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Kinetic Study of Corn and Sugarcane Waste Oxidative Pyrolysis

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Abstract: The behavior of the kinetics and pyrolysis of the corn and sugarcane waste (cob corn, husk corn, and bagasse) produced in Colombia have been evaluated in a thermobalance as a step toward their valorization, in order to recover this type of waste. For this, a kinetic model has been developed consisting of a multicomponent mechanism that seeks to describe the formation of volatile materials. This model evaluates the decomposition of hemicellulose, cellulose, and lignin from three parallel and independent reactions network. It also involves the production of other products such as fixed coal and ashes. The evaluation of the model from the kinetic parameters and the thermogravimetric curves were compared with other types of waste, in the same way the chemical characteristics of the studied waste were determined. Although the wastes of this study are completely different, it was found that the degradation behavior of the residues of this study are very similar to other lignocellulosic materials, which demonstrates again that the pyrolysis valorization is possible.

Keywords: waste; biomass; kinetics; thermogravimetry; corn; sugarcane bagasse

1. Introduction

Within the production of biofuels, chemicals, and energy, biomass is considered a promising alternative to fossil fuels. Among the types of biomass are wood, algae, municipal organic waste, and crop waste, among others [1,2]. An important characteristic of the biomasses are the differences in their properties according to their nature, the ecosystem where they developed, and the region where they are located. Nowadays, biofuels are classified as first, second, third, and even up to fourth generation according to the technology used and the raw materials [3–5]. Biofuels produced from food crops are considered to be "first-generation" biofuels. Feedstock for these fuels can be categorized into starch, sugar crops, and oilseeds [5]. Sugarcane, rice, maize, wheat, soybean, oil palm tree, and barley are some of these feedstocks [6–8]. Second-generation fuels are produced from waste and lignocellulosic materials. Their main advantage is that they do not compete with food/food supplies [6,9].

Crop wastes are mainly used as alternative raw materials to fossil fuels due to the increase in food production for the population. According to Amutio et al. [10], in recent years, biomass conversion routes have increased for the production of chemical products and biofuels. This conversion is part of the broad concept of biorefinery [11–13]. The concept of biorefinery can include different processes such as biological gasification and thermochemical, such as pyrolysis and combustion [13]. Of these technologies, pyrolysis has been highlighted, which is characterized as a conversion process that presents a degradation between 300–600 °C compared to the combustion that occurs between 800 and 1000 °C. A large number of pyrolysis products can be obtained such as char, bio-oil, and noncondensable and condensable gases [14–16].

In the improvement of the pyrolysis, different technologies have been investigated. This included fluidized bed reactors, circulating fluidized beds, ablative reactors, conical spouted bed reactors, and drop tube furnace, among others [14,17,18]. Currently, studies are focusing on applying knowledge on an industrial scale rather than keeping the findings in the academic setting. During the study of scaling of technology, important challenges have been found such as the supply of energy, especially that for heating the raw material and the process fluidization gas [16,19–22]. Some authors have found that heat inside the reactor could be partially supplied by the gas fluidization temperature due to certain limitations of this mechanism such as low flexibility of the flow velocity and the gas inlet temperature and bypassing gas in the reactor [14,23]. Amutio et al. [10] have recommended oxidative pyrolysis as an alternative to pyrolysis, because this involves the addition of low oxygen concentrations in order to cause effects of combustion reactions in the final step of process. Adopting this type of procedure is an important step on the industrial scale; this is because the necessary energy is supplied by the combustion of the pyrolytic products in order to make the pyrolysis process efficient.

Consequently, the oxidative pyrolysis of biomass for biofuels production is an appropriate technology for the advance and application of a project that seeks to use corn and sugarcane waste. Worldwide, 1.6 billion metric tons of sugarcane are produced, with Brazil and India being the main producers, having an estimated production of 190 kg of sugarcane waste produced per ton [24,25]. Additionally, about 961,080 metric tons of corn waste are produced worldwide, with the United States and China being the main producers, followed by Brazil and the European Union. Some studies have reported that 640 million tons of corn production is associated with the generation of 45 million tons of corn husks [26,27]. In developing countries, these wastes are an environmental problem due to their poor disposition and their lack of use. So there is an opportunity to transform these wastes into energy [28].

The use of thermobalance for kinetic studies is considered adequate in determining the intrinsic kinetics of the biomass oxidative pyrolysis [10,14,29]. Despite the fact that the scale of thermogravimetric process compared to large-scale pyrolysis is very different in terms of heating speed, gas residence time, and particle size among others [30]. Multicomponent mechanism and one component have been used to describe the formation of volatile main products in the pyrolysis [10,30,31]. Multicomponent consists of the devolatilization reactions of the primary components present in the biomass, i.e., hemicellulose, cellulose, and lignin. Although there are important interactions between their devolatilization, these components are considered parallel and independent [10]. In many cases, these mechanisms consider only the devolatilization reactions, although certain researchers also consider the reactions of char formation. The kinetic oxidation of biomass, coal, tires, and plastics has been studied, resulting in the determination that the kinetic oxidation path is different for each solid fuel, and that it can be the result of the particle ignition dominated by either burning volatile matter or heterogeneous oxidation [14,32–37]. Thus, this study aims to determine the kinetics of degradation of cane and corn residues, which are fundamental for large-scale automatic thermal operation, and aims to be a first step in the development of a technology based on the conical spouted bed reactor.

2. Materials and Methods

In this study, two types of lignocellulosic biomass from the agroindustry (corn and sugarcane) were used. These biomasses are the amount of waste produced from corn and sugarcane that have been inadequately managed in areas where they are widely cultivated. Moreover, the criteria used to choose these types of biomass are as follows: (1) Raw material that is not used and is poorly disposed of; (2) they are waste from agricultural species; (3) waste as a byproducts of crops; and (4) they are waste produced in great quantities, exceeding 500 million metric tons per year and constituting a problem for their disposal in landfills. Proximate and ultimate analyses were carried out in the Vario–Macro of Elementar and TGA Discovery 5500 of TA Instrument. The high heat value (HHV) was measured in a Parr 6200 isoperibol bomb calorimeter.

The characteristics of the biomasses are shown in Table 1. It was observed that both the husk and the cob have similar contents both in the proximate and ultimate analyses, which indicated that the residues of both types of biomass have a similar composition. These observations demonstrate the biofuel potential of these sources.

Table 1. Properties of the two biomasses used in the study (C_1: Bagasse sugarcane, C_2: Husk corn, C_3: Cobs corn).

Properties	C_1	C_2	C_3
Ultimate Analysis (%wt)			
Carbon	48.64	46.82	46.51
Hydrogen	5.87	5.74	5.68
Nitrogen	0.16	0.66	0.47
Oxygen	42.82	41.36	44.13
Proximate Analysis (%wt)			
Moisture	5.72	6.37	7.18
Volatile matter	74.43	71.72	73.42
Fixed carbon	16.08	20.70	20.04
Ash	5.01	2.74	0.92
HHV (MJ kg^{-1})	17.92	17.35	16.92

A kinetic study was carried out using thermogravimetry in a TGA Discovery 5500 thermobalance. Pyrolysis experiments were conducted by subjecting the sample (15 mg approximately) to a heating ramp of 15 °C min^{-1} from room temperature up to 800 °C, using a nitrogen flow rate of 50 mL min^{-1}. The biomass particle size used in the runs was less than 0.2 mm [30,31].

3. Kinetic Model

For this study, the same kinetic model that Saldarriaga et al. [32] used was applied, which consisted of a multicomponent mechanism which described the formation of volatile matter through the degradation of hemicellulose, cellulose, and lignin as parallel and independent reactions. The study considered the oxidative pyrolysis process in two stages. The first based on a pyrolysis and heterogeneous oxidation and the second on the combustion of coal. Therefore, the influence of oxygen occurred after the pyrolysis process.

$$\left(\frac{1}{W_0 - W_\infty}\right)\left(\frac{dW}{dt}\right) = \sum_{i=1}^{n} c_i k_i \left[\frac{(W_i - W_{\infty,i})}{W_{0,i} - W_{\infty,i}}\right]^{n_i} \tag{1}$$

X is the biomass conversion, is defined as:

$$X = \frac{W_0 - W}{W_0 - W_\infty} \tag{2}$$

and W mass at a given time, W_o initial mass of the sample on dry basis and W_∞ mass at the end of the pyrolysis stage. The conversion of the constituents in the biomass can be defined as:

$$X = \frac{W_{0,i} - W_i}{W_0 - W_\infty} \tag{3}$$

As noted, the kinetic model proposed in this work is different from other studies that have been carried out since this one does not consider cellulose pyrolysis with a step for the formation of char [38,39]. Other authors have reported that the contribution of hemicellulose and cellulose to the formation of char is small and that the main responsible component is lignin [40]. According to Saldarriaga et al. [32], the lignin content is associated with the deconvolution of the lignin peak, and the mass of carbon remaining at the end of the pyrolysis stage (at the end of the isothermal period 800 °C). While, for cellulose and hemicellulose, at the end of the pyrolysis stage they are completely volatilized ($W_{\infty,HC}$ and $W_{\infty,C}$, respectively). Therefore, they are assumed to have zero content. Likewise, the mass of lignin remaining in the particle ($W_{\infty,L}$) is the mass of the sample minus the ash content.

Some authors have proposed a first order kinetic equation for the degradation of polymeric materials [41–43] which is defined below:

$$\frac{dX}{dt} = \sum_{i=1}^{n} \frac{dX_i}{dt} = \sum_{i=1}^{n} c_i k_i (X_{i,\infty} - X_i) \tag{4}$$

where k_i is the kinetic constant corresponding to the degradation of each one of the three polymers (cellulose, hemicellulose, and lignin). The kinetic constants are defined using the reparametrized Arrhenius equation, as follows:

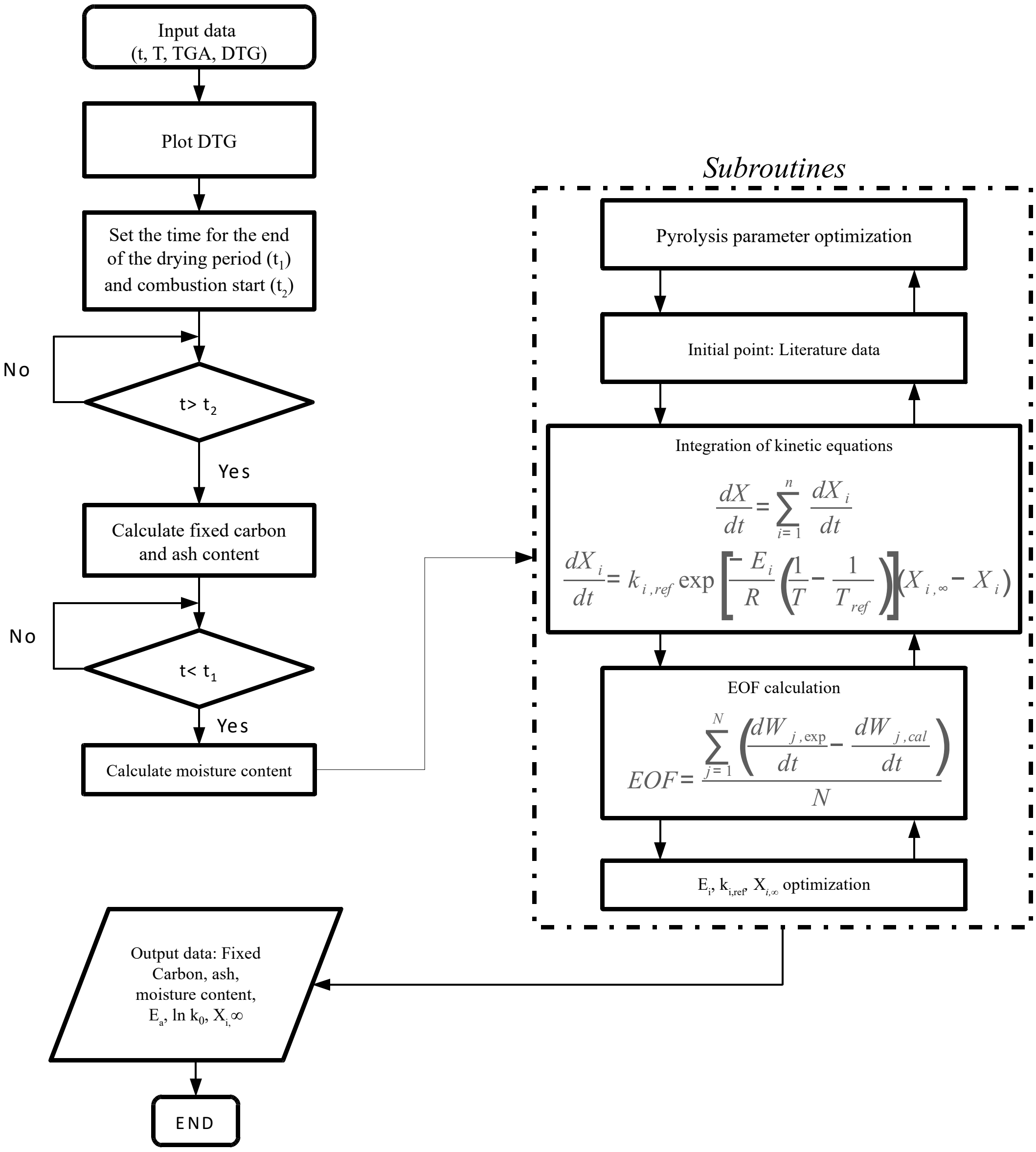
$$k_i = k_{i,ref} exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{5}$$

where $k_{i,ref}$ is the kinetic constant at the reference temperature T_{ref} (500 °C).

With the proposed model, the two kinetic parameters were obtained: The kinetic constant at the reference temperature and the activation energy. Likewise, the content of the three natural polymers was obtained. The objective function to be optimized in this work was defined as the sum of the squared differences between the experimental and calculated data of the DTG:

$$EOF = \frac{\sum_{j=1}^{N}\left(\frac{dW_{j,exp}}{dt} - \frac{dW_{j,cal}}{dt}\right)^2}{N} \tag{6}$$

where N is the number of experimental data. For model development, an algorithm written in Scilab was used (Figure 1), which adjusts the Xi calculated and experimental value. The target function is minimized by an optimization subroutine *fminsearch* (based on the Nelder–Mead algorithm).



$$\frac{dX}{dt}=\sum_{i=1}^{n}\frac{dX_i}{dt}$$

$$\frac{dX_i}{dt}=k_{i,ref}\exp\left[\frac{-E_i}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right](X_{i,\infty}-X_i)$$

$$EOF=\frac{\sum_{j=1}^{N}\left(\frac{dW_{j,\exp}}{dt}-\frac{dW_{j,cal}}{dt}\right)}{N}$$

Figure 1. Flow charts of the algorithm designed for DTG deconvolution.

4. Results and Discussion

Figure 2a,b show the degradation and conversion curves for the three residue biomasses that were studied. Several shoulders can be distinguished in the graphs which evidence the same behavior observed by other authors such as Amutio et al. [10], in which the pyrolysis processes began with the evaporation of humidity at 105 °C followed by a main curve with a maximum peak of weight loss at approximately between 350–370 °C. The first shoulder was assigned to the hemicellulose, the main, and very highest to the cellulose, and the long shoulder at the end is related to the decomposition of the lignin. Some authors indicate that the heterogeneous nature of lignin causes a degradation over a wide range of temperatures, which at low temperatures is overlapping with the degradation of the other two components, while at high temperatures the total mass loss is attributed completely to the lignin [14,44].

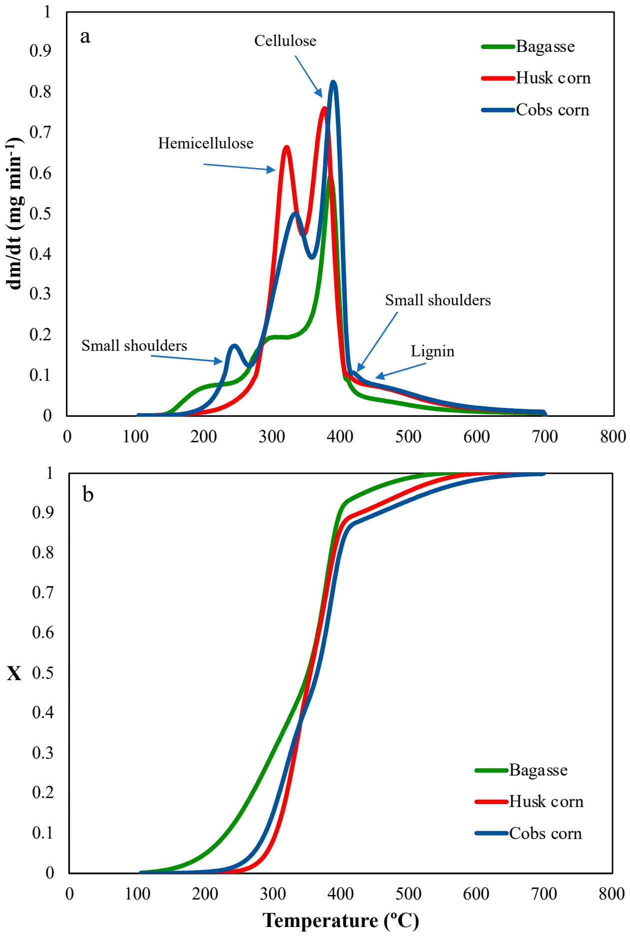


Figure 2. Evolution of the DTG curve (**a**) and conversion (**b**) with temperature for the three biomass materials.

In Figure 2a, small shoulders can be observed close to the curves that were attributed to the hemicellulose and lignin, which, according to Mészáros et al. [45], were caused by the extractive compounds that were released as fatty acids, hydrocarbons, carbohydrates, and other substances. This decomposition was described mainly in temperatures ranging from 130 °C to 250 °C, and 250 °C to 500 °C (Amutio et al.) [14].

It can also be observed in Figure 2a how the behaviors of the three biomasses were significantly different. The bagasse showed a slightly pronounced shoulder to the left that can be attributed to the hemicellulose and other components. However, both the husk and cob of the corn waste presented a very pronounced peak to the left that can be generated by the hemicellulose and a higher one in the center that can be attributed to cellulose. Moreover, it can be observed that both corn waste products presented other compounds. Figure 2b also demonstrates that the conversions of the three residues evaluated were very different from each other in regard to the final temperature, with bagasse being close to 500 °C, while for the other residues it was between 600 °C and 650 °C.

As mentioned above and according to different authors, the degradation of lignin begins at low temperatures and extends over a wide range of temperatures [46]. This investigation demonstrated a similar behavior to that found by Saldarriaga et al. [32] and was different from that reported by Sebio-Puñal et al. [47] in which cellulose does not have a higher thermal stability than either hemicellulose or lignin due to its crystalline structure. Saldarriaga et al. [32] found that, in certain biomass types (e.g., *Pinus insignis*, miscanthus, and pellets), lignin begins its degradation at the same time or even faster than cellulose, while cellulose is the last polymer to degrade. In the same way, it has been proven that once the cellulose degradation begins, the process is very fast and a characteristic peak is produced in the deconvoluted DTG curve (Figure 3).

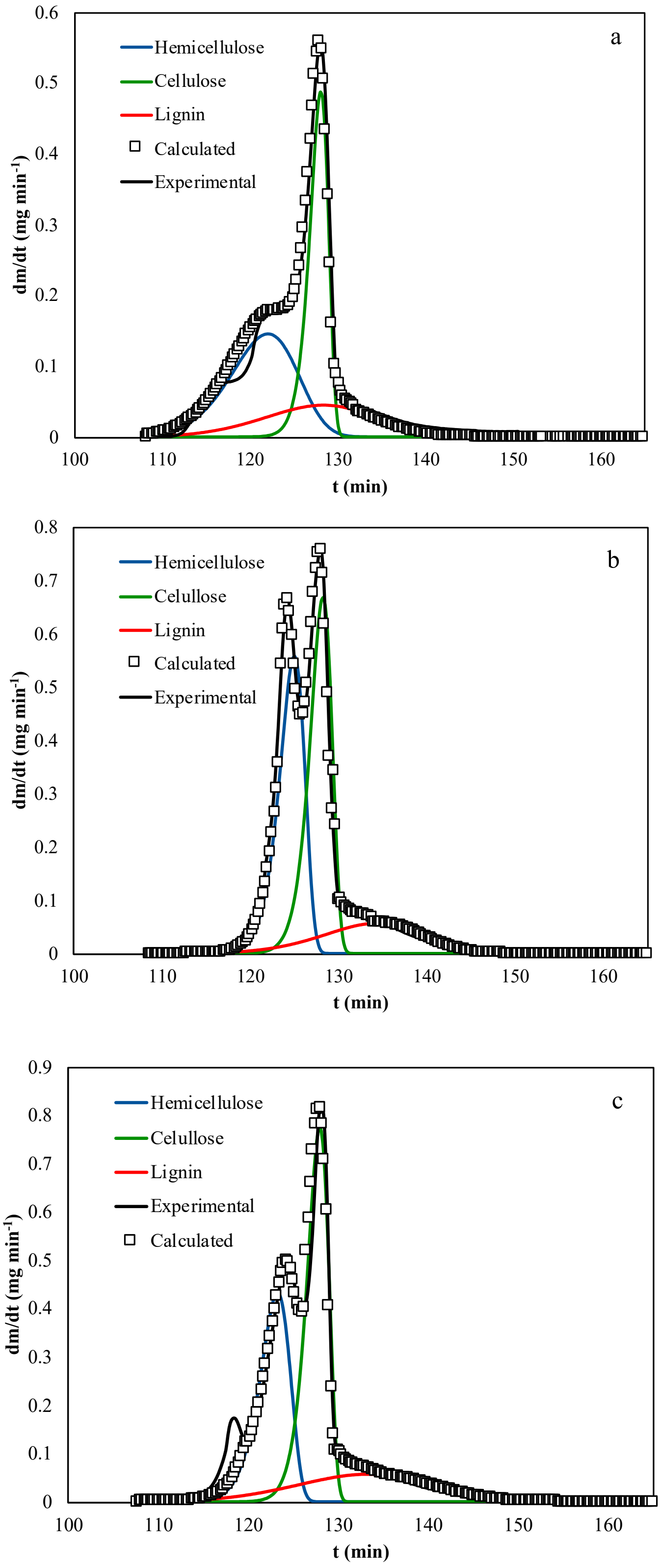


Figure 3. Comparison of experimental results and those estimated using the kinetic model for DTG curve: (**a**) Bagasse, (**b**) husk corn, and (**c**) cob corn.

Furthermore, Conesa et al. [48] found discrepancies in the results of the pyrolysis of the biomasses treated, which have been attributed to the differences in the experimental methodology in terms of the data analyzed and the kinetic calculation parameters used. Many authors have shown that the kinetic reactions of pyrolysis are complex and cannot be described as a simple mechanism [10,32]. Moreover, the use of biomass components provided the model with physical significance [49,50]. According to Amutio et al. [10], and with the results of this work, it can be assumed that biomass materials are composed of pseudo-components, with a degradation process according to the pyrolysis behavior of cellulose, hemicellulose, and lignin [50]. This behavior, which can be observed in the DTG curve of different biomasses, indicates that the identities of the individual components are maintained during pyrolysis [49].

Figure 3 shows the deconvolution curves of the three analyzed residues. Likewise, the figures show the experimental and calculated results within the kinetic model for all biomasses and pseudo-components. It can be observed that the curves do not reach a complete conversion given that the pyrolysis was defined at 700 °C. Similarly, the proposed model assumes the real conversion of the three main components of biomass (lignin, hemicellulose, and cellulose), and the rest of the components are the compounds with the lowest composition, fixed carbon, and volatiles. In addition, it is evident that the proposed model adjusts adequately, although with certain deviations among the three biomasses: In the bagasse it was between 140 °C and 250 °C, in the maize (husk and cob) it was between 280 °C and 330 °C and 380 °C and 550 °C, respectively. As mentioned above, the peaks related to the extractive components were not considered. Despite this, the adjustment was found to be adequate, and the use of a simple kinetic model is suitable for comparing the volatilization data of the different types of lignocellulose materials. However, the objective of this work was to acquire a preliminary description and a better understanding of the pyrolysis processes of these types of materials for later application in a pyrolysis for the production of char or bio-oil. As did other authors, this study proved that this reaction scheme can be applied to all types of organic wastes with lignocellulosic contents, thus demonstrating that this technique can be standardized to all lignocellulosic biomass to determine their pyrolysis kinetics [14,29,30].

Figure 4 shows that the evolution of conversion of the three biomasses as seen in the kinetic model was appropriate because it considered the actual conversion of the pseudo-components as well as the extractive compounds of each of the wastes analyzed, in addition to the fixed coal, the volatiles, and the performance of the char and ashes. In the same way, in Figure 2b, it can be observed that complete conversion was achieved at 700 °C, indicating that this type of waste is suitable for flash pyrolysis. The fitting was optimal and the use of a simple kinetic model was better to compare the volatilization of the different treated wastes, as has been confirmed by other authors [32,37]. In addition, the main objective of this work was achieved, which was to obtain a preliminary description and a better understanding of the pyrolysis processes of this waste, to encourage its application in a pyrolysis reactor for the production of different byproducts.

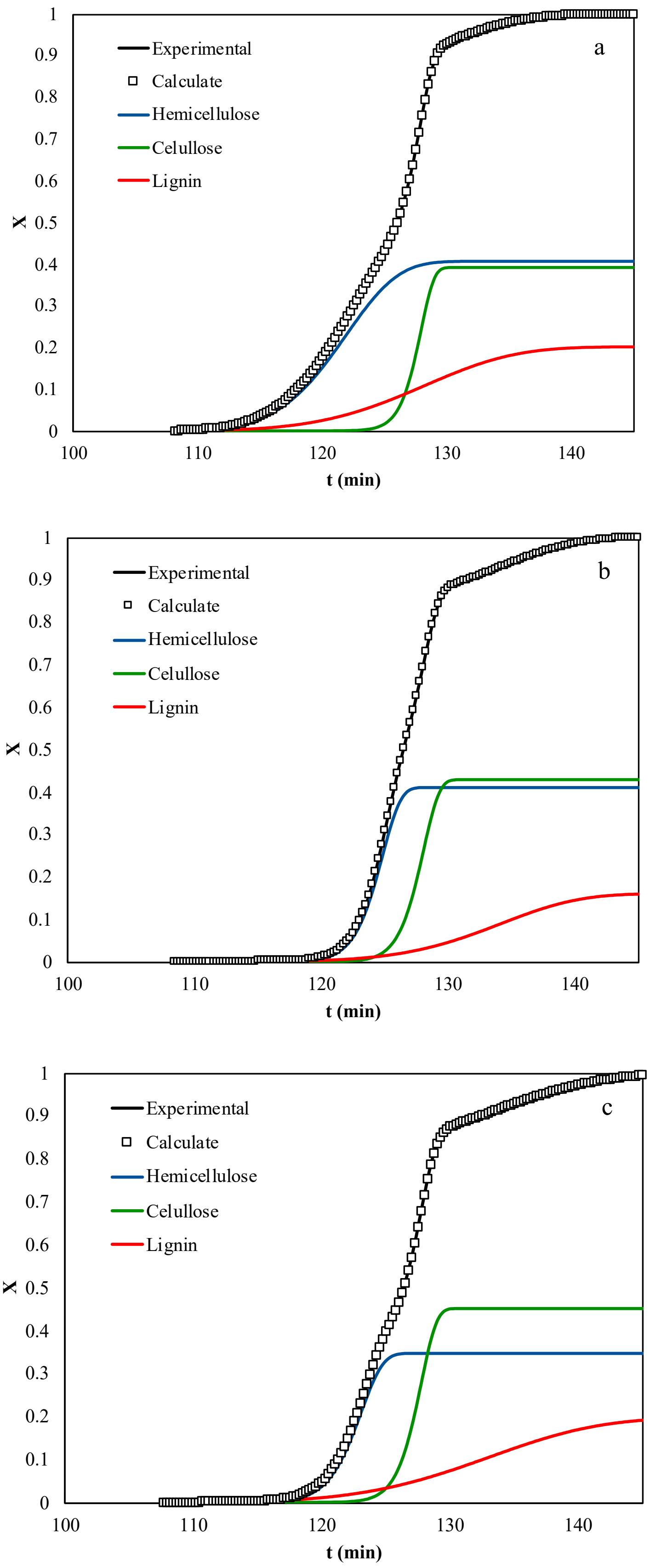


Figure 4. Comparison of experimental results and those estimated using the kinetic model for evolution of conversion with temperature: (**a**) Bagasse, (**b**) husk corn, and (**c**) cob corn.

Table 2 summarizes the kinetic parameters obtained by means of the adjustment (activation energy and kinetic constant), as well as the mass fraction of each of the pseudo-components. It was observed that the obtained kinetic parameters, k_0 and E, are quite different for the three residues studied, even those of corn (cob and husk). Which, according to the ultimate and proximal analysis (see Table 1), were very similar. These differences in the kinetic parameters are possibly due to the contents of other compounds in each of the parts. Despite this, the three biomasses presented high hemicellulose and cellulose content, which makes them potentially useful for energy.

Table 2. Pyrolysis kinetic parameters (values of frequency factor, $k_{0,}$ and activation energy, E) and pseudo-components contents.

Biomass	Kinetic Parameters	Hemicellulose	Cellulose	Lignin
Bagasse (C_1)	Log k_0 (s^{-1})	4.14	39.70	0.50
	E (kJ mol^{-1})	45.16	237.06	35.23
	Content (wt.%)	30.81	29.52	15.70
Husk corn (C_2)	Log k_0 (s^{-1})	26.04	32.69	2.99
	E (kJ mol^{-1})	148.77	199.37	52.30
	Content (wt.%)	30.54	32.04	12.51
Cob corn (C_3)	Log k_0 (s^{-1})	16.09	31.83	0.42
	E (kJ mol^{-1})	100.00	194.00	36.93
	Content (wt.%)	26.84	34.86	15.84

With values between 194 to 237 kJ mol^{-1}, cellulose was the component with the highest activation energy, followed by hemicellulose and finally lignin, which was the component with the lowest activation energy (Table 2). The results also show that, according to other investigations in kinetic studies of three parallel reactions corresponding to lignin, cellulose, and hemicellulose, these were within the same range. According to Amutio et al. [29], the differences that can be observed in the results of the kinetics were due more to methodological differences in data analysis used, rather than to any difference in the nature of the raw material. Also, the activation energy ranges for different types of biomass are very similar to those found in this study. This can be demonstrated with the sawdust of *Pinus insignis*, which has an activation energy for lignin, cellulose, and hemicellulose of 28.2 kJ mol^{-1}, 221.5 kJ mol^{-1}, and 117.4 kJ mol^{-1}, respectively [32]; bagasse fiber [51], with 127, 252, and 33 kJ mol^{-1}, respectively; and sugarcane bagasse [52,53], with activation energies of 90–170, 199–256, and 21–77 kJ mol^{-1}, respectively. Finally, that the findings of this work and that of other scientists are further evidence that the reaction orders lead to higher values of activation energy, mainly in hemicellulose and lignin in many types of biomass [54–56].

5. Conclusions

Corn and bagasse residues are easily available, with their high production of waste, which makes them efficient raw materials to produce fuels and chemical products. This could be an alternative for the management of waste generated in these monocultures worldwide and would contribute to technological development. This study provided clear bases for the valorization of this type of waste by pyrolysis processes in order to improve renewable energy sources in the country.

The proximate and ultimate analyses in conjunction with the calculation of the high heat value of corn waste and bagasse from sugar cane provided useful information for evaluating the possibility of valorizing these residues by means of oxidative pyrolysis. The three reaction models based on the decomposition of hemicellulose, cellulose, and lignin describe approximately the degradation of the studied residues, confirming that it is possible to study different lignocellulosic residues by means of this kinetic model. According to the results, it can be inferred that, although both materials are heterogeneous even among corn residues, their pyrolytic behavior is similar.

The viability of recovery of the evaluated wastes is demonstrated in this study from the kinetic parameters that indicate that the pyrolysis route is very similar. On the other hand, this model, which has already been tested by other authors [32,37], demonstrated once again that it is possible to determine the approximate content of hemicellulose, cellulose, and lignin in the raw materials.

Author Contributions: Study conception and design: J.F.S. and I.E.; acquisition of data: F.R., Y.C., I.E., and J.F.S.; analysis and interpretation of data: F.R., Y.C., I.E., and J.F.S.; drafting of manuscript: F.R., Y.C., I.E., and J.F.S.; critical revision: F.R., Y.C., I.E., and J.F.S.

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Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

EOF	objective function to be optimized
DTG	derivate thermogravimetric
$\mathrm{c_i}$	mass concentration of i component (wt.%)
E_i	activation energy of i constituent (kJ mol^{-1})
k_i	kinetic constant for the weight loss of each i constituent (s^{-1})
$k_{i,ref}$	number of experimental data
N	number of experimental data
t	time (min)
R	gas constant
T	temperature (°C)
W, W_0, W_∞	weight of biomass sample at t time, at the beginning of pyrolysis and at the end of pyrolysis, respectively (mg)
W_i, $W_{0,i}$,$W_{\infty,i}$	weight of i constituent in the sample at t time, at the beginning and at the end (mg)
X	conversion of the biomass sample by mass unit of pyrolysable mass
X_i, $X_{\infty,i}$	conversion of i constituent at t time and at the end

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