

Comparative Study of the Reaction Kinetics of Three Residual Biomasses

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Kinetic analysis for the combustion of three agro-industrial biomass residues (coconut husk, corn husk, and rice husk) was carried out in order to provide information for the generation of energy from them. The analysis was performed using the results of the data obtained by thermogravimetric analysis (TGA) at three heating rates (10, 20, and 30 K/min). The biomass residues were characterized in terms of proximate analysis, elemental analysis, calorific value, lignin content, α -cellulose content, hemicellulose content, and holocellulose content. The biomass fuels were thermally degraded in an oxidative atmosphere. The results showed that the biomass thermal degradation process is comprised of the combustion of hemicellulose, cellulose, and lignin. The kinetic parameters of the distributed activation energy model indicated that the activation energy distribution for the pseudocomponents follows lignin, cellulose, and hemicellulose in descending order. The activation energy values for each set of reactions are similar between the heating rates, which suggests that it is independent of the heating rate between 10 K/min and 30 K/min. For all the biomass samples, the increased heating rate resulted in the overlap of the hemicellulose and cellulose degradation events.

Keywords: Biomass; Combustion; Kinetic parameters; DAEM

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INTRODUCTION

The shortage of conventional fossil fuels and the environmental problems that arise from their use, such as global warming and acid rain, have become a cause of concern for their contribution to climate change. Biomass is an alternative renewable and clean energy resource that can alleviate pollution problems, so it has received increasing attention from researchers (Demirbaş 2001; Yaman 2004). There are many conversion technologies to utilize biomass, such as direct combustion, gasification, pyrolysis, flash pyrolysis, and anaerobic digestion, among others (Song *et al.* 2004).

In the literature, the combustion characteristics of different biomasses have been studied primarily through thermogravimetric analysis (TGA) (Kok and Ozgur 2017; Mlonka-Mędrala *et al.* 2019). Thermogravimetric analysis has been used to identify different polymeric lignocellulosic fractions present in biomass residues and to determine the reactivities of carbonized residues in presence of reactive atmospheres (Wilk *et al.* 2019; Sher *et al.* 2020). The kinetic study is considered an important criterion for the measurement of the reactivity potentials of coals and biomass residues that are used as fuels. The distributed activation energy model (DAEM) has been widely used to describe the thermal degradation of different biomasses (Hu *et al.* 2016; Oliveros *et al.* 2019) and

to obtain precise kinetic parameters such as the apparent activation energy (E) and the other thermodynamic parameters calculated from E , including the pre-exponential factor (A).

In this sense, agrobusinesses constitute an important line of the Colombian economy, since they add value to the products of the field. One of the peculiarities of this line of the economy is the large amount of biomass produced as a by-product during the transformation of the raw material; In some cases, the amount of waste generated during harvesting and processing can be as high as 50% of the tons produced, such as corn, coconut, and rice husk waste. These wastes, as they do not receive adequate treatment, end up in rivers and streams, or in garbage dumps and sewers in cities, causing serious environmental and solid waste management problems.

Although they are currently considered waste, they have a high potential due to their composition. Some potential uses are being studied so that they can become an important source of energy or fuel if used properly.

The objective of this study was to estimate the kinetic behavior of the combustion of rice husk, coconut husk, and corn husk by the DAEM, from the thermogravimetric curves obtained using a TG analyzer under three heating rates (10, 20, and 30 K/min). The results associated with this type of study are of great importance, since they provide information that can be used for the kinetic modeling of the combustion process for the generation of energy from biomass.

EXPERIMENTAL

Methods

Figure 1 outlines the general methodology of this work.

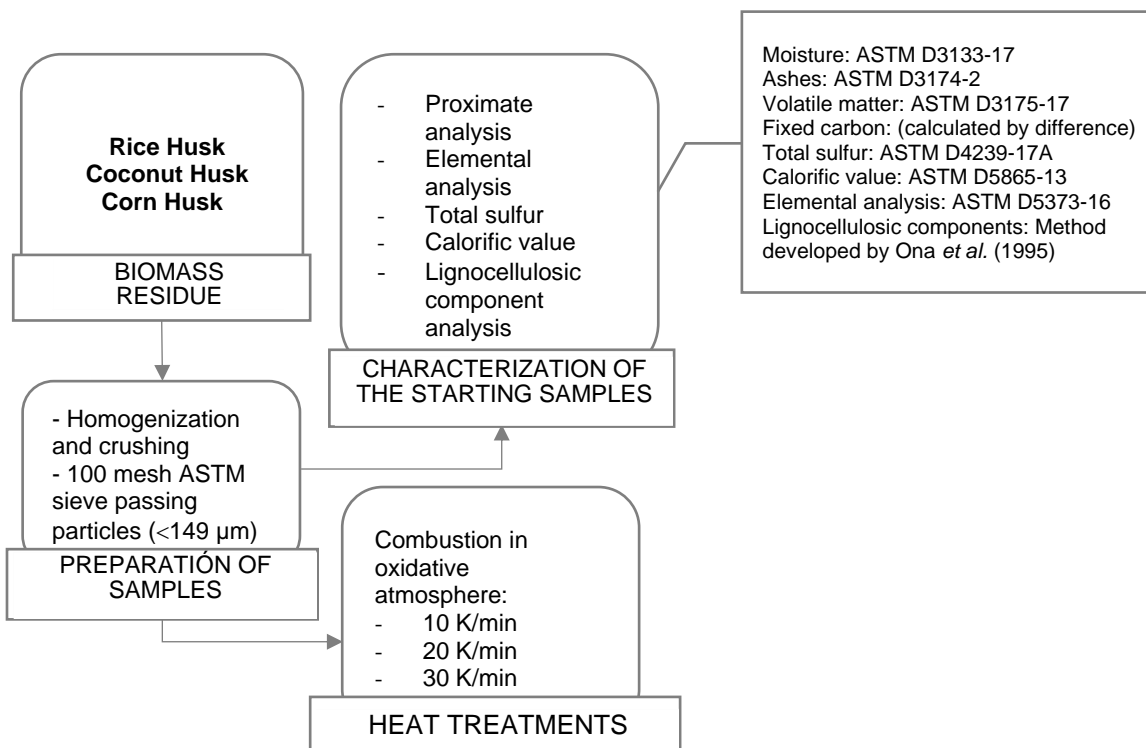


Fig. 1. Methodology

The stages in which the methodology was divided to be carried out are shown in Figure 2.



Fig. 2. Stages of methodology

Biomass Characterization

Three industrial-waste biomass samples were selected for this study: rice husks, coconut husk, and corn husks, all of which were obtained from Atlántico, Colombia. In the proximate analysis, total humidity, the ash content, and the volatile matter were determined using the ASTM standards D-3173 (2017), D-3174 (2002), and D-3175 (2017), respectively. The fixed carbon (by difference) was also calculated. The elemental analysis quantified the content of the carbon, hydrogen, nitrogen, and oxygen using the ASTM standard D-5373 (2016). The total sulfur was calculated according to the ASTM standard D-4239, method A (2017) and the calorific value was determined according to the ASTM standard D-5865 (2013).

The major component analysis determined the percentage of cellulose, hemicellulose, lignin, and extractives according to the method developed by Ona *et al.* (1995). Figure 3 presents images of the biomass characterization.

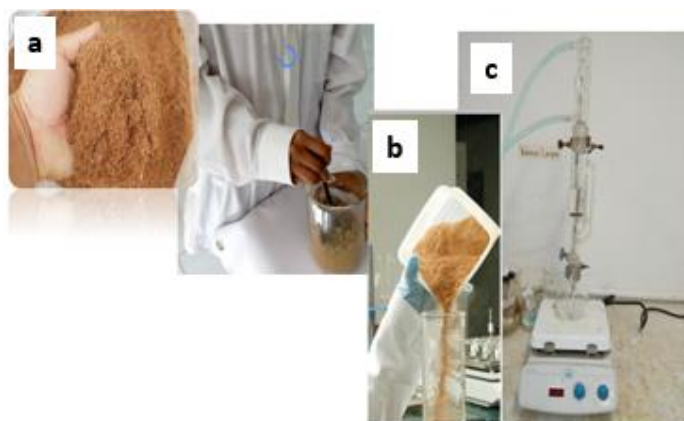


Fig. 3. Biomass characterization (a) preparation of samples, homogenization and crushing process (b) sieve passing particles (<149 μm) (c) disposition of the equipment to carry out the lignocellulosic components analysis

Thermal Treatments

Biomass fuels were thermally degraded in an oxidative atmosphere using a SETSYS Evolution TGA-DTA/DSC thermal analyzer (Setaram, Caluire-et-Cuire, France) in the TG mode (Fig. 4). Ten to 20 mg of sample with a particle size less than 150 μm were placed to ensure complete combustion (Ninduangdee and Kuprianov 2014; Mlonka-Mędrala *et al.* 2019) in an alumina sample holder. Synthetic air was used as stripping gas

with a flow of 30 mL/min and three heating rates (10, 20, and 30 K/min) were evaluated in a temperature range between ambient temperature (approximately 298 K) and 1273 K.



Fig. 4. SETSYS Evolution TGA-DTA/DSC

Kinetic Analysis Using the DAEM

The DAEM has been used successfully to describe the thermal degradation of various solid materials (Várhegyi *et al.* 2002; Hu *et al.* 2016; Oliveros *et al.* 2019). Whether in an inert or oxidative atmosphere, the entire process of thermal degradation consists of a series of irreversible reactions of the first order occurring successively.

In this model, the first derivative of a thermogravimetric curve (DTG) is calculated according to Eq. 1,

$$Y^{Calc}(t) = -\sum_{j=1}^M c_j dx_j/dt \quad (1)$$

where x_j is the unreacted fraction of the material, represented by the kinetic equation of order j , c_j represents the contribution of the j -th partial reaction of the measured quantity, and M corresponds to the number of pseudo-components or the set of reactions that can be described through the same probability distribution function. The model assumes a first-order kinetic model and an Arrhenius dependency for the kinetic constant.

Oxidative degradation for hemicellulose and cellulose occurs at lower temperatures compared to lignin, given that their structures are amorphous, random, and more "soft"; these differences in their chemical structures lead to different reactivities (Ren *et al.* 2018; Carrier *et al.* 2011), and therefore, the activation energy required to carry out the combustion of these organic polymers is lower. This means that the activation energy values increase in the order of hemicellulose, cellulose and finally lignin.

The activation energies for the reactions involved are distributed on a Gaussian distribution function with parameters E_{0j} and σ_j . If the solution of a first-order kinetic equation with a given value E is denoted as $X_j(t, E)$, the functions x_j from Eq. 1 are calculated according to Eq. 2,

$$x_j(t) = \int_0^\infty (2\pi)^{-1/2} \sigma_j^{-1} \exp\left[-\frac{(E-E_{0,j})^2}{2\sigma_j^2}\right] X_j(t, E) dE \quad (2)$$

To evaluate the integral corresponding to Eq. 2, a change is made in the lower limit of integration from 0 to $-\infty$ without affecting the results and subsequently the Gauss-

Hermite quadrature rule is used to approximate this new integral, as shown in Eq. 3 and Eq. 4 (Bhavanam and Sastry 2015),

$$\mu_j = \frac{2(E-E_{0,j})}{\sqrt{2}\sigma_j} \quad (3)$$

$$x_j(t) \cong \frac{1}{2\pi} \sum_{i=1}^N w_i \exp(0.72\mu_{ij}^2) X_j(t, \mu_{ij}) \quad (4)$$

where w_i , y , and μ_{ij} are the mass and abscissa factors of the Gauss-Hermite quadrature formula. In this equation, the results of the optimization of change of scale proposed by Donskoi and McElwain (2000) and a value of N equal to 80, as suggested by Várhegyi *et al.* (2002), are used. The adjustment was made with a non-linear least squares method, minimizing the sum presented by Várhegyi *et al.* (2002; 2007) in Eq. 5,

$$S = \sum_{k=1}^{N_{exp}} \sum_{i=1}^{N_k} \frac{[Y_k^{obs}(t_i) - Y_k^{cal}(t_i)]^2}{(N_k^{max}(Y_k^{obs}))^2} \quad (5)$$

For each experimental curve, the fit obtained is characterized by Eq. 6,

$$fit(\%) = 100 \frac{[|Y_k^{obs}(t_i) - Y_k^{cal}(t_i)|]^2}{(N_k^{max}(Y_k^{obs}))^2} \quad (6)$$

The previous equations were solved with the help of an algorithm designed by Oliveros *et al.* (2019) in MATLAB[®] software (MathWorks, Natick, MA) using the optimization functions and built-in ODE solvers.

RESULTS AND DISCUSSION

Biomass Characterization

Following the results of the proximate, the elemental analysis and component analysis performed on the samples are presented as described in the methodology and consolidated in Tables 1, 2, and 3.

Table 1. Results of the Proximate Analysis

Proximate Analysis (%) Mass, Dry Basis			
	Rice Husk	Coconut Husk	Corn Husk
Moisture	8.61	8.83	4.62
Ash	22.37	0.49	3.87
Volatile Matter	72.69	92.16	83.78
Fixed Carbon	4.94	7.35	12.35
Sulphur	0.05	0.03	0.10
Calorific value (MJ/Kg)	15.31	24.29	20.56

Table 2. Results of the Elemental Analysis

Elemental Analysis (%) Mass, Dry Basis			
	Rice Husk	Coconut Husk	Corn Husk
Carbon	34.60	47.7	42.30
Hydrogen	4.28	5.44	5.87
Nitrogen	0.30	0.06	0.46
Oxygen	38.37	46.25	47.31

Table 3. Results of the Component Analysis of Biomass Samples

Component Analysis (%) Mass			
	Rice Husk	Coconut Husk	Corn Husk
Lignin	19.58	12.34	5.36
Holocellulose	62.39	74.812	63.66
Alpha-cellulose	60.323	74.45	1.70
Hemicellulose	2.06	0.366	61.96
Extractive	2.35	2.64	13.96

The results obtained from the elemental analysis and the calorific value values shown in Table 2 are typical for these types of samples and are related to those reported in the literature. The calorific value reported by other researchers for rice husk is between 16.35 and 16.44 MJ/kg, for coconut husk it is between 18.23 and 20.01 MJ/kg, and for corn residues it is between 17.96 and 18.41 MJ/kg (Rambo *et al.* 2015; Marafon *et al.* 2019).

It was also observed that a higher ash content decreased the energy density of the biomass (Raveendran and Gasnesh 1996). For example, the rice husk had the highest ash percentage (22.37%) and the lowest power calorific value (15.31 MJ/kg), followed by the corn husk and coconut husk biomasses.

Regarding the results obtained from the chemical composition of the lignocellulosic materials, holocellulose was found to be present as the predominant composition in most of these materials (Xiao *et al.* 2001; Halim *et al.* 2016). According to the result presented in Table 3, the holocellulose content in all the biomass samples comprised more than half of the total solid composition, which shows that cellulose and hemicellulose are the main components of the biomasses under study.

Kinetics Analysis using the DAEM

The experimental data obtained from TGA of the biomass samples was satisfactorily modeled with the three Gaussian functions. This was done under the assumption that during the combustion process, the decomposition of the three main components – hemicellulose, cellulose, and lignin, occurs (Carrier *et al.* 2011; Kok and Ozgur 2017). In general, the three components simultaneously are not clearly defined as independent events, but they appear on the DTG curves as two events in which the phenomena coexist. The temperature range evaluated with the DAEM was 453 to 833 K, in which the event of moisture release was excluded.

The distributed activation energy model (DAEM) has been used successfully to describe thermal degradation of various solid materials (Santander *et al.* 2019). Whether in an inert or oxidative atmosphere, the entire thermal degradation process consists of a series of irreversible first-order reactions occurring in succession and an Arrhenius dependence for the kinetic constant. The activation energies for the reactions involved are considered distributed in a Gaussian distribution function with parameters $E_{0,j}$ and σ_j . (Ren *et al.* 2018). Reaction kinetic parameters are derived from various TGA curves that are typically obtained for experiments at low constant heating rate.

The kinetic reaction parameters were determined from the TG curves that were obtained from the heat treatments at the heating rates of 10, 20, and 30 K/min. Figures 5, 6, and 7 illustrate the fit obtained with three sets of the DAEM reactions the rice husk, coconut husk, and corn husk samples, respectively, at different heating rates. The first peak observed in the profiles of the different biomasses corresponds to the most reactive fraction (hemicellulose), which rapidly degraded at relatively low temperatures (453 K to 623 K),

with the release of volatiles that were oxidized in an air atmosphere and was largely responsible for the generation of combustion gases (Flores and Quiñones 2018). When the temperature increased, the next less soft fraction, attributed to cellulose, was thermally degraded in the temperature range of 548 K to 623 K. Lignin was the most difficult to oxidize fraction, which had a higher temperature range (523 K to 773 K) (Lozano 2009; Flores and Quiñones 2018).

The curve fitting obtained by the DAEM for the rice husk samples shown in Fig. 5 is presented with a dotted line, while the experimental data is shown as a continuous line. The curves referring to each reaction set were represented by the hemicellulose, cellulose, and lignin components of the biomass, which are represented the red, blue, and green dotted lines, respectively. It is possible to observe a good fit of the model to the experimental data at the different heating rates.

As can be seen in Fig. 5, as the heating rate increased, the combustion of the hemicellulose was favored because the conversion rate increased. The cellulose behaved in the same way. However, when comparing the cellulose with the lignin, it was evident that at 30 K/min, the value of $d\alpha/dt$ for lignin was lower. This is corroborated when comparing the values of the kinetic parameters obtained by the DAEM, which are shown in Table 4, specifically in the C_{3norm} value that represents the contribution of the partial reaction of lignin to the measured quantity (Várhegyi *et al.* 2002). In this instance, a heating rate of 30 K/min had a value of 0.13. For the heating rates of 10 K/min and 20 K/min, the values were 0.212 and 0.254, respectively.

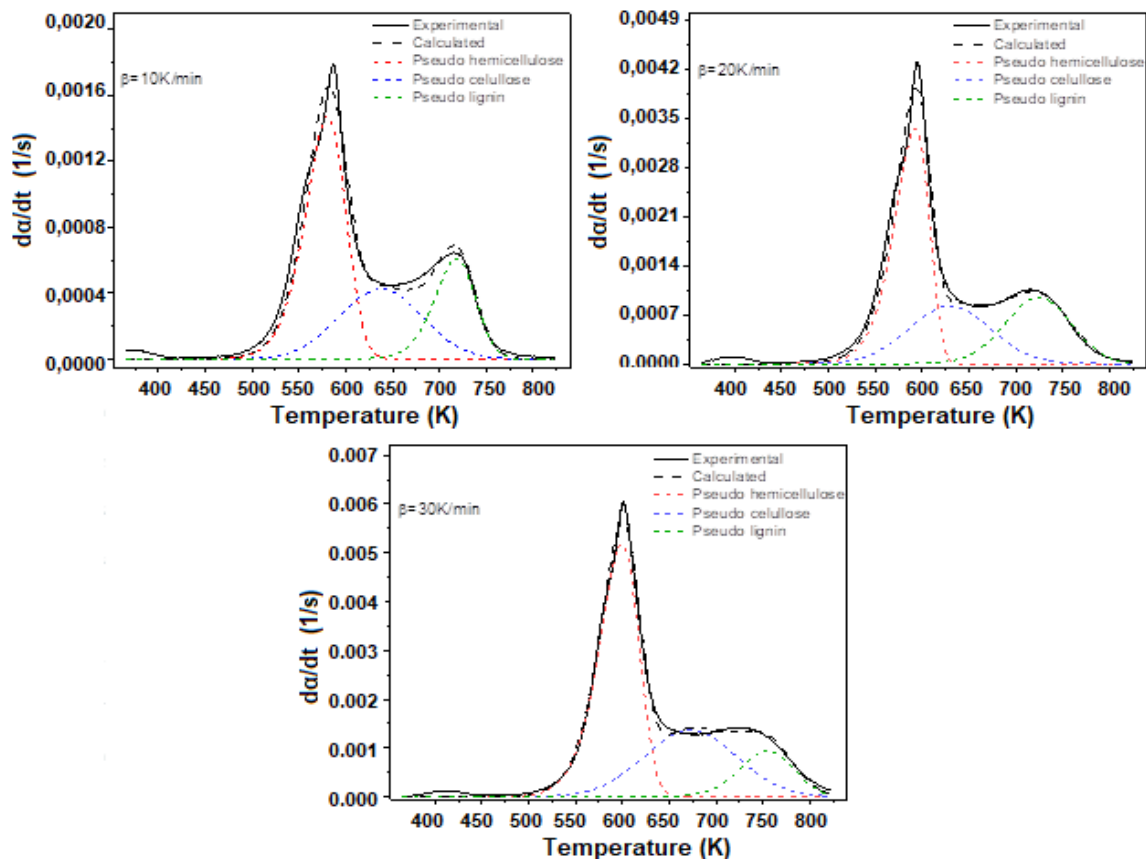


Fig. 5. Fit DAEM to DTG data from the rice husk biomass samples during combustion at different heating rates

Table 4 presents the parameters calculated using this algorithm, where the first activation energy (E_{01}) and the first pre-exponential factor (A_1) will probably correspond to the decomposition of the hemicellulose, while the second parameters (E_{02} , A_2) will correspond to the decomposition of the cellulose. For lignin, the activation energy and the pre-exponential factor parameters will correspond to those denoted as E_{03} and A_3 .

In general, the activation energy required in the combustion of the rice husk samples at different heating rates presented similar values. The activation energy was between 153 and 156 kJ/mol for the first set of reactions, between 185 and 192 kJ/mol for the second set of reactions, and between 261 and 270 kJ/mol for the third set of reactions. This suggests that the activation energy is independent of the heating rate between 10 and 30 K/min.

Table 4. Kinetic Parameters of the Rice Husk Obtained by DAEM

Parameters	Rice 10 (K/min)	Rice 20 (K/min)	Rice 30 (K/min)
C_{1norm}	4.98E-01	4.76E-01	5.37E-01
A_1 (1/s)	5.33E+11	1.05E+12	5.61E+11
E_{01} (kJ/mol)	1.54E+02	1.56E+02	1.53E+02
σ_{01} (kJ/mol)	6.16	7.28E-03	4.18
C_{2norm}	2.90E-01	2.70E-01	3.27E-01
A_2 (1/s)	9.54E+12	1.00E+14	5.52E+12
E_{02} (kJ/mol)	1.85E+02	1.92E+02	1.87E+02
σ_{02} (kJ/mol)	2.36E+01	2.45E+01	2.53E+01
C_{3norm}	2.12E-01	2.54E-01	1.35E-01
A_3 (1/s)	4.13E+17	1.06E+17	5.89E+16
E_{03} (kJ/mol)	2.71E+02	2.62E+02	2.67E+02
σ_{03} (kJ/mol)	1.10E+01	2.24E+01	1.58E+01

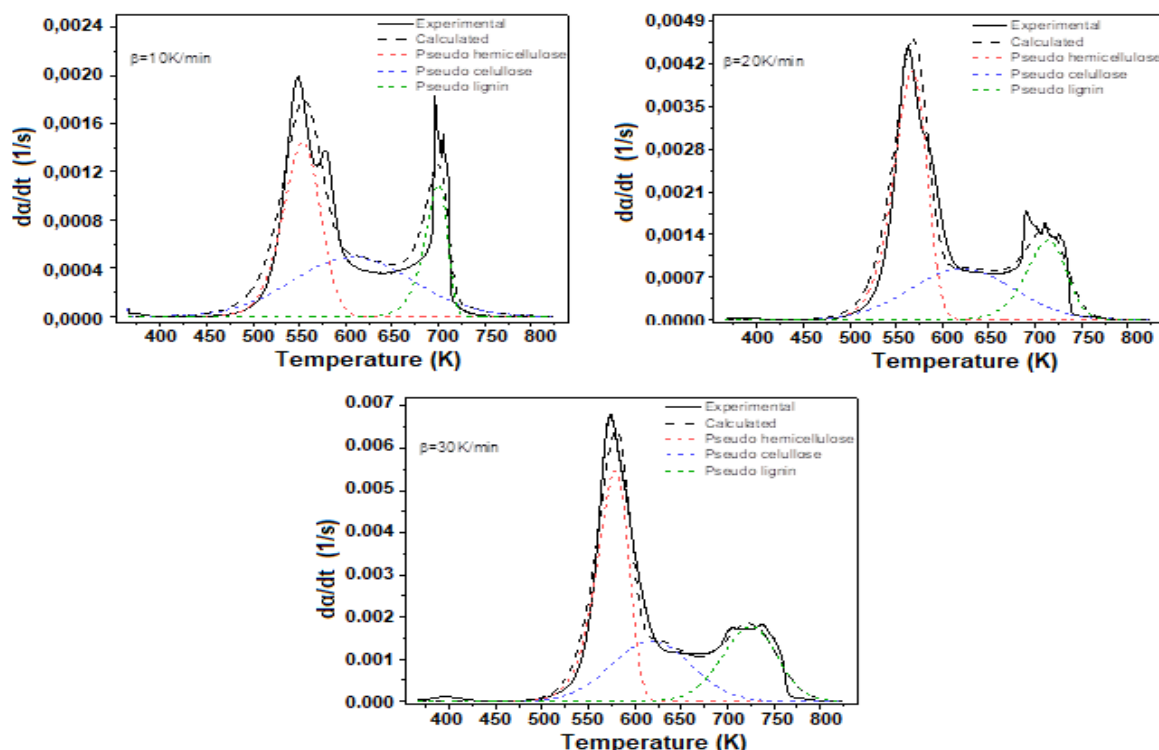


Fig. 6. Fit of the DAEM to DTG data from the coconut husk biomass samples during combustion at different heating rates

Similar to the rice husk samples, as the β of the coconut husk samples increased, the decomposition reaction of the hemicellulose was favored since the value of the conversion rate increased. However, this parameter decreased for the cellulose as the decomposition rate of the lignin increased. Both effects can be seen in Fig. 6, and the results are further corroborated with the values of C_{1norm} , C_{2norm} , and C_{3norm} in Table 5.

Table 5. Kinetic Parameters of the Coconut Husk Obtained by DAEM

Parameters	Coconut 10 (K/min)	Coconut 20 (K/min)	Coconut 30 (K/min)
C_{1norm}	3.91E-01	4.92E-01	4.55E-01
A_1 (1/s)	6.311E+13	7.59E+13	5.75E+13
E_{01} (kJ/mol)	1.68E+02	1.69E+02	1.69E+02
σ_{01} (kJ/mol)	7.90	4.72	2.83
C_{2norm}	4.22E-01	3.11E-01	2.90E-01
A_2 (1/s)	8.44E+13	6.77E+13	4.19E+13
E_{02} (kJ/mol)	1.88E+02	1.87E+02	1.81E+02
σ_{02} (kJ/mol)	3.94E+01	3.25E+01	2.30E+01
C_{3norm}	1.87E-01	1.97E-01	2.56E-01
A_3 (1/s)	9.96E+22	1.73E+16	7.56E+16
E_{03} (kJ/mol)	3.33E+02	2.46E+02	2.57E+02
σ_{03} (kJ/mol)	6.47E-01	8.77E+00	1.70E+01

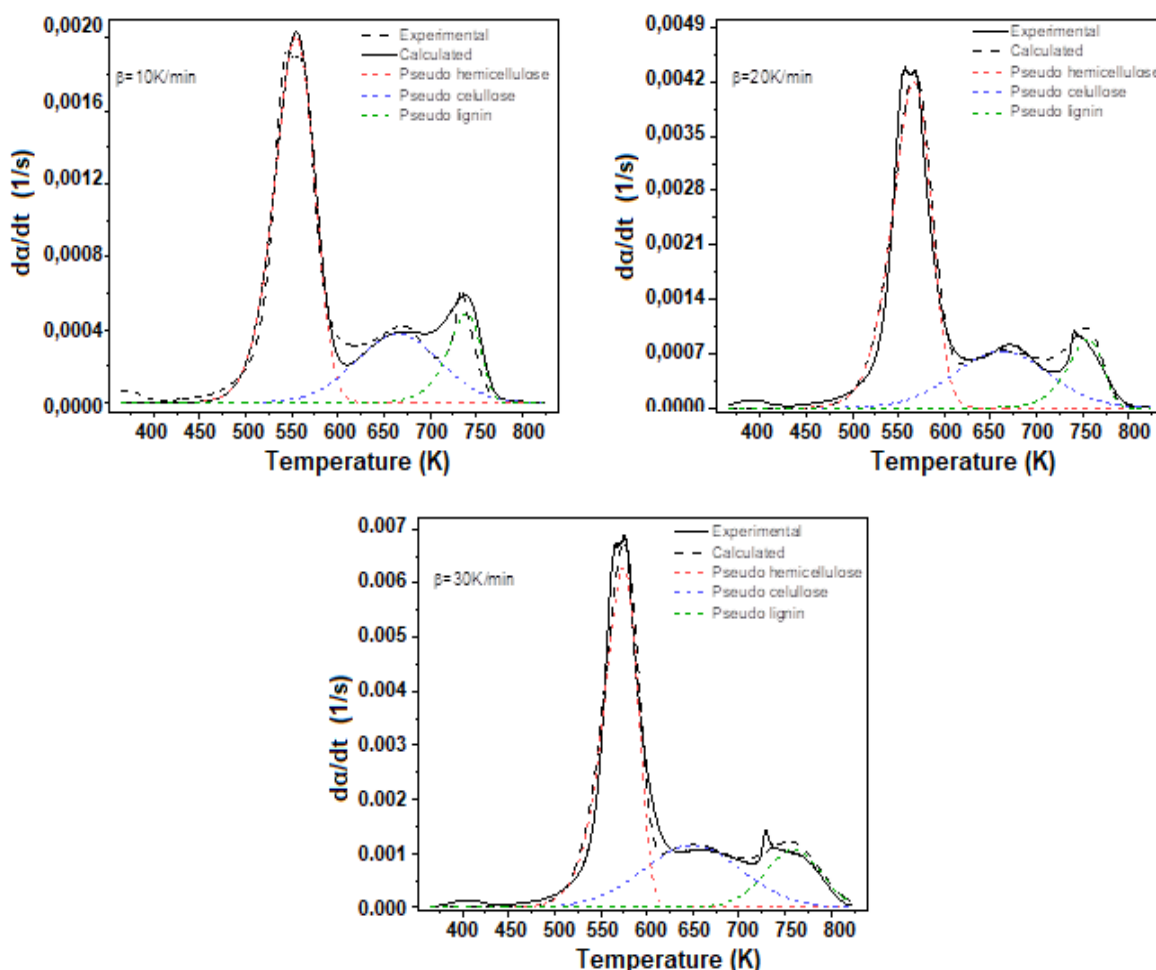


Fig. 7. Fit of the DAEM to DTG data from the corn husk biomass samples during combustion

The activation energy required in the combustion of the coconut husk biomass at different β -values presented similar values. The activation energy was approximately 169 kJ/mol for the first set of reactions, between 181 and 188 kJ/mol for the second set of reactions, and between 246 and 258 kJ/mol for the third set of reactions. For the third set, the smallest adjustment of the data obtained by DAEM to the experimental ones was achieved for the coconut husk sample treated at 10 K/min. For this sample, the activation energy value of 333 kJ/mol was atypical and greater than the activation energy values for the coconut husk at 20 K/min and 30 K/min (Fig. 6).

In the case of the corn husk biomass (Fig. 7), the thermal behavior of the samples was similar to the rice husk and coconut husk biomass samples. It is possible to see an increased in the conversion speed (da/dt) of hemicellulose in the corn husk biomass as the β -value increased. Conversely, the contribution of the volatiles decreased as a result of the hemicellulose degradation denoted as C_{1norm} in Table 6.

Table 6. Kinetic Parameters of the Corn Husk Obtained by DAEM

Parameters	Corn 10 (K/min)	Corn 20 (K/min)	Corn 30 (K/min)
C_{1norm}	6.25E-01	6.15E-01	5.56E-01
A_1 (1/s)	6.73E+11	7.47E+11	2.32E+12
E_{01} (kJ/mol)	1.48E+02	1.48E+02	1.53E+02
σ_{01} (kJ/mol)	6.84	5.72	2.56
C_{2norm}	2.47E-01	2.63E-01	2.89E-01
A_2 (1/s)	2.03E+13	1.06E+13	6.86E+13
E_{02} (kJ/mol)	1.98E+02	1.90E+02	1.94E+02
σ_{02} (kJ/mol)	2.50E+01	2.78E+01	3.06E+01
C_{3norm}	1.29E-01	1.22E-01	1.55E-01
A_3 (1/s)	2.46E+16	2.32E+16	3.95E+16
E_{03} (kJ/mol)	2.61E+02	2.62E+02	2.66E+02
σ_{03} (kJ/mol)	1.43	3.58	16.40

When comparing the DTG profiles and the main components for each biomass, the cellulose reaction range of the coconut husk biomass decreased as the β -value increased, while the reaction zone of the lignin increased. For the corn husk samples, both the cellulose and the lignin reaction ranges increased as the β -value increased. For the rice husk samples, no trend was observed in the reaction zones of the events. It was generally observed that the increased heating rate resulted in the overlapping of the hemicellulose and cellulose degradation events for all of the biomass samples that were studied. This observation was confirmed by the temperature values associated with the maximum point of degradation, shown in Table 7.

In Table 7, T_H , T_C , and T_L are the peak temperatures of hemicellulose, cellulose, and lignin, respectively. Table 7 shows that, for the coconut and corn biomass samples, the difference between the T_H and T_C values decreased as the β -value increased. As for the rice biomass sample, there was no apparent difference in the T_H and T_C values as the β -value increased.

Table 7. Peak Temperatures of Each Main Component of Biomass at Different Heating Rates

Sample	β (K/min)	T_H (K)	T_C (K)	T_L (K)
Rice	10	580	639	718
	20	593	630	726
	30	599	675	756
Coconut	10	553	609	699
	20	567	626	713
	30	578	621	725
Corn	10	555	667	740
	20	567	666	756
	30	574	654	761

The oxidative degradation for the hemicellulose and the cellulose occurred at lower temperatures compared to the lignin (Table 7). This was because their structures were amorphous, more random, and softer. These differences lead to different reactivities, so the activation energy required to carry out the combustion of these organic polymers was lower (Carrier *et al.* 2011; Ren *et al.* 2018). This means that the activation energy values increased in the order of hemicellulose, cellulose, and lignin.

The results of the activation energy for the decomposition of biomass reported in the literature suggest that there is a tendency to increase this parameter as the heating rate increases (Melgar *et al.* 2008; Arango-Muñoz *et al.* 2015). However, the results of this study suggest that the activation energy values for each set of reactions were similar between the speeds (β). As can be seen in Tables 4, 5, and 6, there was no noticeable difference in the activation energies. Yao *et al.* (2008) found that, in the thermal decomposition of natural fibers, such energy does not show remarkable variations, or it varies shortly after the process starts.

Thermogravimetric parameters deduced from the curves obtained from the combustion of the different biomasses are shown in Table 8.

Table 8. Peak Temperatures of Each Main Component of Biomass at Different Heating Rates

Sample	β (K/min)	T_0 (K)	T_f (K)	MR (%)	da/dt (s ⁻¹)
Rice Husk	10	522	752	22.75	0.00174
	20	530	776	28.65	0.00423
	30	535	798	27.51	0.00601
Coconut Husk	10	512	714	0.00	0.00190
	20	522	739	0.00	0.00442
	30	530	766	0.00	0.00677
Corn Husk	10	507	759	5.70	0.00195
	20	513	789	5.05	0.00438
	30	519	805	3.99	0.00688

Characteristic temperatures: T_0 (initial temperature), and T_f (final temperature),
Residual mass after reaction (RM)
Maximum conversion speed (da/dt).

The T_0 values did not represent significant differences between biomasses, but it is notable that the T_f values for the coconut husk samples were lower compared to the corn husk samples and in turn with the rice husk samples.

The temperatures of maximum mass losses, for the first event, follow a tendency to increase directly with the increase in the heating rate; this behavior is not evident for the samples in the second event or reaction zone. In general terms, the coconut husk samples are those with the lowest peak temperature for this last event. Regarding the values of maximum conversion speed, for the three biomasses, values are close and follow the trend to increase with the increase in the heating rate. Similar maximum temperatures, reaction intervals and thermal profiles have also been observed in the literature (Kok and Ozgur 2017).

Of the biomasses studied, residual mass or ash values were higher for rice husk biomass (within the range 22 to 29%), followed by samples of corn husk, the ash content of which was between 5 and 6%; coconut husk samples did not leave any residue after oxidation. These values are related to the results obtained in the characterization of each biomass found through proximate analysis.

Results of the characterization showed that for biomasses the main component is holocellulose. In particular, the rice husk showed a high ash content (22.37%), which has as a consequence a considerable decrease in its calorific power when compared to the other two biomasses studied. The highest calorific value was presented by the coconut husk with a value of 24.29 MJ/kg, which makes it very attractive for its direct use in energy processes.

CONCLUSIONS

1. The results show that the biomass thermal degradation process is made up of the combustion of hemicellulose, cellulose, and lignin. Model kinetic parameters (DAEM) indicated that the activation energy distribution for the pseudocomponents follows the order of: E_{03} (lignin) > E_{02} (cellulose) > E_{01} (hemicellulose).
2. The activation energy values for each set of reactions were similar between the heating rates. For all the biomass samples, the increased heating rate resulted in the overlapping hemicellulose and cellulose degradation events.

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