

Determination of the Kinetic Parameters of the Slow Pyrolysis of Coconut Shell from Ivory Coast

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Résumé

Les coques de noix de coco constituent des déchets abondants difficilement biodégradables dans les pays tropicaux et particulièrement en Côte d'Ivoire. Pourtant, en dépit de leurs potentielles sources d'énergies, elles sont peu étudiées. Leurs caractéristiques cinétiques restent pratiquement ignorées. Dans la présente étude, nous nous sommes intéressés à leurs paramètres cinétiques qui ont été déterminés à l'aide de la thermogravimétrie. Ces données gravimétriques sont traitées par la méthode différentielle de Kissinger et la méthode d'intégration de Flynn – Wall – Ozawa. Les résultats obtenus montrent que la dégradation des coques se fait en deux étapes et que l'énergie de la première étape est plus faible que celle de la deuxième. En tenant compte des domaines de décomposition du xylane, de la cellulose et de la lignine ; constituants essentiels des coques de noix de coco d'une part et de ceux des coques elles-mêmes d'autre part, nous interprétons la décomposition des coques de noix de coco comme étant la décomposition de l'hémicellulose en première étape et de celle conjointe de la cellulose et de la lignine en deuxième étape.

Mots clefs : Energie d'activation, Pyrolyse, Thermogravimétrie, Paramètres cinétiques

Summary

The coconut shells don't constitute an easy biodegradable abundant waste in the tropical countries and particularly in Ivory Coast. However, in spite of their potential sources of energy, they are not sufficiently studied. Their kinetic characteristics remain practically unknown. In the present study, we are interested in their kinetic parameters which are given by using thermogravimetry. These gravimetric data are treated through Kissinger's differential method and the method of integration by Flynn – Wall – Ozawa. The results obtained show that the degradation of the shell is made in two stages and that the energy of the first stage is weaker than that of the second. By taking into account the fields of decomposition of xylan, cellulose and lignin; essential components of the coconut shells on the one hand and those of the shells themselves on the other hand, we interpret the decomposition of coconut shells as being first the decomposition of hemicellulose and then that of cellulose and lignin.

Keywords: Activation energy, Pyrolysis, Thermogravimetry, Kinetic parameters, coconut shell

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1. Introduction

In Ivory Coast, charcoal remains the principal source of energy in domestic sector. It is competed with more and more by the butane gas. Moreover, it is very much used in the craft industry namely in potteries and bakeries. In rural areas, the demand in wood was satisfied thanks to wood extracted directly from the forest. However the regulation on the forest products gradually limited families' wood supply. Nevertheless, the demand for charcoal remains unsolved. This is the reason why the producers are turning to another source of energy: coconut shells. Indeed, after extraction of the coconut milk, the coconut shells are highly regarded as waste. This waste accumulates and is not easily biodegradable.

So far, the manufacture of charcoal is made in a traditional way. Also, to better answer the demand in view of optimizing the production from coconut shell, it is essential to replace the old methods of manufacture by more adapted technologies.

The physical and chemical properties of various wood species and the kinetic parameters of the wood pyrolysis were studied ^[1,2]. However, that of coconut shells are still not very accessible and the publications on their pyrolysis are recent ^[3].

Whatever the starting biomass, it is possible to choose experimental favourable conditions for the production of solids ^[4]. Such as the final temperature of pyrolysis and the temperature heating rate. According to R. Capart and *al.* ^[5], a final temperature of pyrolysis lower than 600°C and a low temperature heating rate (less than 11°C.mn⁻¹) lead to good outputs. These authors conclude that the limit of thermal transfer is thus negligible at these heating rates.

In this work, we were interested in the study of the thermal behaviour of coconut shells under experimental conditions

favourable to an important production in solid. To better include the thermal behaviour of coconut shells, we will compare it with that of xylan, cellulose and lignin. The kinetic parameters of pyrolysis will also be studied.

2. Experimental

2.1. Raw materials

The matters subjected to the heat treatment in this study are:

- Lignin (Aldrich, organosolv, CAS 8068 – 03 – 9), xylan (Sigma, from Birchwood CAS 9014 – 63 – 5) and microcrystalline cellulose (Merck, Cat. N° 102330).
- Coconut shells from the Ivory Coast (Africa). Its biochemical composition as determined classically is (wt. % dry matter): cellulose 51; hemicellulose 27 and lignin 20. Before fractionation and thermogravimetric experiments, the coconut shell was ground to a size range less than 200µm.

In order to study the principal coconut shell constituents, we use a fractionation method combining the approaches used by Müller – Hagedorn and *al.* ^[6] and Collura and *al.* ^[7]. This technique allows the separation of raw material in three fractions respectively rich in cellulose, hemicellulose and lignin by simple water (de-ashing and water extractable products removal), H₂SO₄ 0.7M (hemicelluloses hydrolysis) and KOH 0.5M (lignin and residual hemicellulose degradation) washings. In the case of acid and alkali treatments, samples were washed with distilled water until a neutral pH was obtained and all the salt was removed.

2.2. Apparatus

This study was performed using SETARAM 92 (TG), with crucible (oxide of silicon) and a vertical hung-down thermobalance. Scientific argon was used

as protective/inert carrier gas at 50 mL.min⁻¹. The following temperature program was used:

- i) From ambient temperature to 100°C, at a heating rate of 10°C.min⁻¹, for sample drying;
- ii) Isothermal drying at 100°C, for 10 min;
- iii) From 100 to 600°C at different heating rates (2, 3, 5, 6 and 10°C.min⁻¹);
- iv) Isothermal transformation at 600°C for 10 min.

The mass loss and mass loss rate were recorded online by specific software designed by SETARAM, as functions of time and temperature.

In order to determine the pyrolysis kinetics parameters obtained through thermal analytical techniques, different methods are available^[8,9]. They are based on different assumptions in order to simplify the complexity of the several reactions that occur during the devolatilisation process. In this study, the detailed investigation of thermal decomposition of coconut shells containing flame retardant components is concerned. The kinetic parameters were determined by various methods from the results of thermogravimetric analysis.

3. Mathematical theory

In the non-isothermal experiments carried out with a thermobalance, the sample mass is measured as a function of temperature. The reaction rate in TGA studies can be defined as the variation of degree of conversion (α) according to time or temperature and the conversion is typically calculated as^[10]:

$$\alpha = \frac{w_o - w_t}{w_o - w_f} \quad (1)$$

where w_o , w_t and w_f are, respectively, weight at the beginning of the degradation step, actual weight at each point of the curve and the final weight measured after the specific degradation process considered.

All kinetic studies^[3, 10 - 12] assume that the isothermal rate of conversion, $\frac{d\alpha}{dt}$, is a linear function of a temperature – dependent rate constant, $k(T)$, and a temperature – independent function of the conversion, (α) i.e.,

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (2)$$

where $f(\alpha)$ depends on the mechanism of the degradation reaction. The function $k(T)$ is usually described by Arrhenius equation:

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where A, E, R and T are the pre-exponential factor (min⁻¹) assumed to be independent of temperature, the activation energy (J.mol⁻¹), the gas constant (8.314 J.mol⁻¹ K⁻¹) and the absolute temperature (K), respectively.

Several methods were suggested to determine the kinetic parameters of the above equation. In this study, we use Kissinger's method^[13] and Flynn – Wall – Ozawa's method^[14].

3.1. Kissinger's method

Kissinger's method is one of the differential methods that have been used to determine the activation energy of solid state reactions from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments. The beauty of this method is that even without a precise knowledge of the reaction mechanism, the activation energy can be determined using the following equation:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln\left(\frac{AR}{E}\right) + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E}{RT_{\max}} \quad (4)$$

where β is the heating rate, $T_{\max}$ is the temperature corresponding to the inflection point of the thermal degradation curves which corresponds to the maximum rate, A is the pre-exponential factor, E is the

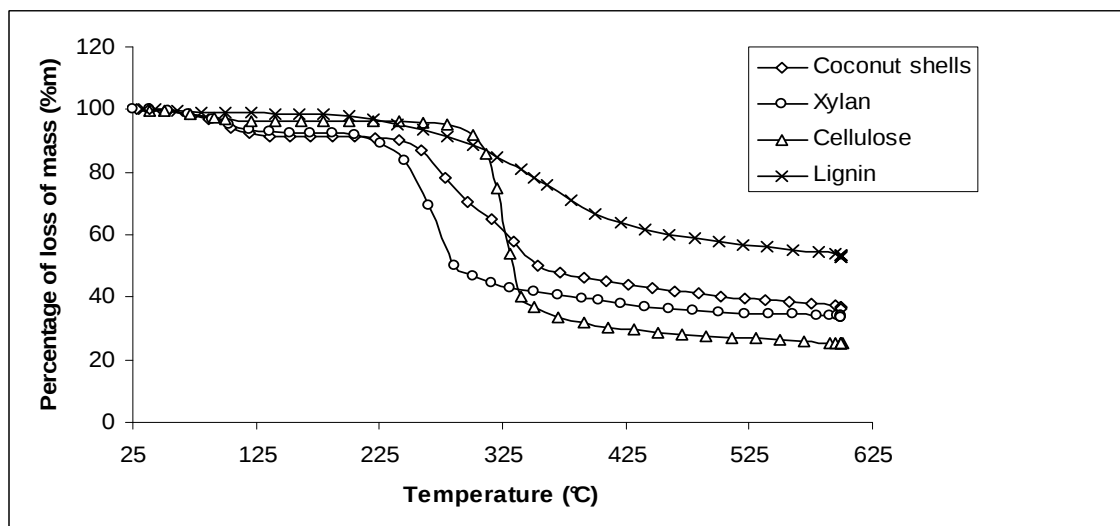


Figure 1: Thermogravimetric analysis of coconut shells and its components essentials at $5^{\circ}\text{C}.\text{min}^{-1}$

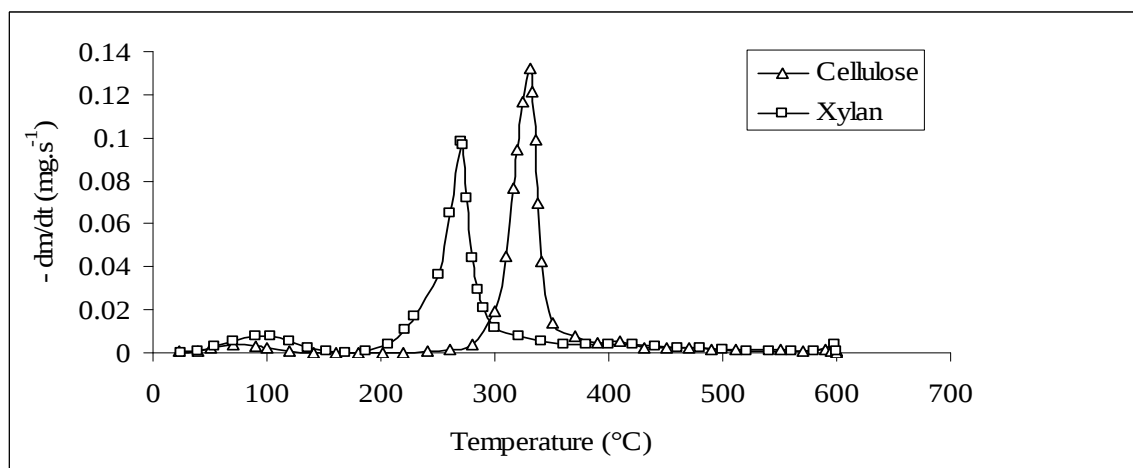


Figure 2: DTG of xylan and cellulose at $5^{\circ}\text{C}.\text{min}^{-1}$

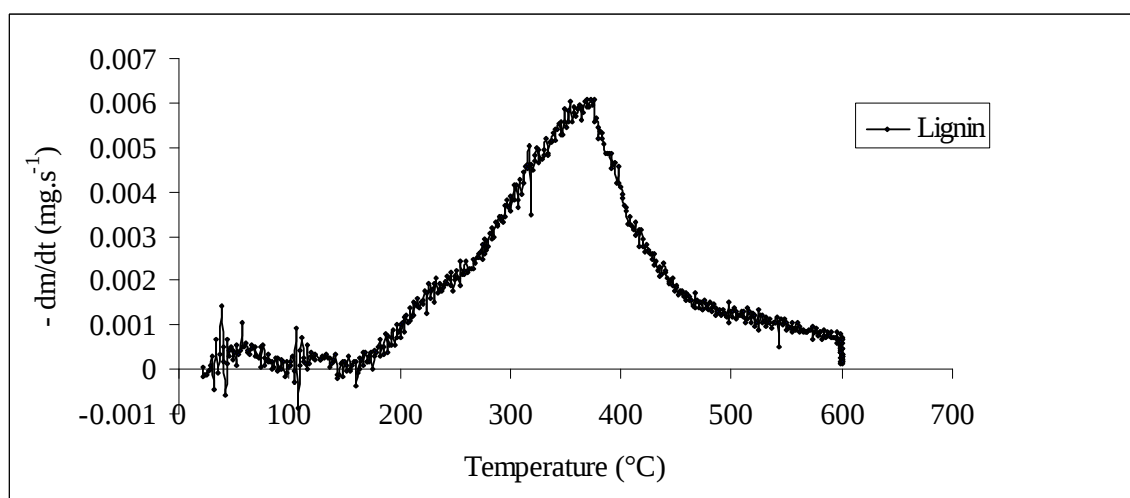


Figure 3: DTG of lignin at $5^{\circ}\text{C}.\text{min}^{-1}$

activation energy, $\alpha_{\max}$ is the maximum conversion and n is the order of the reaction.

From a plot of $\ln\left(\frac{\beta}{T_{\max}^2}\right)$ versus $\frac{1}{T_{\max}}$ and fitting to a straight line, E can be calculated from the slope $\frac{E}{R}$.

3.2. Flynn – Wall – Ozawa's method

This isoconversional integral method suggested independently by Ozawa^[15] and Flynn and Wall^[16] uses Doyle's approximation^[17] of the temperature integral. By using this approximation, they obtain:

$$\log \beta = \log\left(\frac{AE}{g(\alpha)R}\right) - 2,315 - 0,457 \frac{E}{RT} \quad (5)$$

where β , A , E , R and T have their usual significance.

Thus, for $\alpha \approx \text{constant}$, the plot of

$\log(\beta)$ versus $\frac{1}{T}$ obtained at several

heating rates should be a straight line whose slope can be used to evaluate the activation energy. Indeed, the line obtained

has as a slope $-0,457 \frac{E}{R}$. From the

knowledge of this slope, we deduce E .

4. Results and discussion

4.1. Characteristics of pyrolysis

The curves of thermogravimetric analysis of the studied matters are given in Figure 1. As the curves show it, xylan starts to be degraded before cellulose and lignin, in agreement with the majority of work of the literature^[18,19] which indicates that hemicellulose breaks up before cellulose and lignin. To the best of our knowledge, F. Kifani – Sahban and *al.*^[1] and Khezami^[5] noticed that lignin undergoes decomposition before xylan and cellulose. Figures 2 and 3 show the mass loss rate (derivative thermograms) for the three essential components. A clear difference

between lignin pellets thermogram and the other two biomass samples thermograms is noticeable. The DTG curves of xylan and cellulose (Figure 2) present the same form. Whereas lignin (Figure 3) differs from the two preceding ones, it presents a shoulder at the low temperatures. Authors^[6,20] also showed that the peak to lignin is broad. According to A. J. Tsamba et *al.*^[3], lignin decomposition is distributed along a wide range of temperature interval and its peak is not commonly distinguishable. However, it is believed that the long flattail observed at high temperatures is caused by lignin decomposition.

In the case of coconut shells, DTG curve (Figure 4) presents, in the interval 230 – 400°C, a first peak at 274°C and a second at 339°C. Turning to Figure 5, it is possible to allot the rate reached by coconut shells to 274°C and 339°C respectively to the degradation of xylan and consequently to hemicellulose and cellulose. Indeed authors^[21,22] in the study of various materials of biomass showed that the first peak corresponds to the decomposition of hemicellulose and the second peak to cellulose. Even if lignin takes part in pyrolysis in all the temperature range explored (Figure 3), its decomposition in the interval 230 – 400°C is masked by those of xylan and cellulose (Figure 5)

By juxtaposing DTG curves of coconut shell and its essential components (figure 5), we notice that the first peak is in the same temperature range as that of xylan and the second peak is in the same field as that of cellulose. The light shift observed at the level of the second peak could be due to the joint decomposition of lignin.

By comparing the decomposition rates of xylan, cellulose and lignin with coconut shell, we note that xylan and cellulose respectively degrade two and three times more quickly than coconut shell whereas the latter breaks up seven times more quickly than lignin (Table I).

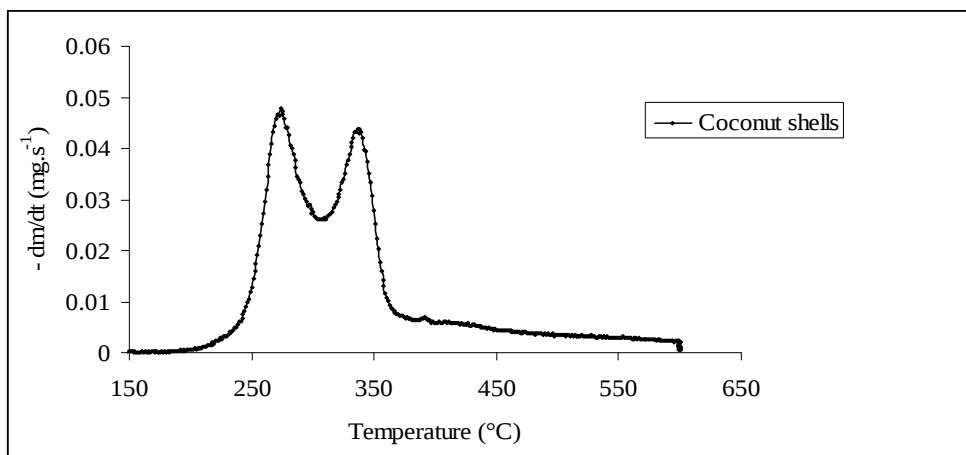


Figure 4: DTG of coconut shells at 5°C.min⁻¹

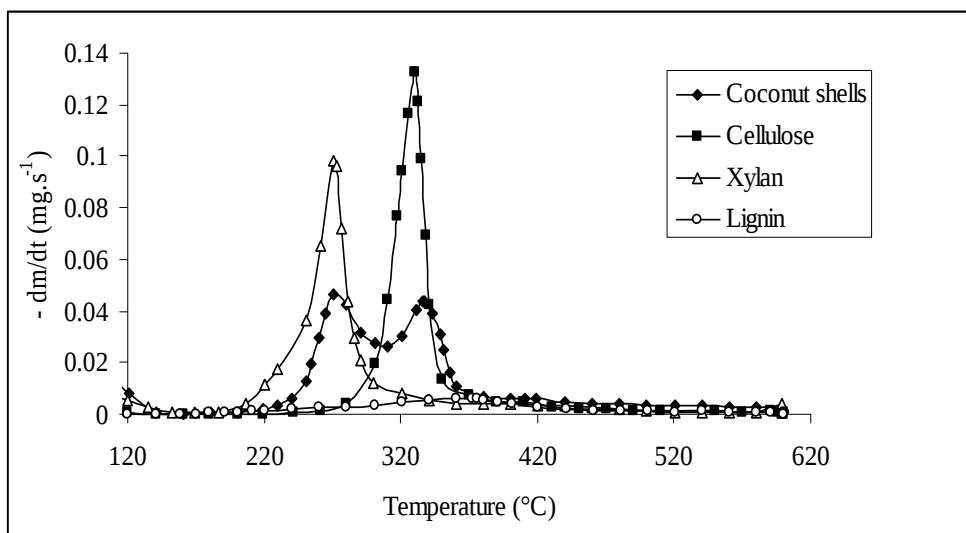


Figure 5: DTG of coconut shells and its essential components at 5°C.min⁻¹

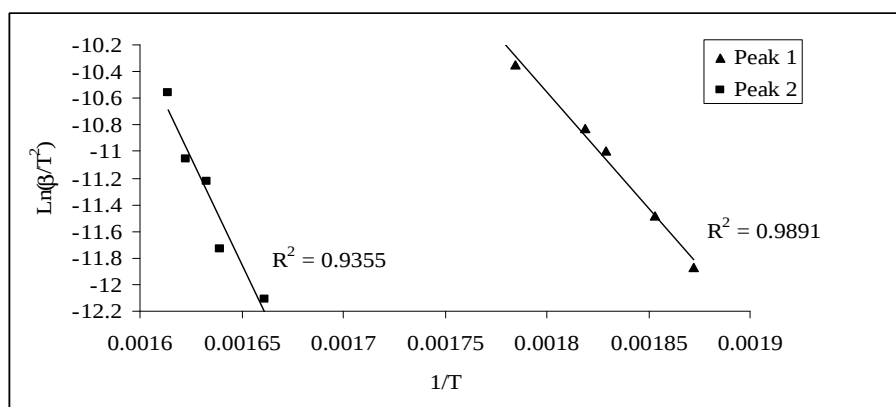


Figure 6: Plots of $\ln\left(\frac{\beta}{T_{\max}^2}\right)$ versus $\frac{1}{T_{\max}}$ of coconut shell for calculating the activation energies by Kissinger's method

Table I: Maximum weight loss rate of coconut shells and its essential components at $5^{\circ}\text{C}.\text{mn}^{-1}$

Raw materials	Temperature ($^{\circ}\text{C}$)	Maximum rate of loss of mass ($10^{-2} \text{ mg.s}^{-1}$)
Coconut shell	274	4.77
	339	4.33
Xylan	270	9.81
Cellulose	329	13.30
Lignin	373	0.61

We think that lignin having a low rate reaction, its decomposition would tend to reduce that of the coconut shell or as, F. Kifani - Sahban and *al.* ^[1] have suggested, the components of nuts would react among themselves, that is to say in the course of their degradation. Indeed, according to Vamvuka and *al.* ^[20], the DTG peak height is directly proportional to reactivity and the corresponding temperature is inversely proportional to the chemical parameters. It is possible also that the reactions of thermal degradation of these three components are preceded by parallel reactions degradation of coconut shell in these components initially associated. The percentages in residues at 600°C of coconut shell at various heating rates are found in Table II.

Table II: Output of solid at 600°C according to the heating rate

heating rate ($^{\circ}\text{C}.\text{min}^{-1}$)	2	3	5	6	10
% Residues	35.08	35.87	36.57	36.39	35.05

The outputs are nearly the same whatever the heating rate. That could be thus explained: the char yield notably decreases with increasing heating rates but increases with shorter reaction times and the two effects compensate. The best yield of coal is obtained at $5^{\circ}\text{C}.\text{min}^{-1}$.

4.2. Output of volatile matters and solids
Volatile matter and the coal yields of the various studied matters were given starting from the thermograms of Figure 1 and are

given in Table 3. The coal yield of lignin is definitely higher than that of the xylan which is higher than that of cellulose.

The coal yield of coconut shell is 37%. It is rather close to that of xylan. This value starts to be reached starting from 450°C (Figure 1). This temperature could be selected like maximum temperature of pyrolysis.

The output in residues of coconut shell is definitely higher than that of the eucalyptus ^[1] which is 20%. According to Heikkimen and *al.* ^[23], the output in residues of wood is approximately 22%. The output obtained of coal on the level of coconut shell consolidates us on our starting assumption according to which coconut shell would constitute a source of energy better than the charcoal. Its use is thus for the State of Ivory Coast a major asset for the protection of the flora and the energy saving.

Table III: Comparison of the volatile matters and solids outputs at 600°C of various matters studied and of those of certain authors

Raw materials	Residues	Volatile matters
Xylan	33%	67%
Cellulose	25%	75%
Lignin	53%	47%
Coconut shells	37%	63%
Eucalyptus [1]	20%	80%
Wood [23]	22%	78%

4.3. Kinetic parameters

The kinetic parameters of coconut shells are given. We give in table 4 the recorded temperatures when the kinetics of degradation is high.

Table IV: Temperatures T_{max} at the maximum weight loss rate.

Rate	2	3	5	6	10
T_{max} of peak 1 ($^{\circ}\text{C}$)	261	267	274	277	287
T_{max} of peak 2 ($^{\circ}\text{C}$)	329	337	339	343	347

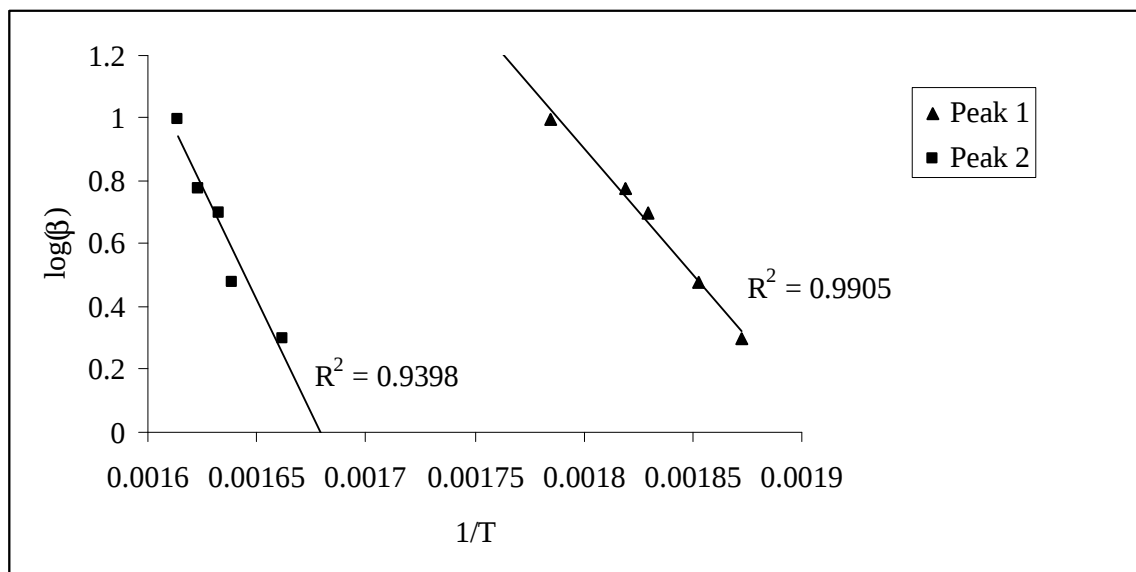


Figure 7: Plots of $\log \beta$ versus $\frac{1}{T}$ of coconut shell for calculating the activation energies by Flynn – Wall – Ozawa's method

Table V: Comparative activation energies results from different authors

Authors	Raw materials	Parameters		
		Interval of temperatures (°C)	Activation energies (kJ.mol ⁻¹)	
F. Kifani – Sahban <i>et al.</i> [1]	Xylan	195 – 280	179.50	
	Cellulose	300 – 375	228.60	
	Lignin	184 – 400	40.71	
	Eucalyptus	220 – 300	130.17	
		300 – 360	226.72	
A. J. Tsamba <i>et al.</i> [3]	Hémicellulose	250 – 380	172.75	
	Cellulose	380 – 450	248.64	
Our results	Coconut shells	Stages (°C)	Kissinger method (kJ.mol ⁻¹)	Flynn – Wall – Ozawa method (kJ.mol ⁻¹)
		Peak 1 230 – 300	145.15	146.59
		Peak 2 300 – 400	265.96	262.39

The four components are degraded in the interval 230 – 450°C (figures 1 and 5). This interval was used to determinate the kinetic parameters.

As mentioned before, Kissinger and Flynn – Wall – Ozawa methods are applied. As shown in figure 1, the different reactions in the temperature interval where the main pyrolysis process in both biomass species takes place, from 230°C to 400°C, are evident, suggesting that different lignocellulosic components, first, hemicellulose and then cellulose, are degraded ^[20-22]. These stages are approximately from 230 to 300 °C and from 300 to 400 °C, respectively. This subdivision is observed in both biomass samples at both heating rates considered in the study. These two intervals constitute the main focus of the present study.

The curves obtained following these two methods are given in figures 6 and 7 and the kinetic parameters obtained are gathered in Table IV.

As mentioned before, DTG curves of coconut shell present two steps and the curves obtained by Kissinger and Flynn – Wall – Ozawa methods are two lines from which the slopes are different. The thermogram of coconut shell presents two peaks which were modelling in our case by two successive reactions. Collura and *al.* ^[7] obtained the same results with *Miscanthus x Giganteus*.

The coconut shell presents two lines, characteristics of two reactions for which we specified the kinetic parameters. These values indicate that the shells are degraded in two stages. Activation energy of the first stage is much weaker than that of the second. Work of the literature ^[1,3] showed that the activation energy of hemicellulose is generally weaker than that of cellulose. The thermal decomposition of coconut shell can be presented by a simple combination of its components decomposition; we allot the first stage to hemicellulose and the second to cellulose and lignin.

For our part, we think that the first stage could be attributed to hemicellulose. Because the activation energy obtained for this stage is of the same order to hemicellulose activation energy existing in the literature (Table V). That of the second stage is on the same order to the sum of activation energies of cellulose and lignin. It would be thus due mainly to the decomposition of cellulose and lignin.

5. Conclusion

Coconut shell and its component essentials pyrolysis were successfully characterised. Differences and similarities between these biomass wastes and wood pellets were found and discussed. The activation energy of the first stage is weaker than the activation energy of the second stage. Coconut shell pyrolysis presents clearly different and distinct peaks for hemicellulose (first) and for cellulose (second) differing from the ordinary one overlapping peak normally found in most of the woody biomass pyrolysis. To obtain a better coal yield, the maximum temperature of pyrolysis must be fixed at approximately 450°C.

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