%. Comparatively, the cellulose presents a very high yield of 86.9%.

The pore size distributions of the corresponding activated carbons are shown in Fig. 4. The activated carbon from hemicellulose presents the broadest PSD (ranging from 0.5 to 1.6 nm) while those from cellulose and lignin are quite similar in shape. The two PSDs of the activated coconut shell and the corresponding activated synthetic mixture are very similar (Figures not shown), particularly in the range of the largest pore sizes (over 0.8 nm). Therefore, the use of synthetic mixtures of H., C. and L. to study the carbonization and activation of lignocellulosic materials is validated.

#### 3.4. Predictive calculation: contribution of each component to the chars

Considering the data obtained for the three basic components, it would be of great interest to be able to evaluate their respective contributions to the mass and the porosity of the activated natural coconut shell and synthetic mixture. This approach, outlined in Fig. 5 in the case of coconut shell, is based on calculations using the chemical compositions given in Fig. 1. The initial weight fractions associated to the carbonization yields of each individual compo-

**Table 2**

Microporous properties of the different chars and activated carbons obtained from H., C., L., artificial mixture and coconut shell

	Yield (%)	$W_t$ ( $\text{cm}^3 \text{g}^{-1}$ )	$W_0$ ( $\text{cm}^3 \text{g}^{-1}$ )	$E_0$ ( $\text{kJ mol}^{-1}$ )		$L_0$ (nm)		
				Adsorption	Desorption	Adsorption	Desorption	
<i>Carbonization</i>								
H.	23.5	0.09	0.09	24.0	36.2	0.86	0.44	
C.	19.1	0.19	0.19	28.5	29.6	0.63	0.59	
L.	44.9	0.15	0.15	23.4	34.4	0.90	0.47	
MIX.	32.7	0.10	0.10	19.4	38.8	1.35	0.40	
CS	25.6	0.19	0.18	24.5	31.0	0.83	0.55	
<i>Activation</i>								
H.	75.7	0.24	0.20	26.7	–	0.71	–	
C.	86.9	0.32	0.32	29.9	–	0.58	–	
L.	77.8	0.30	0.28	29.6	–	0.59	–	
MIX.	71.5	0.38	0.30	25.7	–	0.75	–	
CS	76.3	0.39	0.35	27.3	–	0.68	–	

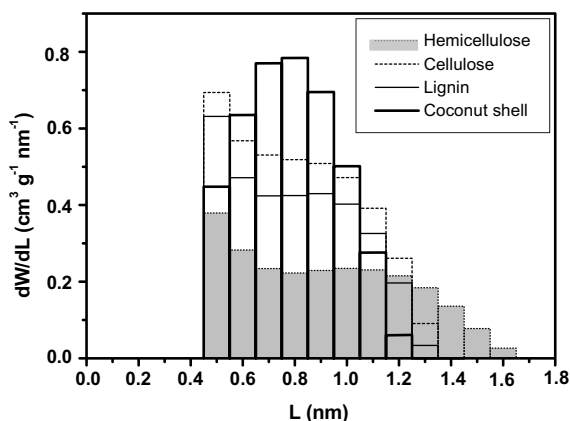


Fig. 4. Pore-size distributions ( $\text{CO}_2$  at  $0^\circ\text{C}$ ) of hemicellulose, cellulose, lignin and coconut shell activated carbons.

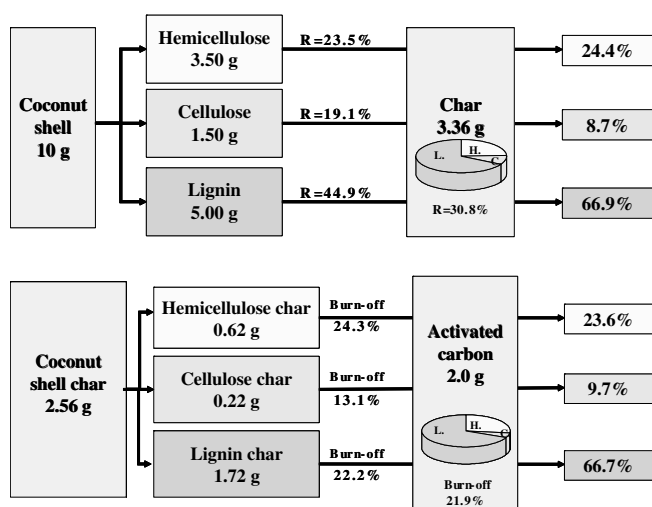


Fig. 5. Diagram of predictive calculation for carbonization and activation steps.

ment lead to the carbonization yield of the raw material and by cumulative effect to their respective char.

Under those experimental conditions, the yield  $Y$  (in %) of char is calculated using the following equation:

$$Y(\text{wt}\%) = 100 - [(1 - x) \times 100] \quad (3)$$

with

$$x = H \times y_{c,H} + C \times y_{c,C} + L \times y_{c,L} \quad (4)$$

which corresponds to the calculated char mass after carbonization where  $H$ ,  $C$  and  $L$  are, respectively, the percentage of compounds in the precursor (in %) and  $y_{c,i}$  are the carbonization yield of each individual component (in %).

In the Table 3 are gathered similar calculations for the different experimented natural lignocellulosic precursors. For the particular composition of the experimented coconut shell, the predicted yield is 30.8% against an experimental value of 25.6%. Comparatively, the synthetic mixture presents a yield of 32.7% for which the estimated value of 33.5% is much more relevant. Those results illustrate the fact that under carbonization and in term of mass production, the three basic fractions within a synthetic mixture behave like when isolated. In the other hand, their structural arrangement and chemical bonds within a natural precursor as well as the presence of particular residue induce a significant increase in weight loss under carbonization.

As the standard deviation for each material is less than 5%, the experimental and estimated results are in good agreement and the approach can be considered as relevant.

By taking into account the raw material initial mass, the contribution of each basic component can be calculated by the followed equation (for example to the lignin) :

$$L_c = \left[ 1 - \frac{x - (L \times y_{c,L})}{x} \right] \times 100 \quad (5)$$

where  $L_c$  is the lignin products after carbonization (in %),  $x$  is the calculated char mass after carbonization and  $y_{c,L}$  are the carbonization yield lignin (in%).

Nevertheless, the calculated yields do not take into account the amount of residue. The weight contribution of the hemicellulose ranges between 14.1% and 24.5%, the cellulose from 5.6% and 27.6% and the lignin from 55.0% to 79.0%. According to those values (Table 3), lignin can be considered as being the major weight contributor to all chars and the cellulose and hemicellulose weight contribution not negligible.

### 3.5. Predictive calculation: contribution of each component to the activated carbon

Similar calculations have been achieved for the activation step from the experimental burn-off of each isolated basic compound leading to the estimation of their respective contributions to the weight of an activated natural lignocellulosic precursor.

The carbonization products and the activation burn-off of each individual component lead to the burn-off of the raw material and by cumulative effect to their respective activated carbons productions (Fig. 5).

Under those experimental conditions, the burn-off (B.O.) is estimated by the following equation:

$$\text{B.O.} (\%) = (L_c \times (1 - y_{a,L}) + C_c \times (1 - y_{a,C}) + H_c \times (1 - y_{a,H})) \times 100 \quad (6)$$

where B.O. is the burn off (in %),  $H_c$ ,  $C_c$  and  $L_c$  are respectively the  $H$ ,  $C$  and  $L$  products after carbonization (in %) and  $y_{a,i}$  is the activation yield of each individual component (in %).

The corresponding weight fractions inherited from the three basic compounds are used for the estimation of their respective pro-

Table 3  
Contribution of each fraction in chars composition estimated by the predictive calculation

	H. products ( $H_c$ %)	C. products ( $C_c$ %)	L. products ( $L_c$ %)	Calculated yield (%)	Experimental yield (%)	Standard deviation (%)
CS	24.4	8.7	66.9	30.8	25.6	2.6
AP	23.1	18.8	58.0	16.2	25.7	4.8
PP	15.4	5.6	79.0	22.2	25.9	1.9
PS	15.1	14.1	70.8	31.1	24.6	3.3
OS	14.1	10.7	75.3	25.1	30.9	2.9
TOS	16.2	19.0	64.8	29.1	27.4	0.9
SW	17.4	27.6	55.0	24.9	21.3	1.8
MIX.	24.5	8.5	66.9	33.5	32.7	0.4

ductions of activated carbon following the equation (for example to the lignin):

$$L_a = \left[ 1 - \frac{(L \times y_{c,L} \times y_{a,L} + C \times y_{c,C} \times y_{a,C} + H \times y_{c,H} \times y_{a,H}) - (L \times y_{c,L} \times y_{a,L})}{(L \times y_{c,L} \times y_{a,L} + C \times y_{c,C} \times y_{a,C} + H \times y_{c,H} \times y_{a,H})} \right] \times 100 \quad (7)$$

where  $C_a$ ,  $H_a$ , and  $L_a$  are the H., C. and L., products after activation (in %).

In the Table 4 are gathered similar calculations for the different experimented natural lignocellulosic precursors. For example, 66.7% of the steam activated coconut shell could be attributed to lignin, 23.6% to hemicellulose and 9.7% to cellulose. The estimation of the whole burn-off under activation leads to 21.9% while the corresponding experimental value is equal to 23.7% (Table 4). Those two results are very close together and the observed variation can be mainly attributed to the residues neglected in the calculations but corresponding to 8% of the total weight of the raw material.

The weight contribution of the hemicellulose ranges between 13.6% and 23.6%, the cellulose from 6.2% and 30% and the lignin from 53.5% to 78.8%. The contributions of the three basic compounds to the activated carbons and chars weights are similar in a same precursor. In comparison to the results obtained for the chars, the burn-off deviations under activation range between 0.1% and up to 27.5% in the case of the plum pulp. As the standard deviation for materials without residues (except for PS and TOS) is less than 5%, the experimental and estimated results are in good agreement and the approach can be considered as relevant.

### 3.6. Microporous properties of the chars and activated carbons from various lignocellulosic precursors

In the Table 5 are presented the microporous properties of the different chars and activated carbons obtained from natural lignocellulosic precursors. According to the experimented operating conditions of carbonization, only the CS, TOS and SW chars are microporous with corresponding  $W_0$  in the range of 0.16–0.21  $\text{cm}^3 \text{g}^{-1}$ .

Fig. 6 represents the evolution of the mean pore size versus the specific microporous volume. This graph is of particular interest to estimate the contribution of hemicellulose, cellulose and lignin to the microporous properties of the chars and subsequent activated carbons.

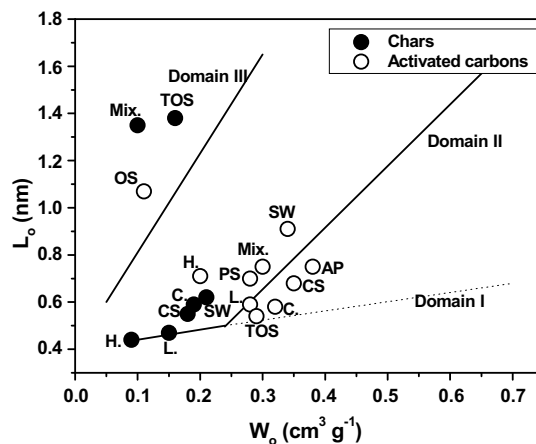
Only the chars from hemicellulose, cellulose, lignin, CS and SW are gathered on the domain I typical of initial narrow and well developed microporosity. This illustrates the fact that the proposed carbonization procedure is particularly efficient for these precursors. In the other hand, the chars from treated olive stone TOS and the synthetic mixture Mix. are gathered on the domain III characteristic of low rank porosities.

Concerning the corresponding activated carbons, only the material elaborated from untreated olive stone is in the domain III of

**Table 5**

Microporous properties of the different chars and activated carbons obtained from natural lignocellulosic precursors

		B.O.(%)	$W_t$ ( $\text{cm}^3 \text{g}^{-1}$ )	$W_0$ ( $\text{cm}^3 \text{g}^{-1}$ )	$E_0$ ( $\text{kJ mol}^{-1}$ )	$L_0$ (nm)
CS	Chars	–	0.19	0.18	24.45	0.83
	AC	23.7	0.39	0.35	27.30	0.68
AP	Chars	–	–	–	–	–
	AC	57.5	0.44	0.38	25.75	0.75
PP	Chars	–	–	–	–	–
	AC	77.0	–	–	–	–
PS	Chars	–	0.05	0.05	–	–
	AC	22.2	0.34	0.28	26.80	0.70
OS	Chars	–	–	–	–	–
	AC	70.6	0.11	0.11	21.50	1.07
TOS	Chars	–	0.16	0.16	19.20	1.38
	AC	20.8	0.30	0.29	31.30	0.54
SW	Chars	–	0.21	0.21	28.90	0.62
	AC	38.5	0.54	0.34	23.30	0.91



**Fig. 6.** The evolution of  $L_0$  with  $W_0$  ( $\text{N}_2$  at  $-196^\circ\text{C}$  (77 K)): lines I, II or III correspond to specific regimes discussed elsewhere [24]. (chars ●), (activated carbons ○).

low rank porosity. In the contrary, the other activated carbons are all gathered around the beginning of the domain II and some are very close to the domain I. Each component (H., C., L) within the raw precursor contribute to the porosity of the chars and activated carbons whatever is its weight contribution.

## 4. Conclusions

The study of physical activation by steam ( $800^\circ\text{C}$  for 120 min) of hemicellulose, cellulose and lignin separately, following carbonization under well defined conditions, shows that it is possible, to some extent, to predict the contribution of each component to the mass and the microporous properties of chars and activated carbons derived from lignocellulosic materials on the basis of their composition.

**Table 4**

Contribution of each fraction in activated carbons composition estimated by the predictive calculation

	H. products ( $H_A$ %)	C. products ( $C_A$ %)	L. products ( $L_A$ %)	Calculated B.O. (%)	Experimental B.O. (%)	Standard deviation
CS	23.6	9.7	66.7	21.9	23.7	0.9
AP	22.2	20.7	57.1	21.0	57.5	18.3
PP	14.9	6.2	78.8	22.0	77.0	27.5
PS	14.5	15.6	69.9	21.2	22.2	0.5
OS	13.6	11.8	74.6	21.5	70.6	24.6
TOS	15.4	20.9	63.6	21.0	20.8	0.1
SW	16.5	30.0	53.5	20.1	38.5	9.2
MIX.	23.6	9.7	66.7	21.9	28.5	3.3

These results show clearly that lignin is the major contributor of all chars and activated carbons. Each component (H., C., L.) within the raw precursor contribute to the porosity of the chars and activated carbons whatever is its weight contribution.

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