

CARBONIZATION KINETICS OF COCONUT SHELL AND PLUM STONE

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Introduction

In the last decades, many efforts have been focused on agricultural and industrial residues thermochemical transformation to generate energy, chemicals or activated carbons. Nevertheless, the working parameters of the conventional carbonization procedures are not well optimized yet. Activated carbons can be produced by two different routes : the chemical activation involving a sole thermal step and the physical activation including two thermal steps : a first carbonization treatment followed by an oxidation in the presence of the activating gas at elevated temperature. The textural properties of the obtained adsorbents depend not only on the nature of the precursor but also on the working parameters of the carbonization and activation steps. The porosity, in terms of mean pore size (L_o), potential specific microporous volume (W_o) and pore size distribution, is already partly established at the char level before the activation itself [1,2].

The carbonization leads to a char mainly composed of carbon, it can be proceeded at a temperature level of 800 to 1100°C under an inert gas flow and without any chemical agent. At this stage, the porosity of the adsorbent is not fully developed. Pyrolysis products like tars have to be removed by mean of the subsequent activation step to open all the potential porosity of the material. Nevertheless, the activation procedure usually induces an inhomogeneity of the pore size distribution due to the competition between diffusion and chemical phenomena. Therefore, the improvement of the carbonization procedure can reduce the amount of needed activation agent, the pore size distribution widening and the cost of the whole elaboration process.

The present study is focused on the coconut shell which is a major industrial lignocellulosic precursor and on the plum stone. These materials are mainly composed of hemicellulose, cellulose and lignin the thermal decomposition of which form the carbonaceous structure of the char precursor of the subsequent activated carbon. Despite an extensive literature in the subject, the decomposition kinetics of those fractions are still badly understood [3]. Their contributions to the obtained whole char are supposed to be of great influence upon the activated carbon properties [4]. Therefore, we have studied their thermal decomposition separately and within a synthetic blend and natural ones, the coconut shell and the plum stone. The obtained data have been analyzed by mean of a kinetic model in which the number of adjustable parameters have been reduced.

Experimental

Non-isothermal pyrolysis experiments have been proceeded using a Setaram 111 thermogravimetric differential scanning calorimeter at atmospheric pressure. Samples of 50 mg have been heat treated under nitrogen flow of 0.50 L/min in order to remove the pyrolysis gaseous products.

A serie of ground and sieved coconut shell powders (40, 160, 200 and a mix<200 μm) have been heat treated from the room temperature up to 800°C at different heating rates and kept at the final temperature during one hour. The different experimented heating rates values are : 1-5-10-20-25 and 30 K \times min.

Same experiments have been also achieved on the three major fractions known to be present in a coconut shell : cellulose (C.), hemicellulose (H.) and lignin (L.). Those components have been supplied by Aldrich : lignin 8072-93-3, cellulose 9004-34-6 and Xylan 36,355-3.

The model has been developed with the coconut shell data and has been also applied to plum stone data.

For char porosity characterizations, higher char amounts are needed. Therefore, experiments under the same conditions have been proceeded in an horizontal conventional furnace with sample loading of 10 g. The porosity characterization of the obtained chars was proceeded by conventional nitrogen adsorption/desorption isotherms at 77 K on samples of 0.2 g following outgasing at 523 K for 24 h and under a residual vacuum of less than 10^{-4} Pa [2]. The microporosity has been characterized following to the Dubinin's theory. From the linear part of the Dubinin-Radushkevich (DR) plots were estimated both the specific microporous volumes W_o and the mean pore sizes L_o . As the solids have low external surface areas ($S_e < 20\text{-}25 \text{ m}^2 \times \text{g}^{-1}$), the total pore volume (W_t) could be estimated directly from the amount adsorbed at relative pressure $p/p_s = 0.95$.

Results and discussion

The coconut shell and the plum stone used in this study are composed respectively of 35%wt. and 22%wt in hemicellulose, 15%wt. and 25%wt in cellulose and 50%wt. and 53%wt in lignin (courtesy G.Chambat *CERMAV-CNRS*). The composition of the raw lignocellulosic materials used in this study is given in Table 1 (courtesy *Service Central d'Analyse du C.N.R.S*). The composition results are different from those from the literature [5,6].

sample	C (%)	H (%)	O (%)	N (%)	S (%)	Water (%)	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
Plum stone	50.7	6.3	41.1	0.86	<0.3	3,8	0.9
Coconut	48.7	5.8	42.5	<0.3	<0.3	380 ppm	5.0
Mix.art.	50.1	5.9	38.3	0.5	<0.3	6.5	4.9

Table 1 . Composition of the raw materials

Coconut shell and plum stone compositions are nearly similar. According to the respective weight loss measured on each isolated component, 65% of the coconut char mass has to be attributed to its lignin fraction, 10% to its cellulose fraction and 25% to its hemicellulose fraction.

sample	Δm %	W_t (cm ³ ×g ⁻¹)	W_o (cm ³ ×g ⁻¹)	L_o (Å)
Hemicellulose char	76.5	0.09	0.09	4.4
Cellulose char	80.9	0.19	0.19	5.9
Lignin char	55.1	0.15	0.15	4.7
Plum stone char	75.4	-	-	-
Coconut char	74.4	0.18	0.18	5.5
Mix. char	67.3	0.10	0.10	4.0

Table 2 . char characteristics (5 K min⁻¹, T_f= 800°C, 1 h.)

In Table 2 have been gathered the microporous properties of the chars obtained from the three separated fractions (hemicellulose, cellulose, lignin), the plum stone, the coconut shell and the synthetic blend. The textural properties of those chars evidence that the three fractions do not lead to the same type of porosity. Moreover, the coconut shell char porosity is well correlated to the mean value of the lignin and cellulose.

In the Figure 1 are illustrated the weight loss curves (TGA curve) of the coconut shell for different particle diameter values. Obviously, there is no effect of the particle diameter on the pyrolysis. Therefore, the corresponding data can be considered under chemical limitation without any diffusion effect.

In Figure 2, the rate of decomposition of the coconut shell is illustrated in term of differential weight loss (DTG profile) against temperature for a heating rate of 10 K/min⁻¹. On the same figure have been drawn the deconvolution of the DTG profile by three theoretical kinetics contributions corresponding to the three major fractions and their summation for comparison with the experimental curve. On the DTG profiles of the coconut shell, the respective decomposition domains of the three major fractions are very easy to observe. Even the lignin fraction, which is known to decompose over a wide temperature range while the two other fractions decompose over some 100°C, is easily identified by the last 680-800°C tail.

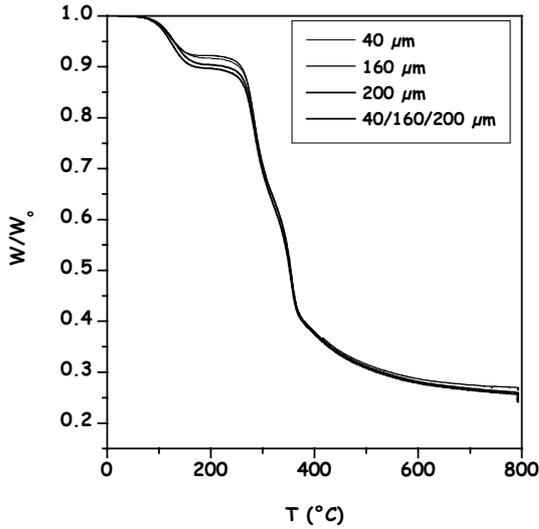


Figure 1. coconut TGA curves
50mg, 10 K. min⁻¹, 40-160-200μm-
mix.<200μm.

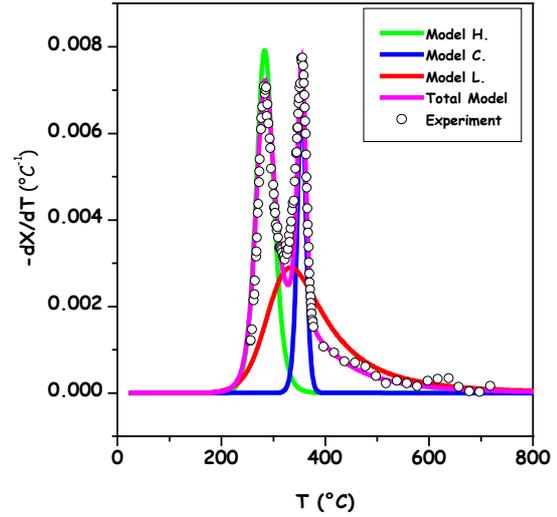


Figure 2. coconut DTG profile
50mg, 10 K. min⁻¹.

In Figure 3 are gathered the experimental DTG profiles of the three isolated fractions, cellulose hemicellulose and lignin, and their mixing in the proportions of the coconut shell (35% hemicellulose, 15% cellulose, 50% lignin).

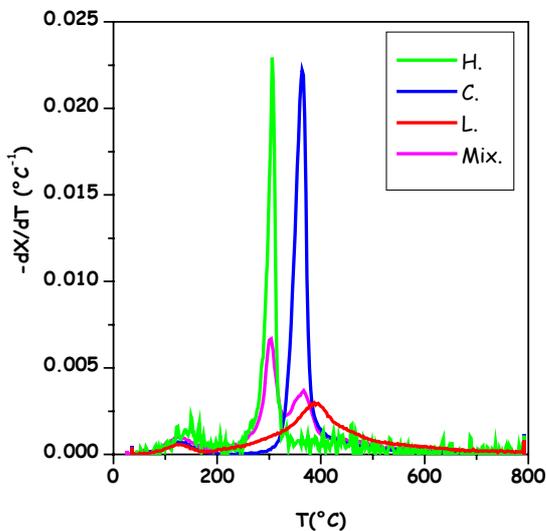


Figure 3. DTG profile of the H C L
fractions and their mixing (35, 15, 50 %),
50mg, 10 K. min⁻¹.

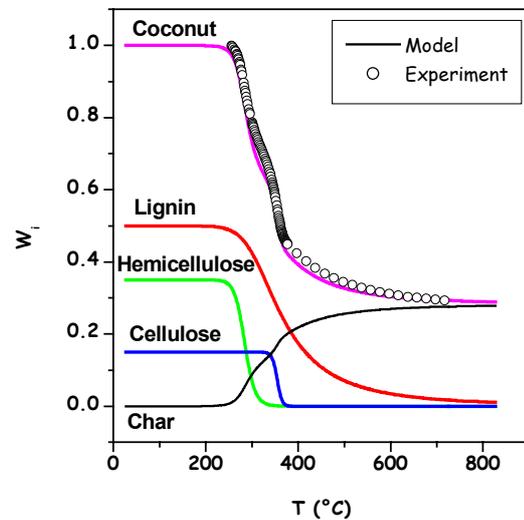


Figure 4. experimental coconut TGA
curve and model, 50mg, 10 K. min⁻¹.

The observed DTG profiles of the isolated compounds are in perfect agreement with the proposed deconvolution of the coconut DTG profile of Figure 2 and the corresponding decomposition temperature ranges of each fraction too.

The hemicellulose and cellulose fractions react over narrow temperature ranges of 250 to 325°C and 300 to 400°C respectively while the lignin fraction decomposes over a wide temperature range of 200 to 800°C. In term of kinetics, the cellulose

decomposition rates presents the most higher value followed by the hemicellulose fraction the decomposition rate of which is a third less important and by the lignin presenting a very low decomposition rate. Those kinetics observations are in perfect agreement with previous studies available in the literature.

In Figure 4 are illustrated the calculated weight loss curves of the three fractions, the associated char weight increase and the corresponding whole weight curve according to the coconut composition. The experimental results obtained on the real coconut are very well predicted by the model.

In Figure 5, the rate of decomposition of the plum stone is illustrated in term of differential weight loss (DTG profile) against temperature for a heating rate of 10 K/min^{-1} . On this DTG profile, the respective decomposition domains of the three major fractions are also very easy to observe and are in perfect agreement with the observed DTG profiles of the isolated compounds. In term of kinetics, the hemicellulose and cellulose decomposition rates in coconut and plum stone are different. Nevertheless, as shown in Figure 6, the experimental results obtained on the plum stone are also very well predicted by the model.

One can clearly see in figures 4 and 6, the different weight loss curves of the three fractions in both materials with a nearly similar composition.

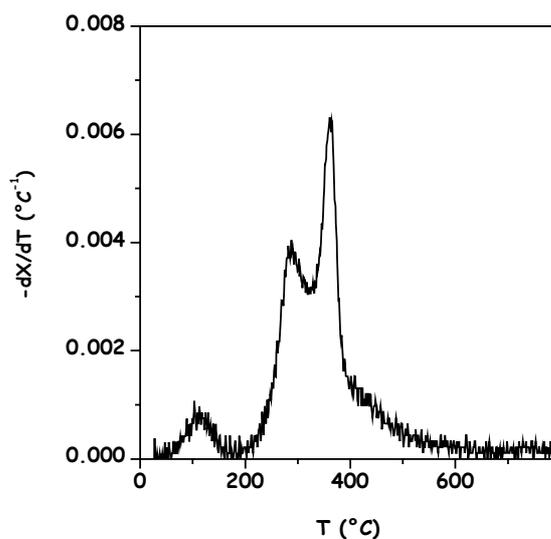


Figure 5. plum stone DTG profile
50mg, 10 K. min^{-1} .

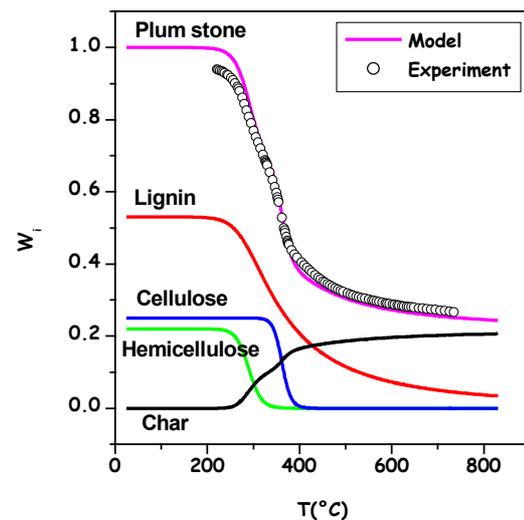


Figure 6. experimental plum stone TGA
curve and model, 50mg, 10 K. min^{-1} .

Kinetics

The non-isothermal decomposition kinetics of a lignocellulosic material is difficult to study. The thermal decomposition of the major component (lignin in term of weight fraction) is partly hidden by the two much more reactive fractions (cellulose and hemicellulose). Therefore, a deconvolution of the DTG curve in three independant contributions is needed to allow any kinetic analysis.

The decomposition kinetics of each of the three fractions are well correlated by independent power-law expressions [7].

The overall pyrolysis rate (equation 1) is equal to the sum of each of the fraction decomposition kinetics balanced by their respective weight fractions and the corresponding chars formation rates (W_{ci}) balanced by their stoichiometric coefficients.

$$\frac{dW}{dT} = \sum_i \left(\frac{dW_i}{dT} + \nu_i \frac{dW_{ci}}{dT} \right) \quad [1]$$

The stoichiometric coefficients of the chars inherited from each of the three compounds have been identified from the yield measured on the decomposition of the isolated hemicellulose, cellulose and lignin. Those coefficients linked to the respective weight of each fraction have to agree with the overall yield of the lignocellulosic material or mixing.

$$W_\infty = \sum_i W_{ci} \quad [2]$$

$$W_{ci} = \nu_i (W_{i0} - W_i) \quad [3]$$

In most of the published studies, the contribution of the char to the overall kinetics is neglected. This is due to the usual failure to appreciate the initial composition of the lignocellulosic material and the char stoichiometric coefficients. Therefore, the decomposition rates are usually under-estimated and the corresponding identified kinetics parameters erroneous.

In the present model, the decomposition rates are written in term of weight fraction variations taking as a reference the initial anhydre lignocellulosic material weight.

$$\frac{dW_i}{dT} = \frac{k_{ci0}}{\beta} \times W_{i0}^{n_i-1} \times W_i^{n_i} \times \exp\left(-\frac{E_i}{R \times T}\right) \quad [4]$$

This kinetics model is based on 15 adjustable parameters the values of which have to be identified using the available experimental data. This number of parameters is too high to lead to a sole set of solutions. Nevertheless, the natural deconvolution of the experimental coconut TGA profile allows to define several additional constraints which have to be fulfilled by the model. Then, the number of adjustable parameters is reduced.

The first constraint is defined at the top of each peak where the second derived of the weight has to be zero and its first derivative equal to the experimental decomposition rate at the observed temperature.

By the application of this principle to each fraction, the model is reduced to 3 adjustable parameters. Considering that the literature is quite homogeneous in term of activation energy values, we have chosen to use those parameters as adjustable ones.

The reduced model illustrated in Figures 2 and 4 is in very good agreement with experimental data and the corresponding kinetic parameters with the literature.

Conclusions

A kinetic model for the thermal decomposition of the coconut lignocellulosic material has been validated. This model can also be applied to the thermal decomposition of

the plum stone. This model is based on a deconvolution of the TGA profile in three contributions corresponding to the three major components : cellulose, hemicellulose, lignin. The deconvolution method has been checked by the comparison between the experimental thermal decomposition of the three isolated compounds and their mixing. A particular technique is proposed to reduce the number of adjustable parameters needed in the model from 15 to 3.

This model will be extended to particles of bigger size tacking into account the mass and heat transfer kinetics. Then, the whole model will be used for optimization of the carbonization protocole of lignocellulosic material with respect to the obtained microporous properties.

References

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