

Investigation into the kinetic behavior of biomass combustion under N₂/O₂ and CO₂/O₂ atmospheres

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Abstract Isoconversional kinetic method (model-free kinetics) was used in this study to determine the activation energies (E_a) of the combustion process of five different biomass samples, namely pine sawdust, sugarcane bagasse, coffee husk, rice husk and *tucumã* seeds, widely available in Brazil. Two different atmospheres with 20 % O₂:N₂/O₂ (conventional combustion) and CO₂/O₂ (typical oxy-fuel combustion) were studied. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were used to obtain experimental data on the thermal degradation behavior of the biomasses, and the activation energy values were obtained for hemicellulose, cellulose and residual lignin separately. The results show that the E_a obtained for N₂/O₂ ranged from 68 to 236 kJ mol⁻¹ for hemicellulose, 119 to 209 kJ mol⁻¹ for cellulose and 87 to 205 kJ mol⁻¹ for residual lignin, depending on the type of biomass. Under CO₂/O₂ atmosphere, E_a showed decreases, in average, 35 % for hemicellulose and 26 % for cellulose, in comparison with N₂/O₂ atmosphere. However, a 6 % increase was observed for the residual lignin. These changes can be understood by differences between CO₂ and N₂ gas properties. However, the results show that the variation in the E_a is more dependent on the type of biomass than on the atmosphere at which the combustion takes place.

Keywords Activation energy · Biomasses · Kinetic method · Thermal analysis

Introduction

Urbanization, population growth and the development of new technologies in both developed and developing countries have increased the demand for electrical power. A direct consequence of such a demand is the increase in the consumption of fossil fuels (oil, coal and natural gas) and gradual atmospheric pollutant emissions [1]. There has been a growing global consensus that the environmental damages (global warming, acid rain and urban smog) are caused by gaseous emissions, which intimately affect both climate changes and human health [2]. The development of new technologies aims at mitigating this situation, considering the reduction in the environmental impacts and also the CO, CO₂ and NO emissions.

A promising alternative to reduce gaseous emissions is the use of renewable fuels for the production of energy [3]. In this sense, Brazil has advanced programs for the implementation of different types of biomass. Their utilization appears as an opportunity to collaborate with power supply systems [4]. In some regions, large parts of biomass wastes are still used only for boiler feeding in power plants for vapor generation. Among the several forms of biomass thermal conversion for energy, the most used ones are direct combustion, gasification and pyrolysis [4]. The knowledge on the biomass thermal behavior is a fundamental issue for the development and optimization of technological processes.

Biomass is an organic solid matrix, and its thermal decomposition involves a large number of parallel reactions, related to heat and mass transfer processes. The

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decomposition of lignocellulosic materials has attracted considerable attention from the scientific community because it is a major step in its combustion process and also the key step in thermal processing methods, such as fast pyrolysis to produce chemical products and bio-oil [5, 6]. The release rate, quantity and composition of the volatile materials present in a biomass influence its flame ignition, stability and temperature profile in the radiant furnace part. Such factors are important in the design of burners for pulverized fuel power stations and impact on NO_x generation mechanisms [6].

Many researchers have conducted studies to elucidate several thermal conversion processes during biomass thermal degradation [3, 5–11]. According to Yang et al. [11], the mass losses of the main components of biomass (hemicellulose, cellulose and lignin) occur in a determined temperature range, which depends on experimental conditions, such as heating rate, heat transfer and biomass type. The chemical differences between these components directly influence their chemical reactivity during the combustion process [12].

The combustion process of biomasses comprises the burnout in an ambient rich in oxygen or air, which considers types and fuel properties, particles size, air flow rate and fuel moisture. Such characteristics affect combustion, reaction rates and generation and transfer of heat [13, 14]. Although the interest in the use of renewable fuels has been growing worldwide, combustion is a process that inherently emits CO₂. An interesting technology to solve this problem is the oxy-fuel combustion, which comprises the recycling of combustion gases, mainly CO₂, which is ready to be captured with increase in its concentration. Although this technology represents a significant advance of decreasing CO₂ emission and can be used as retrofit technology in conventional boilers, the costs are still a barrier for its commercial application [15–19].

However, the successful implementation of the oxy-fuel technology requires fundamental knowledge on the combustion under a CO₂ atmosphere. The determination of kinetics parameters of the thermal degradation of solid fuels is essential for the design of conversion plants with efficient operating systems [7, 20] and for an accurate prediction of their behavior under different conditions.

Several studies have reported different approaches of kinetic methods to describe thermal degradations [7, 21–26]. The determination of the E_a based on the Arrhenius's equation and using thermogravimetric data has been widely applied to the evaluation of the reaction mechanisms in solid phases.

This study investigates the thermal decomposition of five different types of biomass *in natura* (pine sawdust, sugarcane bagasse, coffee husk, rice husk and *tucumã* seed) under both atmospheres: N₂/O₂ (conventional combustion)

and CO₂/O₂ (oxy-fuel combustion). Experiments were performed in a thermogravimetric balance, and data were applied to a mathematical model (isoconversional kinetic method—model-free kinetics) for the determination of the activation energies of the combustion processes.

Materials and methods

Origin of biomasses

Five *in natura* biomass samples, namely pine sawdust, sugarcane bagasse, coffee husk (from São Paulo State—Southeast region), rice husk (from Maranhão State—Northeast region) and *tucumã* seed (from Pará State—Northern region), were selected for the study. Physico-chemical characteristics of the *in natura* samples after preparation are shown in Table 1.

Samples preparation

The samples were received *in natura* and underwent pre-treatments that consisted in washing for the removal of impurities, dried at 90 °C for 24 h, chopped in a household blender and sieved. The average particle size of 460 μm was selected and obtained by the arithmetic mean of two consecutive ASTM laboratory sieves whose mesh apertures ranged between 420 and 500 μm. Particles of 460 μm average size were used for all the samples and determined based on our previous study [27].

Thermal analysis (TG/DTG)

TG/DTG non-isothermal tests were performed in a *Shimadzu* thermogravimetric analyzer, TGA-50H model for the obtaining of the experimental data. Three steps of thermal degradation related to hemicellulose, cellulose and lignin were evaluated.

The following conditions were used: atmospheres of synthetic air (N₂/O₂–80/20) to simulate conventional combustion and CO₂/O₂ (80/20) to simulate oxy-fuel combustion; 100 mL min^{−1} flow rate; 10.0 ± 0.5 mg samples mass; and five heating rates: 10, 15, 20, 25 and 30 °C min^{−1} from room temperature up to 700 °C.

Figure 1 shows the TG/DTG curves only for the sugarcane bagasse sample in N₂/O₂ atmosphere. For each biomass and atmosphere, the TG and DTG curves exhibited similar behaviors, but with their own characteristics.

Activation energies (E_a) and conversion degree (α) of the thermal degradation steps for hemicellulose (first step), cellulose (second step) and residual lignin (third step) were obtained by model-free kinetics. Each thermal degradation

Table 1 Physicochemical characteristics of the biomasses

	Pine sawdust	Sugarcane bagasse	Coffee husk	Rice husk	Tucumã seed
Proximate analysis/mass% as received					
Moisture	7.3	7.5	9.3	8.2	7.1
Volatile matter	18.3	13.1	22.6	15.0	19.4
Fixed carbon	70.4	75.8	61.5	47.8	69.4
Ash	4.0	3.6	6.6	29.0	4.1
Ultimate analysis/mass% dry-ash-free basis					
Carbon	46.6	45.1	43.1	39.1	48.8
Hydrogen	5.4	4.9	5.0	4.1	6.1
Nitrogen	0.4	0.3	1.6	0.3	0.9
Sulfur	n.d.	n.d.	0.7	0.6	n.d.
Oxygen*	36.3	38.6	33.7	18.7	33.0
HHV**/MJ kg ⁻¹	18.3 ± 0.2	17.5 ± 0.1	16.8 ± 0.1	15.4 ± 0.1	20.8 ± 0.1

n.d. Not detected; * Calculated by difference; ** High heating value

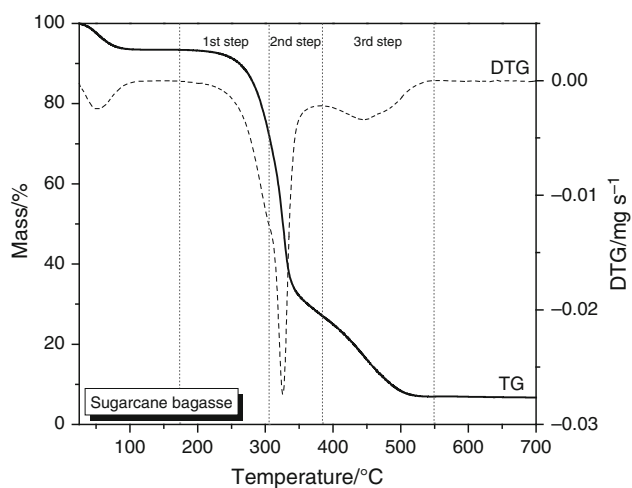


Fig. 1 TG/DTG curves for the sugarcane bagasse sample under synthetic air atmosphere at 10 °C min⁻¹, showing the three thermal degradation steps

step was considered based on the peak separation methods of DTG curves [26].

Determination of the activation energies by model-free kinetics

The activation energies for the combustion processes of five biomasses (pine sawdust, sugarcane bagasse, coffee husk, rice husk and tucumã seed) were obtained using non-isothermal thermogravimetric experiments and model-free kinetics.

The model-free kinetics method enables the evaluation of the Arrhenius parameters. It is based on isoconversional

techniques and calculates the activation energy as a function of conversion ($E_a = f(\alpha)$) [28–32]. The method is supported on the assumption that:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where T is the temperature, t is the time, $f(\alpha)$ is the reaction model, $k(T)$ is the constant of reaction rate, R is the universal gas constant, A is the pre-exponential factor, E_a is the activation energy and (α) is the conversion degree.

Conversion degree is defined as $\alpha = (m_0 - m)/(m_0 - m_\infty)$, where m is the local sample mass that varies with time, m_0 is the initial sample mass and m_∞ is the final sample mass. For simple reactions, the function of conversion, $f(\alpha)$, can be determined, but for complex reactions it is generally unknown [28].

There is a temporal dependence on non-isothermal conditions, which can be eliminated dividing $f(\alpha)$ by the heating rate $\beta = dT/dt$. After rearranging Eq. (1), one obtains:

$$\frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT \quad (2)$$

Integrating Eq. (2) up to the conversion at the local temperature, one has:

$$\int_0^\alpha \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (3)$$

Provided that $E_a/2RT \gg 1$, the temperature integral of the right-hand side can be approximated by

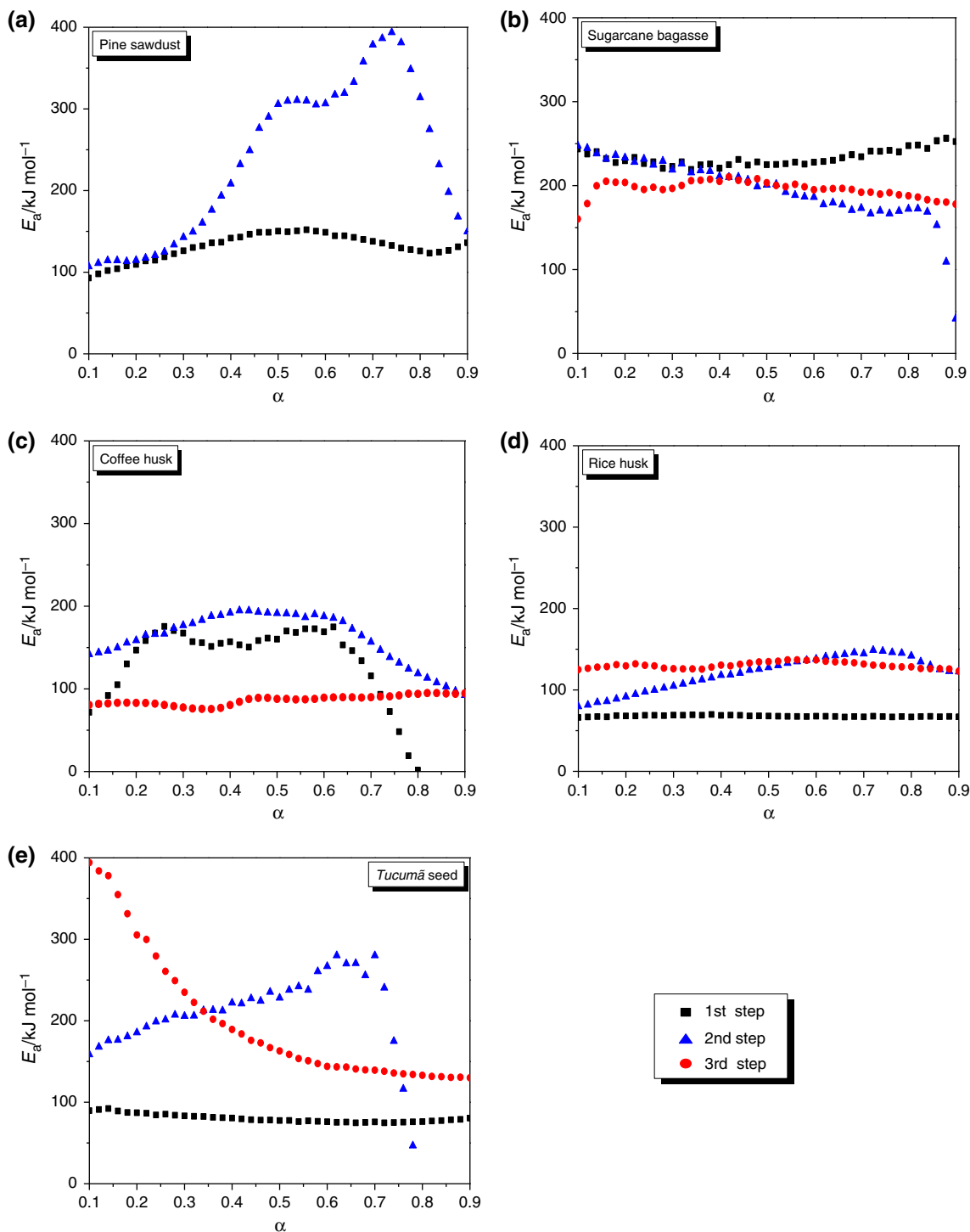


Fig. 2 Activation energy (E_a) versus conversion degree (α) curves for the thermal degradation of five samples under synthetic air atmosphere. The three steps correspond to hemicellulose, cellulose and residual lignin degradations

$$\int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \approx \frac{R}{E_a} T^2 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

Inserting Eq. (4) in Eq. (3), rearranging Eq. (3) and taking the logarithm of the generated expression, one has:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{RA}{E_a g(\alpha)}\right] - \frac{E_a}{R} \frac{1}{T_\alpha} \quad (5)$$

where subscript α represents the values related to a given conversion degree. The activation energies can be obtained graphically by plotting $\ln(\beta/T^2)$ versus $1/T$.

Table 2 Activation energies under synthetic air atmosphere for the thermal degradation steps of the biomasses

Biomasses	Activation energies/kJ mol ⁻¹		
	First step	Second step	Third step
Pine sawdust	127 ± 22	209 ± 77	–
Sugarcane bagasse	236 ± 33	175 ± 83	190 ± 37
Coffee husk	98 ± 77	153 ± 36	87 ± 7
Rice husk	68 ± 2	119 ± 24	129 ± 5
<i>Tucumã</i> seed	81 ± 5	158 ± 109	205 ± 96

Results and discussion

Values of the activation energies for combustion under synthetic air atmosphere

Figure 2 shows the profiles of the E_a versus conversion degree (α) for three thermal decomposition steps under synthetic air atmosphere of the five biomasses (pine sawdust, sugarcane bagasse, coffee husk, rice husk and *tucumã* seed).

Table 2 shows the activation energy (E_a) values obtained by model-free kinetics under N₂/O₂ (80/20) atmosphere for the three thermal degradation steps.

The first, second and third steps correspond to the thermal degradation of hemicellulose, cellulose and residual lignin, respectively. Moisture release, which occurs below 110 °C, was not considered in this study.

Among the samples, only pine sawdust showed two distinct events of mass loss. The first and second events correspond to the hemicellulose and cellulose decomposition together, and the third is related to the decomposition of the residual lignin.

E_a versus (α) for coffee husk (Fig. 2c) of hemicellulose degradation (first step) shows a variation between 3 and 176 kJ mol⁻¹ related to a very heterogeneous thermal degradation. Such a behavior may be indicative of the occurrence of different mechanisms during the thermal decomposition process, which can be explained by the high volatile content ($\approx 74\%$) in the sample [23, 33, 34].

Regarding the thermal degradation of cellulose (second step), pine sawdust and *tucumã* seed samples (Fig. 2a, e) showed a more complex decomposition mechanism with variations of E_a between 105 and 400 kJ mol⁻¹, and 46 and 282 kJ mol⁻¹, respectively. The profiles of the E_a versus conversion curves show that the thermal decomposition of a biomass is considerably influenced by its structural and chemical composition. According to Poletto et al. [7], the crystallinity index and the extractive content can vary from

34 to 43 % and from 4 to 14 %, respectively; such factors can either accelerate or slow the thermal degradation process at low temperatures.

The high variation in the E_a values for pine sawdust, which is a woody sample, can be associated with the high content of organic compounds [35]. For *tucumã* seeds, the high variation of E_a may have been caused by its complex structure, which can be confirmed by means of TG/DTG curves that showed several mass loss events.

The average E_a values achieved in this study are in agreement with values reported in the literature regarding order of magnitude. For example, these E_a values reported to the biomasses ranged between 160 and 280 kJ mol⁻¹ for pine sawdust [23], 76–220 kJ mol⁻¹ and 75–116 kJ mol⁻¹ for sugarcane bagasse [25, 36], 160–250 kJ mol⁻¹ for coffee husk [37] and 120–250 kJ mol⁻¹ for rice husk samples [26, 38].

However, it is worth mentioning that those authors employed TG experiments, but with different kinetic methods and considered the entire process of thermal degradation as one step. Regarding the *tucumã* seed samples, no E_a value for thermal decomposition has been reported in the literature.

Influence of the atmosphere type on the thermal degradation of biomasses

In order to compare the influence of the atmosphere type on the thermal decomposition of biomasses, an atmosphere of 80 % CO₂–20 % O₂ was used, i.e., N₂ was replaced by CO₂.

Under 80 % CO₂–20 % O₂ condition, three different events of mass loss for all samples could be observed in the DTG curves. Under synthetic air condition (80 % N₂–20 % O₂), the pine sawdust samples showed two events and the others showed three events.

The DTG curves are shown in Fig. 3. The presence of CO₂ causes a displacement of the thermal degradation to a higher temperature for two samples (pine sawdust and coffee husk). However, such an effect was not observed for other samples (sugarcane bagasse, rice husk and *tucumã* seed). It seems that the degree displacement depends more on the biomass type than on the atmosphere type.

In both atmospheres, a shoulder around 310 °C was observed for the sugarcane bagasse and rice husk samples. Such a characteristic is indicative of higher hemicellulose content in the samples [23]. For the sugarcane bagasse and rice husk samples, the distinction between hemicellulose and cellulose is possible by means of DTG curves, while

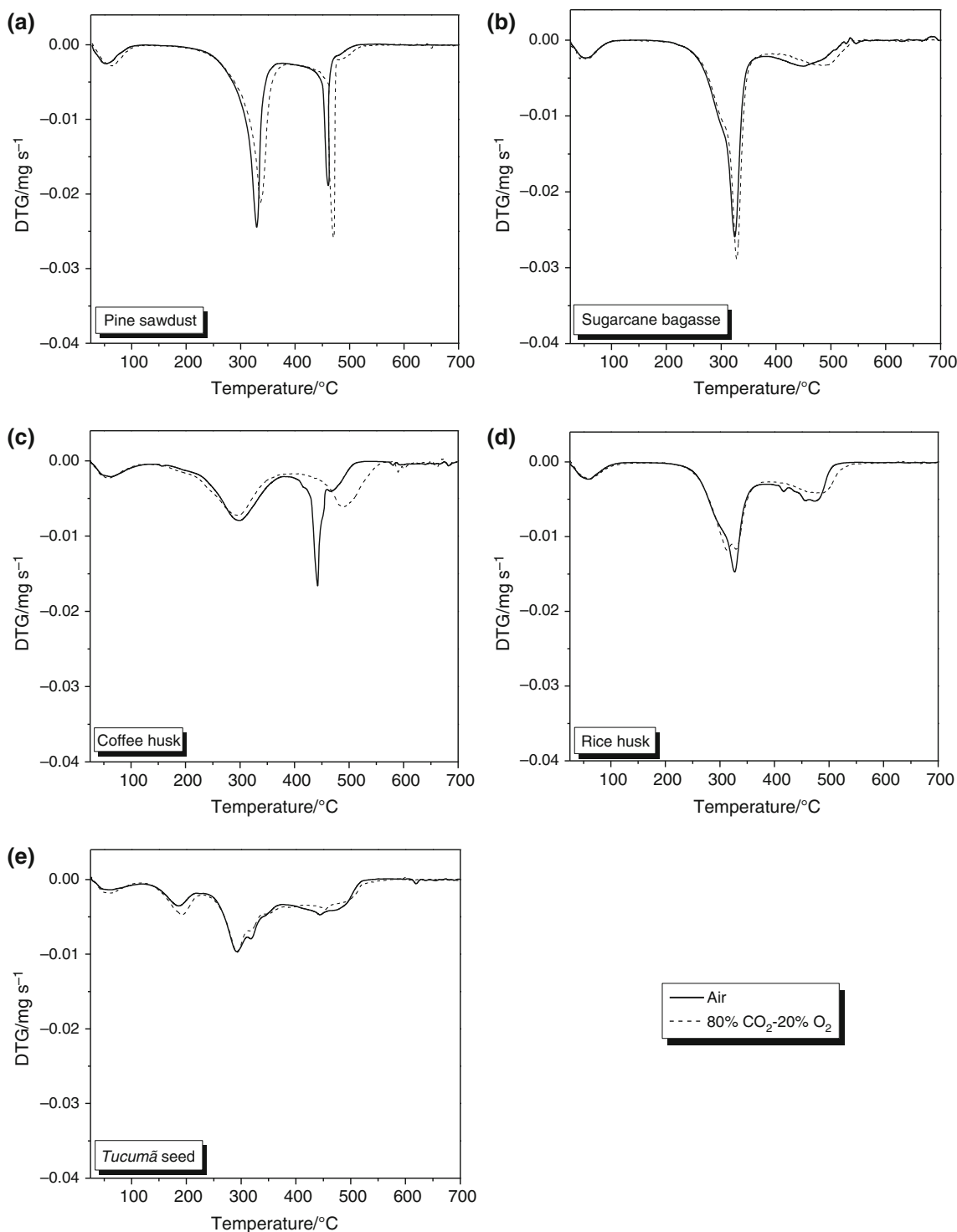


Fig. 3 DTG curves for the biomass samples under synthetic air and 80 % CO₂ atmosphere at 10 °C min⁻¹, showing the thermal degradation steps

for the other samples, such a distinction is not possible due to the overlapping of hemicellulose and cellulose during the thermal process [25].

For most biomasses (pine sawdust, sugarcane bagasse, rice husk and *tucumã* seed) of this study, no significant

effect was observed by replacing N₂ by CO₂ during the combustion process. However, only for the coffee husk sample there was a decrease in the combustion reaction rate accompanied by a displacement to a higher temperature in the second degradation step.

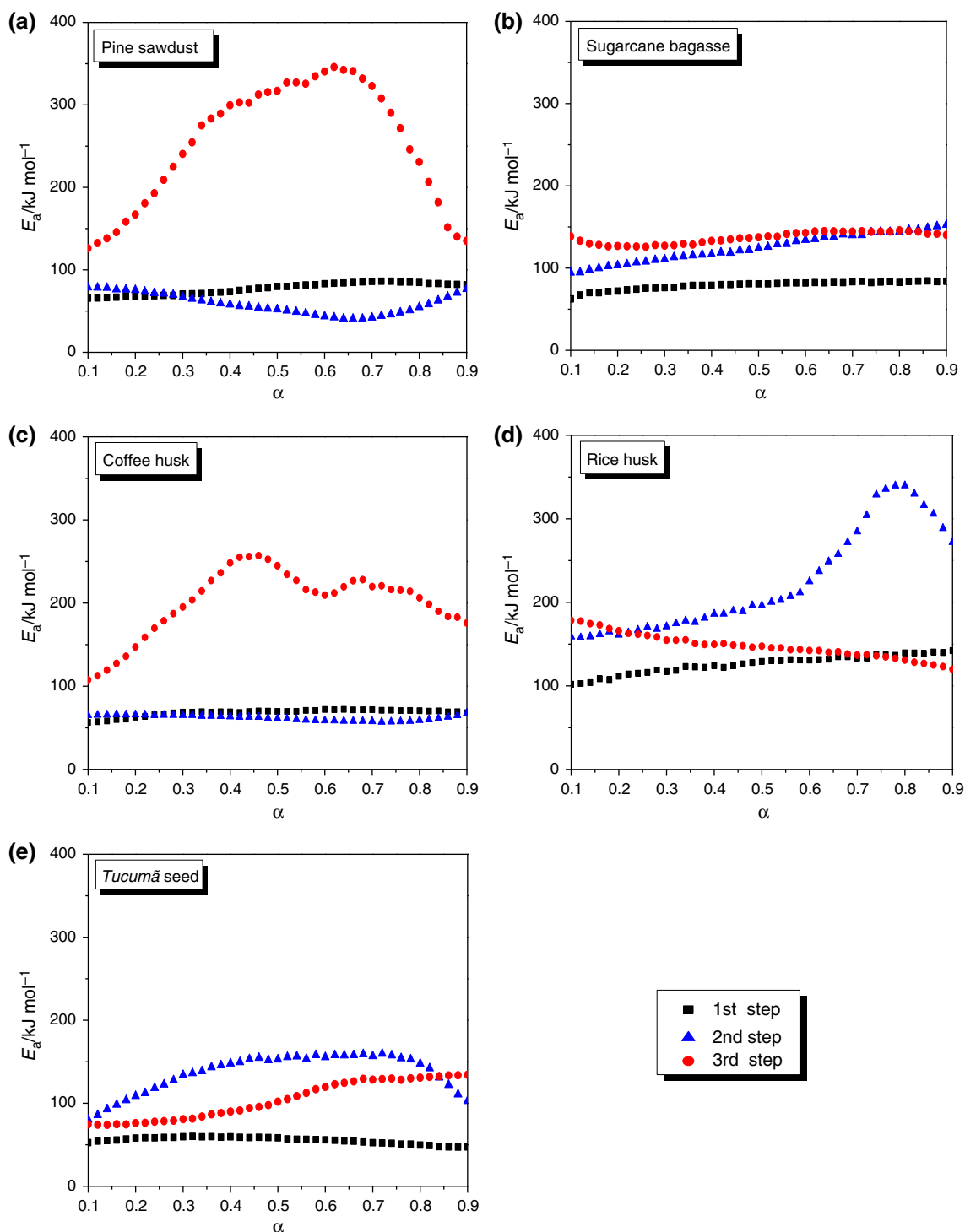


Fig. 4 Activation energy (E_a) versus conversion degree (α) for the thermal degradation of five samples under 80 % CO₂ atmosphere. The three steps correspond to hemicellulose, cellulose and residual lignin degradations

Values of the activation energies for combustion under 80 % CO₂ atmosphere

The activation energies (E_a) were determined for each thermal degradation step separately so that the effect of CO₂ could be understood.

Figure 4 shows the E_a versus (α) curves under 80 % CO₂–20 % O₂ atmosphere for the thermal decomposition steps of the biomasses studied (pine sawdust, sugarcane bagasse, coffee husk, rice husk and *tucumã* seed). All the biomasses showed the three distinct thermal degradation steps.

Table 3 Activation energies under 80 % CO₂ atmosphere for the thermal degradation steps of the biomasses

Biomasses	Activation energies/kJ mol ⁻¹		
	First step	Second step	Third step
Pine sawdust	76 ± 8	64 ± 16	233 ± 80
Sugarcane bagasse	77 ± 11	124 ± 20	140 ± 11
Coffee husk	66 ± 6	69 ± 6	188 ± 48
Rice husk	124 ± 16	219 ± 61	148 ± 22
<i>Tucumã</i> seed	54 ± 5	129 ± 32	104 ± 24

A homogeneous behavior related to the hemicellulose thermal degradation for all biomasses was observed under 80 % CO₂ atmosphere in the first step. A more heterogeneous behavior was observed for the rice husk and *tucumã* seed samples in the second step (Fig. 4d, e). Such heterogeneity is attributed to the high variation in the activation energy, i.e., for rice husk the values are between 150 and 320 kJ mol⁻¹, and for *tucumã* seed the E_a varied from 80 to 150 kJ mol⁻¹.

In the second stage and only for rice husk, there was a significant change in the E_a versus (α) curve when N₂ was replaced by CO₂. In the third thermal degradation step, related to the residual lignin content, the higher activation energy values were observed for pine sawdust and coffee husk samples, as shown in Fig. 4a, c. The E_a values ranged from 120 to 350 kJ mol⁻¹ for pine sawdust and from 100 to 250 kJ mol⁻¹ for coffee husk.

Table 3 shows the E_a under 80 % CO₂ atmosphere for the three thermal degradation steps obtained by model-free kinetics.

No trend was observed when N₂ was replaced by CO₂, and the behavior of each sample is independent of the atmosphere in which the degradation takes place.

Conclusions

This study investigated the effects of two atmospheres on the activation energy values of the thermal degradation steps of five different biomass samples (pine sawdust, sugarcane bagasse, coffee husk, rice husk and *tucumã* seed) at the same oxygen concentrations: N₂/O₂ and CO₂/O₂.

The isoconversional kinetic method (model-free kinetics) was used, and experimental conditions were performed in a thermobalance.

Three different steps were considered, and each decomposition region corresponded to the hemicellulose, cellulose and lignin contents in the samples. Each region was delimited in the TG curves by the peak separation method based on DTG curves.

The results show that the activation energy values varied for each thermal degradation step, atmosphere type and biomass type, and no trend was observed regarding the replacement of N₂ by CO₂ in the environment. For the rice husk sample, the activation energy values in CO₂ atmosphere increased 56 % on average, in comparison with synthetic air atmosphere, which is in agreement with E_a values reported in the literature.

On the other hand, in average, the E_a values for sugarcane bagasse, pine sawdust, coffee husk and *tucumã* seed are lower in CO₂ than in synthetic air atmosphere, i.e., 44, 26, 6 and 36 %, respectively.

Biomass is a complex lignocellulosic matrix and involves several steps during its thermal decomposition process. According to the results, each constituent component of the different biomasses showed a specific thermal degradation mechanism. Such difference was shown in the E_a versus α curves for each step defined. In comparison with the thermal processes conducted at two atmospheres, the mechanisms were distinct, as indicated by the curves profiles and average E_a values.

Although the properties of CO₂ and N₂ gases are different, our findings indicate that the variation in the E_a is more dependent on the biomass type than on the atmosphere in which the combustion takes place.

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