

## Research Article

# Not Reacted Core Model Applied in Palm Nut Shell Pyrolysis

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One of the main sources of activated carbon is biomass which can be transformed into char by pyrolysis. Apart from the obtaining coal, the pyrolysis of biomass can be used for the preparation of fuels, and this is why it is very important to determine its kinetic parameters for modelling. In the present research, the pyrolysis enthalpy of palm nut shells (*Elaeis guineensis*) was determined with the use of a differential scanning calorimetry study (DSC). To determine the kinetic parameters, the Not Reacted Core model was employed. This model considers that there is a heat and mass gradient between the furnace atmosphere and the interface formed during pyrolysis. To obtain the required data for the model, palm nut shells were submitted to pyrolysis in a Nichols furnace under reducing atmosphere. Samples were taken every 10 minutes to calculate char conversion. The experimental pyrolysis enthalpy resulted to be 301.81 J/g and then the monomeric units of cellulose, hemicellulose, and lignin were employed in order to determine the pyrolysis enthalpy per mole. The three biopolymers react with different mechanisms at different temperatures. The molecular weight resulted to be 172.38 g/mole, and the enthalpy for pyrolysis was 52.03 kJ/mol. For the application of the Not Reacted Core model, the amorphous char heat transfer coefficient was selected, and the value is 1.6 J/s·m·K. The reaction rate constant was  $6.64 \times 10^{-9}$  1/s assuming a first-order reaction, whereas the effective diffusion across the char layer was  $4.83 \times 10^{-7}$  m<sup>2</sup>/s.

## 1. Introduction

The search for new sources of energy has provoked the general interest for the use of biomass. The pyrolysis of biomass is a complex thermal process that allows obtaining fuels [1]. However, the process is very complex, and it depends on several factors. It should also be noted that each lignocellulosic material to be used tends to vary enormously in its chemical composition. As it is of general knowledge, biomass is composed of several components, and the three more representatives are cellulose, hemicellulose, and lignin [2]. According to biomass chemical composition, pyrolysis could be endothermic or exothermic. Generally, lignocellulosic materials that have a higher concentration of lignin will tend to show endothermic pyrolysis. On the contrary, lignocellulosic materials have a lower concentration of lignin and a greater quantity of cellulose and hemicellulose, and they will show an exothermic behaviour during pyrolysis. Usually, the lignocellulosic substances that come from the

stems have a higher concentration of lignin in their structure [3].

In order to understand the pyrolysis of lignocellulosic materials such as palm nut shells, it is necessary to understand how the decomposition of the main constituents occurs. Thus, the process of pyrolysis of palm nut shells can be divided into four major stages: dehydration of the bean, decomposition of hemicellulose, decomposition of cellulose, and decomposition of lignin [4]. Depending on which component is in greater concentration with respect to the others, biomass will have an exothermic or endothermic behaviour during pyrolysis. Thus, in many articles, it is frequently discussed whether the nature of the pyrolysis is exothermic or endothermic. According to several authors, if the content of lignin is high, the pyrolysis process will be endothermic [3, 5–7].

Cellulose and hemicellulose may have the same mechanisms of thermal decomposition. The mechanisms proposed for the pyrolysis of cellulose consider dehydration and

depolymerization reactions with breakdown of glycosidic bonds and bonds which produce tar, levoglucosan, furfural, and heterocyclic compounds as well as CO, CO<sub>2</sub>, CH<sub>4</sub>, CnHm, and H<sub>2</sub> [8]. The coal is produced by low temperature dehydration reactions and secondary reactions of repolymerization (reforming). In addition, carbon in the form of graphene layers is produced by aromatization reactions which occur via dehydration reactions that produce coal. These reactions are exothermic, while reactions that generate tar and gases are highly endothermic [9].

Lignin, on the contrary, has a much more complex structure. It is made up of different phenolic molecules and carbonyl compounds, and when they are fragmented during pyrolysis, these molecules give rise to different aromatic compounds. The mechanisms of thermal decomposition of lignin are much more complex [10, 11]. They are based on dehydration and on depolymerization reactions similar to those proposed for cellulose. Due to the chemical composition of the lignin, the production of tar and levoglucosan is less than in the case of cellulose, which results in a higher production of coal in the pyrolysed material. However, there are three components that are repeated throughout the chemical structure with different forms of polymerization. These are *p*-coumaryl alcohol (C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>), coniferyl alcohol (C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>), and synapyl alcohol (C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>) [12, 13].

In the literature, the three organic compounds are accepted as the main components of lignin. These components possess the main functional groups (hydroxyl groups and methoxy groups) that participate in the formation and decomposition reactions of lignin. In fact, it is considered that 90% of the functional groups found in the structure of lignin are the methoxy groups while the remaining 10% correspond to the hydroxyl groups [14]. In order to evaluate the rate of decomposition of biomass in the case of thermogravimetric analysis, the Not Reacted Core model was applied considering simple reactions to succeed simultaneously. According to the reaction mechanisms proposed by several authors, the carbonization reaction of palm nut shells can be simplified as follows:



where Cq(*s*) is the solid reagent (the palm nut shell), Ch(*s*) is the carbonized material (residual solid coal), and Gas(*g*) is gas produced during carbonization.

The mechanism of cellulose carbonization proposed by Zickler et al. [15] considers an unreacted nucleus which is reduced as a function of time, and the phenomenological model proposed for palm kernels pyrolysis is shown in Figure 1.

In the middle, there is the not reacted core represented by Cq. Surrounding the not reacted core is the carbon layer (Ch) formed during palm nut shells pyrolysis. Heat is transferred from the oven to the interface in order to initiate the pyrolysis. Therefore,  $T_o$  (outside temperature) must be higher than  $T_i$  (interface temperature) in order to maintain a gradient. During pyrolysis, several gases are produced which increase  $P_i$  (interface pressure). This pressure must be greater than  $P_o$  (outside pressure) to permit gases to diffuse

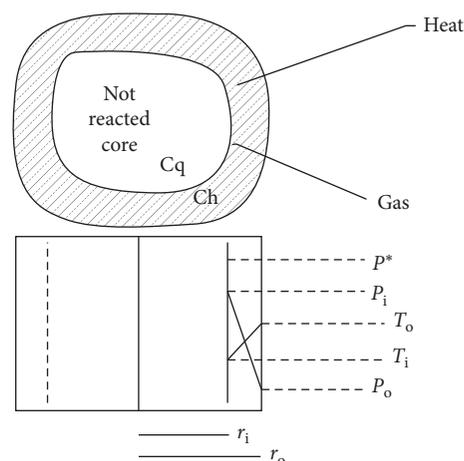


FIGURE 1: Not Reacted Core model (Cq: palm kernel; Ch: coal;  $p^*$ : gas equilibrium pressure;  $P_o$ : atmospheric pressure;  $P_i$ : gas pressure at the interface;  $T_o$ : outside temperature;  $T_i$ : temperature at the interface;  $r_o$ : radius of the particle;  $r_i$ : radius of the interface;  $r_{oc}$ : radius of the particle after decreasing volume).

from the interface to the outside. Thus, heat and mass transport phenomena are crucial stages for palm nut shells pyrolysis.

The mechanism of palm nut shells pyrolysis is very complex; its decomposition rate depends on many different factors, the most significant being the heat transport to the Cq/Ch interface (being endothermic), reaction rates involved in the pyrolysis, and the diffusion of gases through the coal layer that should be porous, pore blockage by tar, reduction of particle size, and fracturing of particles [16–18].

## 2. Materials and Methods

The STA 8000 thermogravimetry equipment was used to obtain the TGA-DSC thermograms. All the samples were subjected to pyrolysis for which nitrogen was used as inert gas. Gas flow of 80 mL/min and a heating ramp of 10°C/min from 50 to 900°C were employed in each experiment. To determine the kinetic parameters, the Not Reacted Core model was employed. This model considers that there is a heat and mass gradient between the furnace atmosphere and the interface formed during pyrolysis. The molecular weight of palm kernels was estimated considering the chemical composition of the monomeric units within each biopolymer. Therefore, glucose, *p*-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol were considered for molecular weight calculation according to their percentage in weight within palm kernels.

To obtain the required data for the model, pilot scale tests were carried out in a 12 kg Nichols furnace. Combustion is carried out in the presence of air and liquefied petroleum gas (LPG), composed by 50% C<sub>3</sub>H<sub>8</sub> and 50% C<sub>4</sub>H<sub>10</sub>, within a burner which has a heat capacity of 315 000 kJ/h. The oven has a sheet of 4 mm thick and refractory-insulating bricks which comprise a combustion chamber coupled to a 457 mm diameter reaction chamber. This chamber is provided with a

100 mm height blade stirrer with a rotating speed of 4 revolutions per minute. The atmosphere of the Nichols furnace is controlled by the lambda factor ( $\lambda$ ) which is the ratio between the air supplied to the burner and the air stoichiometrically necessary for a complete combustion of the gas. The air is supplied by a fan whose flow rate is  $1.66 \text{ Nm}^3/\text{min}$ . The pilot scale pyrolysis tests were carried out on samples with a particle size between 5 and 20 mm. For each test, the Nichols furnace was heated to the desired temperature (heating rate  $0.7\text{--}1.5$  and  $10^\circ\text{C}/\text{min}$ ) with a reducing atmosphere  $\lambda = 0.76$  (chemical analysis of combustion gases: 10%  $\text{CO}_2$ , 4%  $\text{CO}$ , 11%  $\text{H}_2$ , 0.01%  $\text{O}_2$ , and 9%  $\text{H}_2\text{O}$ ). The samples were loaded at the start of the oven, either in a fixed bed with 12 kg of sample or in mixed bed with 3 or 4 kg. Tests were also carried out by introducing the sample into the preheated oven at the desired temperature. At the end of the test, the material is discharged, cooled in a closed metal container, and weighed. Samples were taken every 10 minutes to calculate char conversion and to incorporate those data in the model. The reaction rate constant and the effective diffusion coefficient across the char layer were calculated as well.

Tests on an industrial scale were carried out in a rotary kiln, which runs on fuel oil with an excess of air of 20% ( $\lambda = 1.2$ ) and whose burner has a heat capacity of  $8 \times 10^6 \text{ kJ/h}$ . The solids were introduced into the furnace by an endless screw that moves in the same direction as the flue gas (cocurrent) forming a layer of about 15 cm in height when the furnace works without lift. Treated solids are discharged at the opposite end of the feed through a water-cooled endless screw, while gases came out at the top and went through an afterburner, a plate heat exchanger, a cyclone, a draft fan, and finally the chimney. The nominal capacity of the solids supply in the oven is  $1 \text{ m}^3/\text{h}$ , and depending on the speed of rotation and the use of the lifters or without the use of the lifters, the residence time can vary between 0.3 and 8.0 hours. Palm kernels of 5 to 20 mm were introduced to a rotary kiln which was heated for 7 days at  $850^\circ\text{C}$  in an oxidizing atmosphere ( $\lambda = 1.2$ ); the fuel oil consumption was 2.650 L/day. In these tests, incoming gases contained 10%  $\text{CO}_2$ , 5%  $\text{O}_2$ , and 15%  $\text{H}_2\text{O}$ . As mentioned above, the tests were performed in the presence or absence of levers, the rotational speed was set at 3 rpm with a feed of 900 kg/h. The duration of each trial was 35 days in order to obtain samples in sufficient quantity to provide them to potential customers. The output rate of the carbonized materials was measured, and their volatile content was measured regularly in order to use in the Not Reacted Core model.

### 3. Results and Discussion

**3.1. Not Reacted Core Model.** In order to develop the Not Reacted Core model, TGA-DSC analysis of pulverized palm kernels were carried out under inert atmosphere of nitrogen. Pyrolyzed samples were analysed by scanning electron microscopy (SEM) to verify the existence of an unreacted core. SEM image of palm nut shells after pyrolysis is shown in Figure 2.

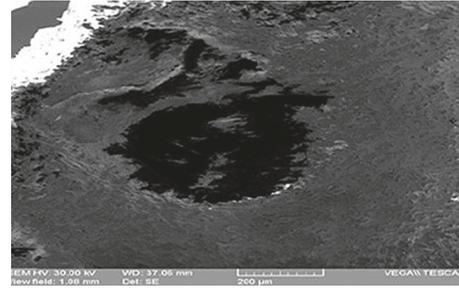


FIGURE 2: Palm kernel's not reacted core SEM image ( $200 \mu\text{m}$ ).

The black core corresponds to the unreacted palm nut shell, whereas the surrounding material is the residual solid coal. This image confirms the idea that biomass pyrolysis occurs according to the not reacted core. At the first stage, heat is transferred through the char layer to the interface up to the interface. Then, chemical reactions of biomass decomposition (different mechanisms for the three biopolymers) occur at the interface which results in the generation of residual coal and various gases. Finally, these gases diffuse through the char layer towards the external atmosphere. The relevance of these model lies in the incorporation of all the three known mechanisms that may occur during biomass pyrolysis: heat transfer, chemical reaction at the interface, and mass transfer.

The Not Reacted Core model for palm nut shells pyrolysis was employed considering that the particles are spherical. Therefore, there is no accumulation of heat and mass during pyrolysis, and the amount of heat carried by the gases is negligible. First, the equilibrium constant of reaction (1) was calculated using the following equations:

$$\Delta G_o = -RT \ln K_{eq},$$

$$K_{eq} = \frac{a_{Ch} \cdot p_{gas}^*}{a_{Cq}} = p_{gas}^*, \quad (2)$$

where  $K_{eq}$  is an equilibrium constant of equation (1),  $a_{Ch}$  is the activity of carbonized product or solid coal (equal to 1),  $p_{gas}^*$  is the partial pressure of the gases produced by carbonization,  $a_{Cq}$  is the activity of solid shells (equal to 1),  $R$  is the universal gas constant ( $8.31 \text{ J/K}\cdot\text{mol}$ ), and  $T$  is the temperature (K).

On the contrary, the conversion ( $\chi$ ) for the carbonization of palm nut shells (equation (1)) can be estimated as the Gas moles/Cq moles ratio assuming that all palm nut shells are spherical. Therefore, the moles of solid shells can be determined by the product between the sphere volume and palm nut shells density:

$$\chi = \frac{\text{gas moles}}{\text{Cq moles}} = \frac{\int_0^t n_{gRx} dt}{(4/3)\pi \cdot r_o \cdot \rho_{Cq}}. \quad (3)$$

For pilot and industrial essays in the Nichols furnace and rotary kiln, respectively, the achieved conversion can be determined by measuring the amount of the volatile material during pyrolysis. The amount of the volatile material is the difference between the initial palm nut shells mass and the

mass weighed at different intervals of time. Equation (4) shows how to calculate conversion in experimental tests for models validation:

$$\chi = \frac{(\% \text{ volatile material})_0 - (\% \text{ volatile material})_t}{(\% \text{ volatile material})_0} \quad (4)$$

In order to estimate the specific reaction rate constant ( $k_r$ ) and the effective gas diffusion ( $D_{ef}$ ), a geometric approach is proposed based on the phenomenological model (equation (1), Figure 1), and the calculation of the number of moles of gas produced by the chemical reaction ( $ng_{Rx}$ ) can be obtained by the following equation:

$$ng_{Rx} = 4\pi r_i^2 \left( -\frac{dr_i}{dt} \right) \rho_{Cq} = k_r (4\pi r_i^2) (p^* - p_i), \quad (5)$$

where  $ng_{Rx}$  is the number of moles of gas produced by the reaction chemical (mole/s),  $r_i$  is the radius of the interface (cm),  $t$  is the time (s),  $\rho_{Cq}$  is the molar density of the shells (mole/cm<sup>3</sup>),  $k_r$  is the specific reaction rate constant (cm/s),  $p^*$  is the equilibrium partial pressure of the gases produced by the carbonization (Pa) (equation (1)), and  $p_i$  is the partial pressure of gases at the interface (Pa).

Grouping the terms of equation (5) and integrating, we get

$$\left( \frac{dr_i}{dt} \right) = -\frac{k_r (p^* - p_i)}{\rho_{Cq}} = -B, \quad (6)$$

$$\int_{r_o}^{r_i} dr_i = -B \int_0^t dt, \quad (7)$$

$$r_i = r_o - B, \quad (8)$$

$$ng_{Rx} = 4\pi \rho_{Cq} B (r_o - Bt)^2. \quad (9)$$

On replacing equation (9) in equation (3),

$$r_o [1 - (1 - \chi)^{1/3}] = B, \quad (10)$$

$$\chi = \frac{3B}{r_o} t - \frac{3B^2}{r_o^2} t^2 + \frac{B^3}{r_o^3} t^3. \quad (11)$$

By solving equation (10), the  $B$  constant is found, and then by solving equation (6), the specific reaction rate constant can be estimated.

Finally, the effective diffusion constant can be determined by solving the next equation:

$$ng_{Df} = 4\pi D_{ef} \left( \frac{p_i - p_o}{(1/r_i) - (1/r_{oc})} \right), \quad (12)$$

where  $ng_{Df}$  is the number of moles of gas leaving the particle by diffusion through the porous coal layer (mole/s),  $D_{ef}$  is the effective diffusion constant of gases through the porous coal layer (cm<sup>2</sup>/s),  $p_i$  is the pressure at the interface (Pa),  $p_o$  is the external pressure (Pa),  $r_i$  is the interface radius (cm), and  $r_{oc}$  is the radius of the particle after volume contraction (cm).

3.2. *TGA-DSC Analysis.* In order to understand palm nut shells pyrolysis, TGA-DSC analyses were performed. In Figure 3, it is shown that the thermogram is obtained.

According to Yang et al., carbonization of the palm nut shells takes place as follows:

- (i) Zone I (<131°C): removal of moisture
- (ii) Zone II (217–335°C): decomposition of hemicellulose
- (iii) Zone III (335–392°C): decomposition of cellulose
- (iv) Zone IV (>392°C): decomposition of lignin

At the beginning, the weight loss is very low since the humidity present on palm nut shells evaporates. Then, the hemicellulose decomposes over 217°C followed by cellulose decomposition. Both biopolymers have the same monomer which is glucose, and over 335°C, this substance transforms to levoglucosan, tar, and several gases such as CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>, among others. On the contrary, pyrolysis enthalpy is calculated from the DSC analysis shown in Figure 4.

Between 50 and 100°C, an endothermic peak can be observed which corresponds to the evaporation of humidity. Afterwards, the other endothermic peak is detected at 243°C which may be assigned to hemicellulose decomposition. Then, a bigger endothermic peak is found upon 400°C and the other at 441°C. Those peaks could correspond to cellulose and lignin decomposition. Finally, it was determined that lignin may decompose upon 392°C (Figure 3), and in our DSC study, we detected the largest endothermic peak upon 500°C, which may be assigned to lignin decomposition.

Then, as it can be observed, palm nut shells pyrolysis has an endothermic behaviour. This result confirms that the content of lignin within biomass determines if pyrolysis is exothermic or endothermic. In this case, the process resulted to be endothermic since the content of lignin within palm nut shells is high (50.4%). Pyrolysis enthalpy was calculated from the DSC analysis which was 301.81 J/g. This value cannot be implemented in the Not Reacted Core model since this model uses values per mole instead of per gram. Thus, palm nut shells molecular weight was estimated considering its chemical composition.

Nevertheless, palm nut shells are not a pure chemical compound; therefore, the molecular weight was estimated considering monomeric units of the three biopolymers that conform to biomass (cellulose, hemicellulose, and lignin). Since lignin is a biopolymer too complex to estimate its molecular weight, it was assumed that all monomeric units of the palm nut shells are involved in pyrolysis. Therefore, glucose is proposed as the monomeric unit of cellulose, and xylene was selected as the monomeric unit of hemicellulose. In the case of lignin, the main monomeric units resulted to be coumaryl, sinapyl, and coniferyl alcohols since they are the major units in this biopolymer. In Table 1, lignin composition of palm nut shells is shown.

Lignin's average molecular weight was incorporated for palm nut shells molecular weight estimation. In Table 2, the molecular weight calculated using palm nut shells chemical composition can be observed.

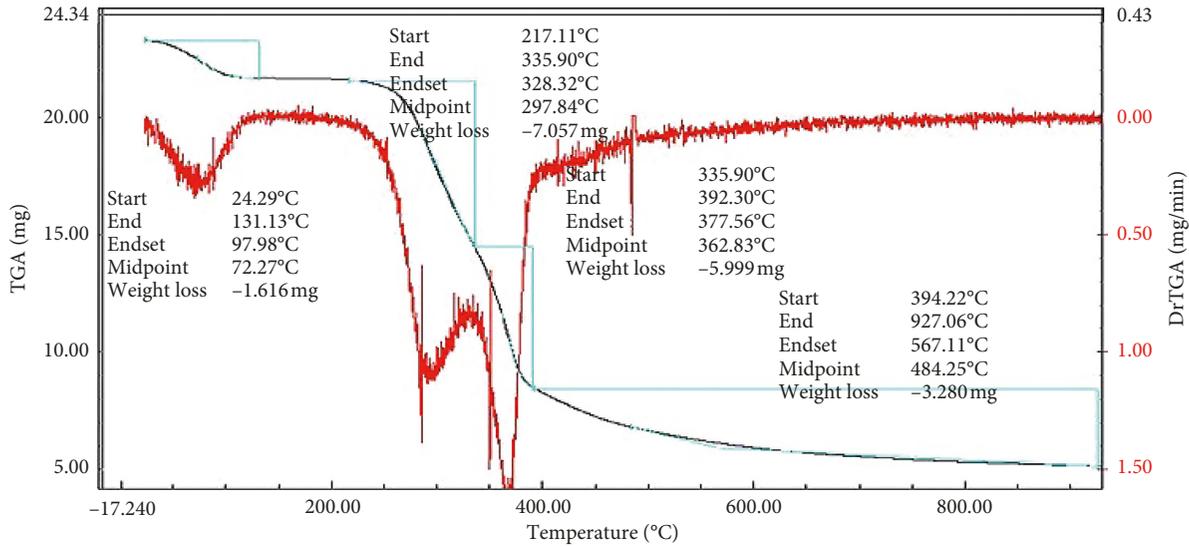


FIGURE 3: Palm nut shells thermogram. Sample: 25 mg; powder: 38  $\mu\text{m}$ ;  $\text{N}_2$  atmosphere: 50 mL/min; heating rate: 10°C/min.

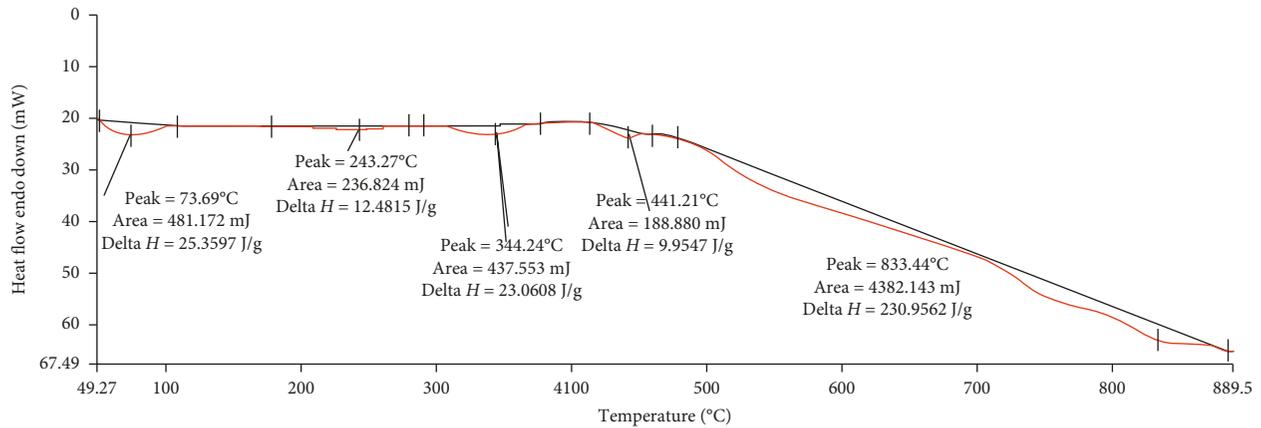


FIGURE 4: DSC analysis. Sample (25 mg); powder (38  $\mu\text{m}$ );  $\text{N}_2$  atmosphere (50 mL/min); heating rate of 10°C/min.

TABLE 1: Lignin composition.

Lignin components	Molecular weight (g/mole)	Composition (%)
<i>p</i> -coumaryl alcohol	150	0.05
Coniferyl alcohol	180	0.39
Sinapyl alcohol	210	0.56
<b>Lignin</b>	<b>193.55</b>	<b>1.00</b>

TABLE 2: Palm nut shells molecular weight.

Palm nut shells monomeric units	Molecular weight (g/mole)	Composition (%)
Glucose	162.00	0.297
Xylene	132.00	0.118
Lignin monomers	193.55	0.504
<b>Palm nut shells</b>	<b>172.38</b>	<b>0.919</b>

The estimated molecular weight resulted to be 172.38 g/mole, and this value was employed to determine the pyrolysis enthalpy per mole in order to incorporate it to the Not Reacted Core model.

**3.3. Not Reacted Core Model's Results and Validation.** The results obtained with the model can be applied for calculating pyrolysis kinetic and thermodynamic parameters. In Table 3, it is shown the results are obtained with the Not Reacted Core model.

Pyrolysis enthalpy was estimated by the product between the enthalpy obtained in the DSC analysis and the molecular weight determined with palm nut shells chemical composition. Pyrolysis entropy was estimated considering the decomposition temperature for each biopolymer found in the TGA analysis. Afterwards, Not Reacted Core models equations were applied for kinetic parameters determination. In this case, the pressure in the equilibrium resulted to be 8.83 atm (894 kPa) which is necessary for gas diffusion. The reaction rate constant was  $6.64 \times 10^{-9} \text{ 1/s}$  assuming a first-order reaction, whereas the effective diffusion across the char layer was  $4.83 \times 10^{-6} \text{ m}^2/\text{s}$ . In order to evaluate the influence of a high carbonization temperature and a high heating rate, pyrolysis tests of palm nut shells were carried out in the Nichols furnace preheated to 850°C. Palm nut shells were fed at this temperature in the reaction

TABLE 3: Not Reacted Core model results.

Parameter	Value	Units
$\Delta H^\circ$	52,074.06	J/mole
$\Delta S^\circ$	85.31	J/mole·K
$\Delta G^\circ$	-13,936.75	J/mole
$p^*$	894,699.75	Pa
Molecular weight estimated	172.38	g/mole
$k_r$	$6.64 \times 10^{-9}$	1/s
Df	$4.83 \times 10^{-7}$	m <sup>2</sup> /s

chamber and at different periods of time, shells are discharged, cooled in a closed metal container, and weighed for volatile material calculation. Afterwards, conversion was calculated with equation (4), whereas equation (3) was employed for conversion estimation with the Not Reacted Core model. In Figure 5, there is a comparison of the volatile material removal efficiencies ( $\chi$ ) calculated by the application of the Not reacted Core Model and those obtained experimentally during pyrolysis of palm nut shells in the Nichols furnace at 850°C.

As it can be observed in Figure 5, this model fits quite well with experimental results obtained during pyrolysis of palm nut shells in the Nichols furnace. Since palm nut shells pyrolysis is highly endothermic, a high heat flux is required at the interface as it is shown in Figure 6. Considering a temperature gradient between the interface and the furnace temperature of 50°C, the amount of heat transported is not sufficient to overcome the energy requirements of the reaction.

These results suggest that palm nut shells pyrolysis is limited by heat transport to the reaction interface. It was possible to prove this hypothesis by industrial tests in a continuous rotary kiln where the gas/solid contact is different compared to that of the Nichols furnace and consequently can also change the heat transport rate to interface and the diffusion of the gases produced by carbonization. Kunni and Chisaki [19] and Perry et al. [20] proposed different methods for calculating the residence time in a rotary kiln, a very important parameter for the control of the quality of the carbonized product. Equation (13), which is an empirical relation, is the most used relation for the estimation of residence time of a solid material in a rotary kiln as a function of its rotational speed:

$$t_{sj} = \frac{1.77L\sqrt{\theta}F}{PDn}, \quad (13)$$

where  $t_{sj}$  is the residence time (min),  $L$  is the oven length (14 m),  $\theta$  is the angle of repose of palm nut shells (34.7°),  $F$  is the characteristic factor of the inside of the rotary kiln (1 for oven without lift; 2 for oven with lifters),  $P$  is the oven slope (2°),  $D$  is the inside diameter of the oven (1.5 m), and  $n$  is the speed of rotation of the oven (revolutions per minute).

With equation (13), which involves the residence time and the kiln length, equation (11) and kinetic parameters listed in Table 3, conversion ( $\chi$ ) can be calculated and compared with the experimental conversions obtained with the industrial rotary kiln as it can be observed in Figure 7.

Given the consistency of the results obtained with the application of the Not Reacted Core model for palm nut

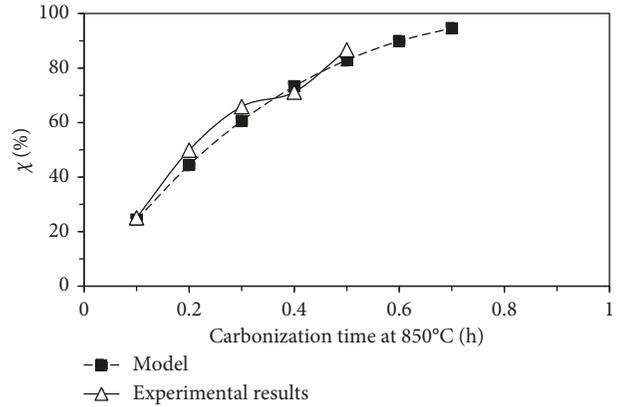
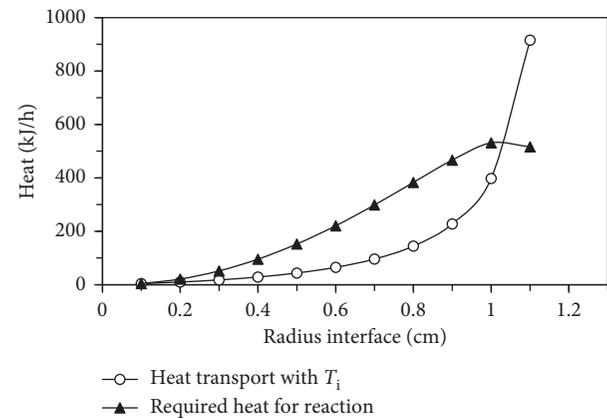
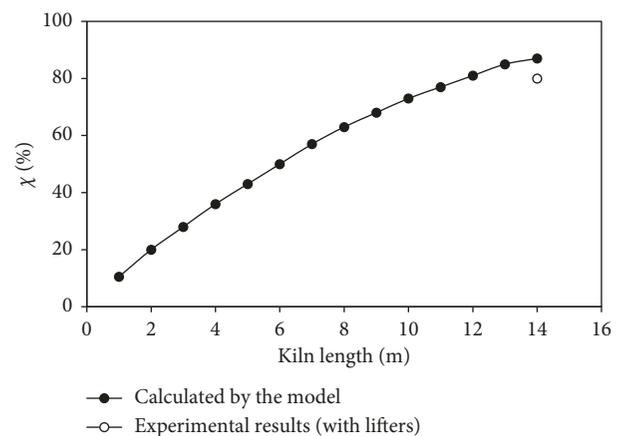


FIGURE 5: Conversion according to experimental results and Not Reacted Core model.

FIGURE 6: Calculation of heat required for reaction and heat transfer to interface as a function of interface radius ( $r_i$ ) during palm nut shells pyrolysis ( $r_o = 1.2$  cm,  $T_o = 850^\circ\text{C}$ ).FIGURE 7: Comparison between experimental conversion in the rotary kiln ( $\chi$ ) with lifters and conversion calculated with the Not Reacted Core model ( $d_{80} = 12$  mm; feed = 900 kg/h;  $T = 850^\circ\text{C}$ ;  $n = 2.9$  rpm).

shells carbonization, this model may be applied to calculate the variation of the flow of gases produced by carbonization as a function of kiln length. These data, very difficult

to obtain experimentally, are useful for the dimensioning and the selection of industrial rotary kiln operating conditions, in order to optimize its geometry as well as the distribution and the position of the lifters. Finally, this proposed model for the carbonization of palm nut shells can be generalized for the carbonization of the other lignocellulosic material.

#### 4. Conclusions

Palm nut shells pyrolysis resulted to be endothermic due to the high content of lignin within its structure. The TGA and DSC analysis demonstrated that palm nut shells present a positive enthalpy of 301.81 J/g. This value accords with several enthalpies presented in literature which suggests that lignocellulosic materials rich in lignin have an endothermic behaviour.

For palm nut shells molecular weight calculation, all monomeric units that conform to the main biopolymers of biomass were considered for the calculation. Therefore, glucose and xylene were chosen as monomeric units for cellulose and hemicellulose, respectively. In the case of lignin, *p*-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol were selected for lignin molecular weight estimation since these substances repeat along its structure. The molecular weight resulted to be 178.38 g/mole, and this value was possible to incorporate in the Not Reacted Core model for thermodynamic and kinetic parameters determination. The reaction rate constant was  $6.64 \times 10^{-9}$  1/s assuming a first-order reaction, whereas the effective diffusion across the char layer was  $4.83 \times 10^{-7}$  m<sup>2</sup>/s.

The validity of the Not Reacted Core model was confirmed with the experimental results obtained in the Nichols furnace and the rotary kiln. During the pilot and industrial tests, the Not Reacted Core model adjusted very well to experimental results. The reason lies in the conceptualization of the model. In this modelling, not only chemical reactions are involved but also heat transfer to the interface and gas diffusion as well. In the case of palm nut shells pyrolysis, heat transfer resulted to be the critic stage during pilot and industrial essays.

The Not Reacted Core model allows to scale-up pyrolysis operations to the industrial scale. During industrial essays with the rotary kiln, conversions obtained experimentally and those estimated by applying the model resulted to be very similar. This finding allows to predict the necessary data for industrial kilns dimensioning.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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#### Supplementary Materials

Data obtained for Not Reacted Core model application are detailed in Table S1. Then, equation (10) was employed for B constant calculation by lineal regression as it is shown in Figure S1. Finally, Table S2 shows conversions obtained with the Not Reacted Core model and those obtained experimentally. These data support the results demonstrated in Figure 5. (*Supplementary Materials*)

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