

Thermochemical Characterization of Biomass

Modelling combustion and pyrolysis kinetic

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ABSTRACT

In this project, it has been studied the kinetic of thermochemical conversion of five biomass samples, eucalyptus branch, eucalyptus splinters, eucalyptus bark, eucalyptus pellets and acacia pellets, prepared in collaboration with University of Aveiro and a pulp and paper company, under oxidizing and non-oxidizing atmospheres and at different heating rates (10, 20, 50 and 100 °C/min). To do so, a thermogravimetric analyser (TGA) with differential scanning calorimetry (DSC) has been used to obtain the mass loss profile, mass loss rate and energy profile during the experiments. TG curves shown differentiated slopes that would correspond to the degradation of the different pseudo-components of biomass: water, cellulose, hemicellulose, lignin and ash. It was studied the conversion of each pseudo-component assuming a first-order reaction.

1. Introduction

There is a growing concern about the pollution of the environment caused by the human activities, in particular in what concerns carbon dioxide accumulation in the atmosphere. In this context, the use of biomass has been increasing in recent years, but despite its tendency to increase, the contribution of bioenergy to world energy consumption nowadays is small; power generation from biomass represents 1.2% of total global power generation capacity and unfortunately, most of this bioenergy is associated with unsustainable biomass use, causing deforestation and soil degradation [2] [3].

One of the challenges facing the evolution of the bioenergy obtained through the use of solid biomass is the implementation of a criterion that ensures the sustainability and economic efficiency of its use. Key

factors that ensure the efficiency of the economics of different conversion routes are the moisture content, dry matter content and energy potential. Therefore, it is necessary to carry out lines of research that provide further information about these processes, in particular the reaction kinetics.

2. Research methodology

2.1 Materials

Table 1 summarizes the samples that were used in the study together with the codes used to designate them.

2.2 Experimental method

Sample	Code
Eucalyptus branch "ramagem de eucalipto"	ER
Eucalyptus pellets "pellets de eucalipto"	EP
Eucalyptus bark "casca de eucalito"	EC
Eucalyptus splinters "estilha de eucalipto"	EA
Acacia pellets "pellets de acácia"	AP

Table 1. Description of the samples and references

The experiments were carried out on a thermogravimetric analyser with a differential scanning calorimetry (STA 6000, PerkinElmer, Inc.). To start all the experiments under uniform conditions and ensure a proper atmosphere within the equipment, a temperature of 30 °C is maintained for 30 minutes.

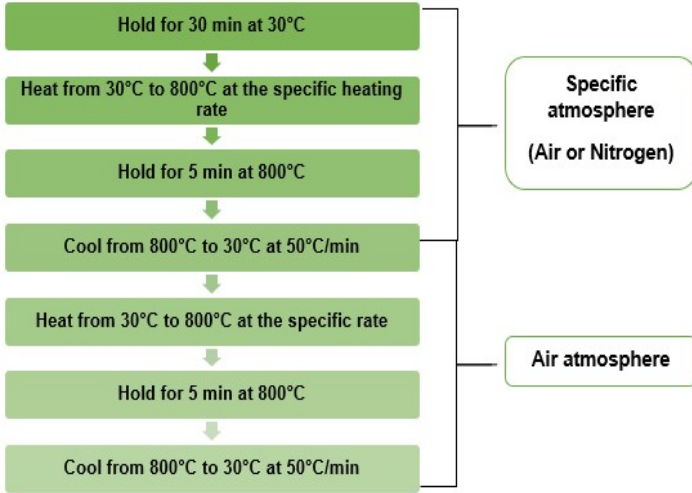


Figure 1. Heating program for all samples

Experiments were carried-out under oxidative conditions, where the sweep gas was air, and non-oxidative conditions, using nitrogen, to obtain pyrolysis conditions with a flow of gas around 20 mL/min at normal temperature and pressure conditions.

To analyse the results of the experiments with different samples, and to ensure a greater accuracy, blank experiments were also conducted, using only the crucible, to obtain the heat flow.

The initial weights of the samples were within the range of 20-30 mg. The experiments were performed for all the samples at four different heating rates (10, 20, 50 and 100 °C / min) and in oxidizing and non-oxidizing atmospheres.

2.3 Data processing

The procedure to calculate the kinetic parameters consist of the following steps:

- I. The experiments are performed according to the experimental procedure in figure 1.

- II. The weight fraction versus temperature is plotted on a graph and a kinetic model is computed in order to simulate the loss of experimental mass. In the context of this work we used a pseudo-component approach to describe the different biomass samples. The different pseudo-components can be tentatively assigned to the expected major components of biomass: water, cellulose, hemicellulose, lignin and ash.

It was assumed that the conversion of each pseudo-component follows a first-order reaction, which is, in a first approach, independent from the other pseudo-components. Thus, the kinetic model describes the kinetics of each pseudo-component according to the expression,

$$-\frac{dW_{comp\ x,n}}{dt} = k(T) \cdot W_{comp\ x,n} \quad (1)$$

Where $k(T)$ is the reaction rate constant given by the Arrhenius equation Eq. (2) and $W_{comp\ x, n}$ represents the change in mass fraction of each individual pseudo-component at given time t_n and Δt is the time lap equal to 0.002 minutes. $W_{comp\ x, n}$ it is calculated by the Euler's method:

$$W_{comp\ x,n} = W_{comp\ x,(n-1)} + \frac{dW_{comp\ x,(n-1)}}{dt} \cdot \Delta t \quad (2)$$

- III. The total modelled mass loss ($W_{model,n}$) it is calculated as the sum of the individual pseudo-components mass loss:

$$W_{model,n} = \sum W_{comp\ x,n} \quad (3)$$

- IV. The values of the activation energy, the pre-exponential factor and the initial mass fraction of each component, were estimated using a least-squares approach and resorting to the Generalized Reduced Gradient (GRG) algorithm for non-linear optimization using the Solver tool in Microsoft Excel.

- V. The objective function to be minimized is

$$f(W) = \sum (W_{exp,n} - W_{model,n})^2 \quad (4)$$

where $W_{exp,n}$ is the experimental mass loss.

3. Experimental Results

3.1 Analysis of thermal decomposition

Thermogravimetric analysis (TGA) measure the mass of the sample over time while the sample is subjected to a controlled heating program in a controlled atmosphere. This thermal analysis provide information of mass loss profile and rate of mass loss.

I. Combustion

TG curves during combustion (Figure 2) shows that the slope of the curve differs at diverse temperature ranges.

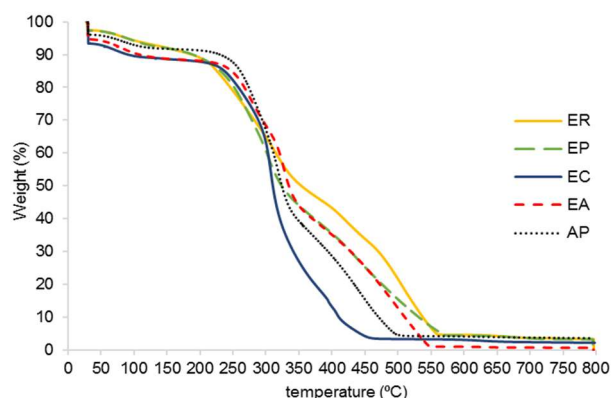


Figure 2. TG curves of combustion at 10 °C/min.

The first stage (30-140 °C), presents a small loss of mass, approximately 6-10% where the moisture contained in the sample and light-weight components are released.

The second stage (140-566 °C) corresponds to the combustion process and during it there is a high amount of mass loss, around 70-80%, when the volatilisation of the components of the sample and its cracking into smaller compounds occur. During this stage the oxidation of the volatiles may also occur. In this range of temperatures there is a first sub-stage (140-345 °C) where the rate of degradation increases and weight loss varies between 42-51% of the residual weight. The second sub-stage occurs at (345-566 °C), where the variation of weight oscillates between 31-48% of the residual weight.

The third stage (>566 °C) correspond to the glowing combustion when the oxidation of the residual char

takes place. In this stage, there is only a very small amount of mass loss, around 0,5-1%.

I. Pyrolysis

TG curves during pyrolysis (Figure 3) shows a first stage (30-137 °C), which presents a small loss of mass, where the moisture contained in the sample and light-weight components are released.

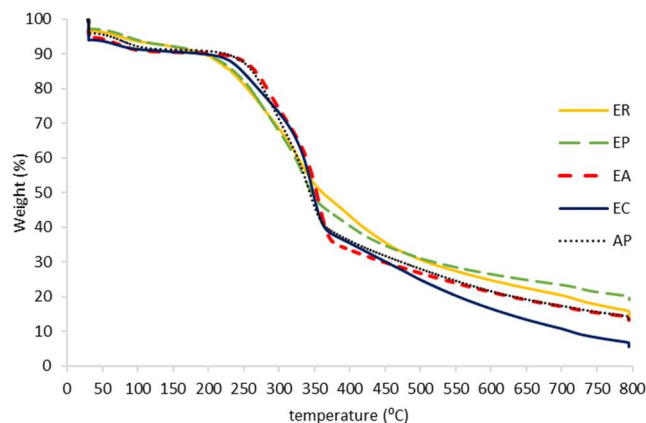


Figure 3. TG curves of pyrolysis at 10 °C/min.

The second stage (137-795 °C) corresponds to volatilization, where the degradation of the long polymer chains of hemicellulose, cellulose and lignin occurs to decompose into char, condensable gases and non-condensable gases. In this second stage, it is estimated that there is a first sub-stage that would correspond to the degradation of hemicellulose, since it has been observed to react at lower temperatures than cellulose or lignin, where the greatest variation in weight occurs between 263-363 °C with a weight loss varying between 4-18%. The second sub-stage (352-454 °C) would correspond to the degradation on cellulose, where the weight loss varies between 13-40% depending on the sample. Last, the degradation of the last component occur in a third sub-stage with a weight loss of 15-39% depending on the sample.

According to kinetic studies, cellulose degradation would occur in the temperature range (315-400 °C) and lignin degradation would occur slowly throughout the process until a temperature of 900 °C [5]. As it can be noticed, more residue is produced in pyrolysis process than in combustion since the volatilization of lignin, favoured at high temperatures during pyrolysis,

produces a large amount of residual solids in the form of carbonaceous material, as already determined in previous studies [7]. The third stage would correspond to the carbonization of the volatiles and the carbonaceous solid.

3.2 Analysis of energy profile

The differential scanning calorimetry (DSC) provide information of the heat flow released or absorbed by the sample during the experiments.

I. Combustion

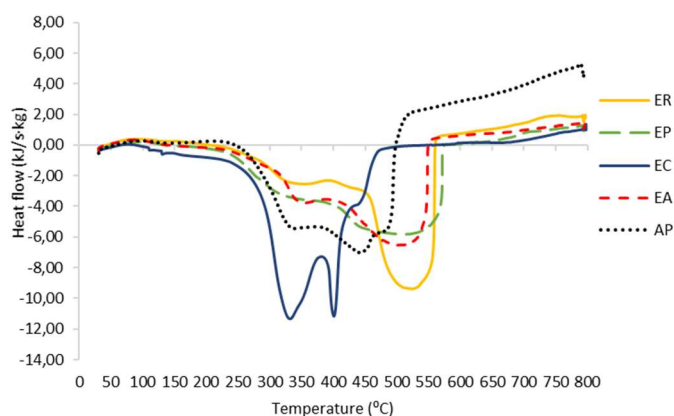


Figure 4. Heat flow profile during combustion at 10 °C/min.

The thermal profile of the samples when submitted to oxidizing atmosphere (Figure 4) shows an exothermic stage at temperatures between (250-550 °C), which would correspond to the combustion of volatiles and, finally, char combustion. After that it takes place a lightly endothermic stage at temperatures above 550 °C, point where the combustion process has already been completed, and may occur the volatilization of some minerals contained in the ash, generally potassium and sodium.

II. Pyrolysis

The thermal profile of the samples when submitted to pyrolysis (Figure 5) is completely endothermic. Despite the endothermic tendency, figure 5 shows peaks and variations along the curve. As mentioned above, once the first dehydration stage occurs, volatilization of the components takes place, which is an endothermic process, and at the same time it can

occur the cracking of volatiles phase already formed into gases, which is an exothermic process [5].

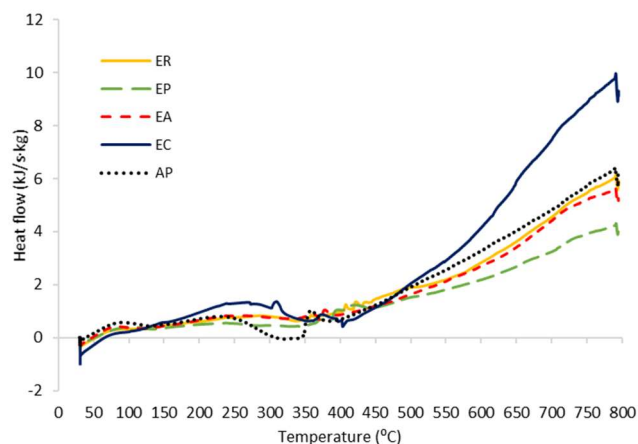


Figure 5. Heat flow profile during pyrolysis at 10 °C/min.

The intermediate peaks and variations in the thermal profile that occur during the process may be since these two stages sometimes overlap, due to limitations in the heat transfer caused by the low thermal conductivity of the woody biomass [1].

3.3 Effect of the heating rate in mass loss profile

In this section, it is analysed the behaviour of each sample at different heating rates. TG/DTG curves of acacia pellets during combustion (Figure 6) and pyrolysis (Figure 7) at different heating rates, show a similar behaviour at low temperatures, with small variations between them.

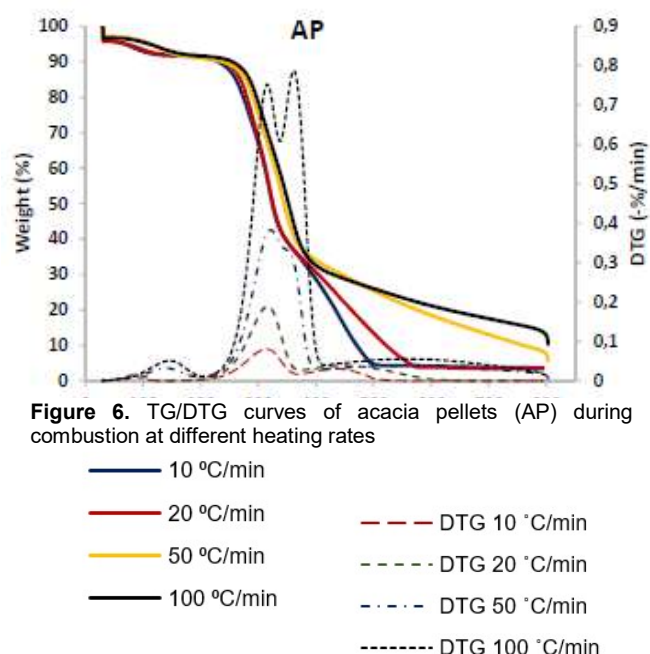


Figure 6. TG/DTG curves of acacia pellets (AP) during combustion at different heating rates

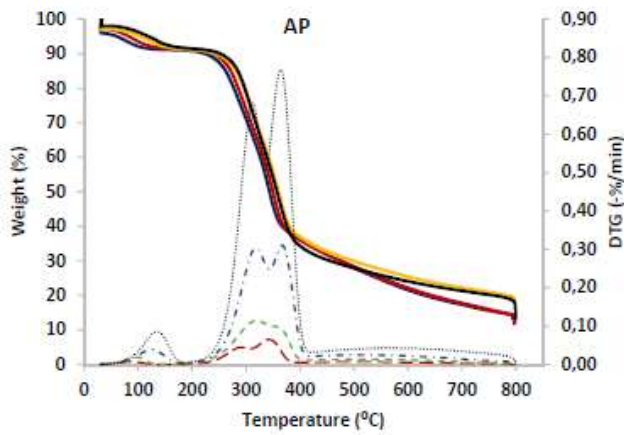


Figure 7. TG/DTG curves of acacia pellets (AP) during pyrolysis at different heating rates



As the temperature increases, the rate of mass loss decreases, which causes the stages to prolong and the slope become lower.

Thus, increasing the heating rate causes the temperature range of the different stages to be larger and consequently the stages overlap. This may occur due to kinetic aspects or because although the heating rate has increased, there is a limitation in the heat transfer due to the thermal resistance of the sample [6].

A slower heating rate improves the heat transfer along the material and ensures a more homogeneous temperature within the particle. As a consequence, the process of cracking is more efficient so more mass is reacting to form volatiles and the mass loss curve is deviated to produce less residue [8].

As for the rate of mass loss, the temperature at which the maximum weight variation is produced is displaced towards higher values. The reason might be that, as there is not an efficient heat transfer, the cracking occurs later than predicted [8].

3.4 Effect of the heating rate in DSC curves

In this section, the results of the differential scanning calorimeter (DSC) are presented at different heating rates.

I. Combustion

Figure 8 represents the heat flow profile of acacia pellets during combustion at different heating rates.

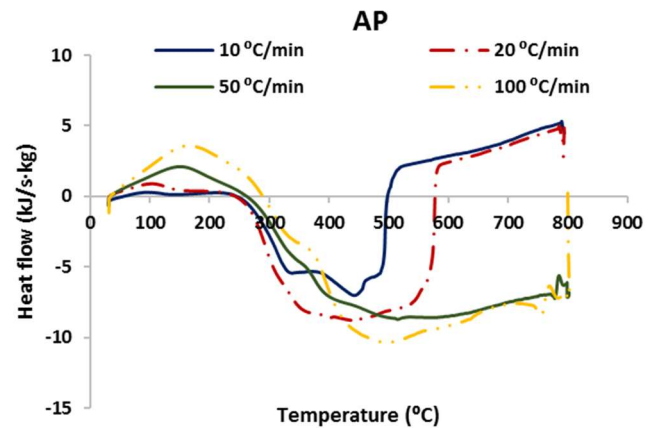


Figure 8. DSC curves of acacia pellets (AP) during combustion at different heating rates.

At low heating rates, generally two peaks can be seen, the first peak represents the combustion of volatiles, and the second peak represents the char combustion [9]. At higher heating rates, the peaks tend to approach each other, and finally at a heating rate of 100 °C/min, the two peaks are completely overlapped, and the curves show a single peak. Table 2 summarizes the curve peaks of the rate of mass loss. The symbol “-” indicates that no peak was found.

		10	20	50	100
	Sample	°C/min	°C/min	°C/min	°C/min
		(°C)	(°C)	(°C)	(°C)
ER	Peak 1	354.43	376.97	556.98	572.91
	Peak 2	523.6	553.5	-	-
EP	Peak 1	399.99	399.99	418.63	516.79
	Peak 2	510.6	517.3	510.51	-
EC	Peak 1	331.94	376.78	410.15	449.92
	Peak 2	401.05	429.31	-	-
EA	Peak 1	355.93	367.36	423.79	496.22
	Peak 2	498.84	456.11	-	-
AP	Peak 1	338.68	447.33	515.14	496.38
	Peak 2	442.09	-	-	-

Table 2. Temperature peaks in DSC curve for combustion at different heating rates

II. Pyrolysis

The heat flow profile during pyrolysis (Figure 9) shows a completely endothermic behaviour at low heating rates, while at high heating rates, the DSC curve shows an exothermic behaviour at around 300-400 °C.

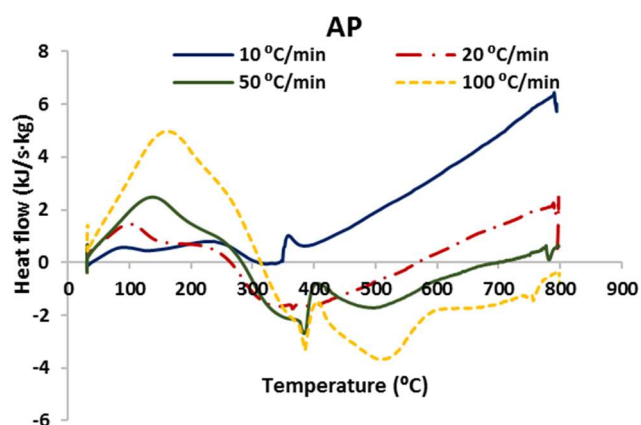


Figure 9. DSC curves of acacia pellets (AP) during pyrolysis at different heating rates.

The peaks seen in the heat flow would be related to the formation of the CO and CO₂ gases that occur simultaneously with the degradation of the sample [4].

3.5 Kinetic parameters

The kinetic parameters estimated by the application of a multi-nonlinear regression model to the data are the activation energy E_a (kJ/mol) and the reaction rate constant, k (min⁻¹), as well as the apparent content of the main pseudocomponents in the samples.

I. Activation energy

The different apparent activation energies (E_a) can be tentatively assigned to the main pseudocomponents of biomass. “ E_{a_w} ” would correspond to the activation energy of the water, since is the first component released during the process. Then, the next activation energies are successively assigned to the decomposition of hemicellulose (E_{a_1}), cellulose (E_{a_2}), and finally lignin (E_{a_3}).

The fourth component that appears in some experiments is related with the remaining lignin that is still degrading. It was added in order to improve the model fitting, as it was noticed that in some cases adding a new component reaction improve the quality of the model.

Combustion

In table 3 are summarizes the average of the different apparent activation energies obtained with the fitting model during combustion experiments at different heating rates (10, 20, 50 and 100 °C/min).

Sample	Parameter	E_{a_w} (kJ/mol)	E_{a_1} (kJ/mol)	E_{a_2} (kJ/mol)	E_{a_3} (kJ/mol)
ER	E_a	48,87	54,88	108,51	57,41
	σ	3,8	9,74	43,71	31,28
	CV	8%	18%	40%	54%
EP	E_a	39,98	69,33	47,84	40,81
	σ	3,41	6,63	2,55	1,41
	CV	9%	10%	5%	3%
EC	E_a	40,49	99,74	149,91	54,98
	σ	4,63	16,87	11,61	34,08
	CV	11%	17%	8%	62%
EA	E_a	50,06	107,26	148,39	52,88
	σ	10,24	29	8,16	19,85
	CV	20%	27%	6%	38%
AP	E_a	51,43	116,54	154,08	42,15
	σ	6,81	22,77	5,79	24,48
	CV	13%	20%	4%	58%

Table 3. Statistical parameters of activation energy obtained at different heating rates during combustion.

Standard deviation (σ) is a measure of data dispersion and the coefficient of variation (CV) provides information of the reliability of the data.

Coefficient of Variation (CV):

- <10% → very acceptable (green)
- 10-20% → acceptable (orange)
- >20% → not reliable (red)

As it can be seen, the first stage remains stable for all samples. It can be noticed that increasing the heating rate causes the activation energy of the first sub-stage to increase.

In the case of the second sub-stage, which would correspond to cellulose degradation, the values are more or less stable, the average value varies from 47.84 kJ/mol of the eucalyptus pellets (EP) to 154.08 kJ/mol of the acacia pellets (AP). The coefficient of variations are quite good for all the samples except the eucalyptus branch (ER).

In the case of the last sub-stage, when degradation of lignin takes place, the difference between the values is higher. This, as commented before, may be due to the deflection in the measurement of temperature of the sample. The discrepancies may also arise from the fact that carbonization process are significantly affected by the heating rate and this reaction is not adequately account to it.

Pyrolysis

Pyrolysis results (Table 4) show better coefficients of variation, which means that the values are closer in pyrolysis experiments than those of combustion at different heating rates.

Sample	Parameter	Ea _w (kJ/mol)	Ea ₁ (kJ/mol)	Ea ₂ (kJ/mol)	Ea ₃ (kJ/mol)
ER	Ea	47,28	71,94	107,57	62,95
	σ	8,81	18,62	6,40	15,62
	CV	19%	26%	6%	25%
EP	Ea	48,74	77,43	108,11	66,41
	σ	5,66	6,56	2,11	8,02
	CV	12%	8%	2%	12%
EC	Ea	42,16	102,03	138,48	27,07
	σ	13,07	5,40	10,03	3,03
	CV	31%	5%	7%	11%
EA	Ea	59,04	106,68	133,00	25,31
	σ	7,39	14,60	10,45	3,91
	CV	13%	14%	8%	15%
AP	Ea	55,46	122,51	150,35	24,47
	σ	6,08	20,29	10,43	1,38
	CV	11%	17%	7%	6%

Table 4. Statistical parameters of apparent activation energies obtained at different heating rates during pyrolysis.

The apparent activation energies obtained in the stages of dehydration and degradation of hemicellulose and cellulose are slightly higher in pyrolysis tests, whereas the last stage of lignin degradation the activation energies are lower in pyrolysis than in combustion.

Despite the comparisons, the reactions that occur during pyrolysis and combustion are different, and therefore, the kinetic parameters will be different.

II. Rate Constant

The apparent rate constant "k₁", corresponding to the decomposition rate of hemicellulose tends to decrease at higher heating rates, while the constant "k₃" corresponding to the degradation of lignin increases at higher heating rates according to figure 10.

The apparent rate constant "k₂" corresponding to the decomposition of cellulose remains more or less constant. The difference in the final stage of the curves at different heating rates might be caused by the deflection in the measurement of the temperature, which produces a deviation in the kinetic parameters. The increment of the rate decomposition of hemicellulose, may be caused by the sensitivity of the fitting model, since the samples do not contain large amounts of water.

Rate Constant	Component
k ₁	Hemicellulose
k ₂	Cellulose
k ₃	Lignin
k ₄	Remaining lignin

Table 5. Description of rate constant codes.

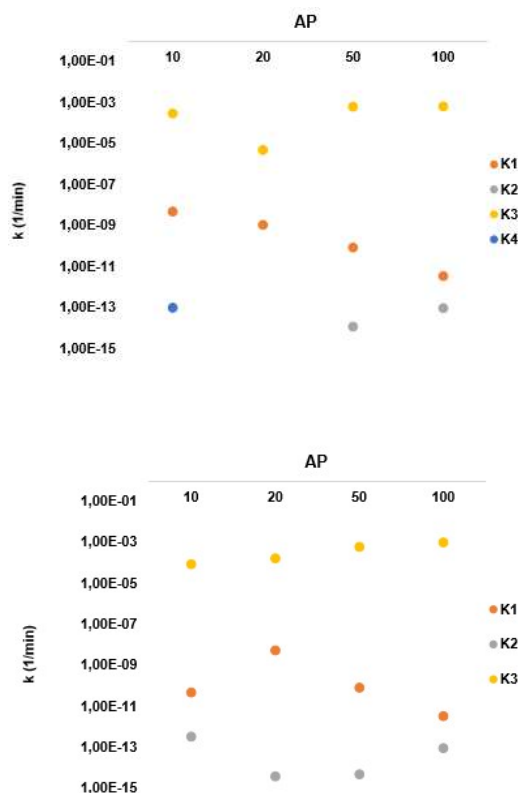


Figure 10. Rate constants during combustion and pyrolysis respectively at different heating rates.

III. Biomass composition

Apart from the fitting of the apparent kinetic parameters, the model was also intended to provide estimates of the different fractions present in the samples. These were estimated from the experimental data for all the transformations.

Sample	HR	W water (%)	W1 (%)	W2 (%)	W3 (%)	W4 (%)	W Ash (%)
ER	10	6.80	45.19	4.59	39.70	-	3.72
	20	6.60	33.46	9.17	33.29	13.11	4.37
	50	8.43	39.45	16.80	32.51	-	2.82
	100	7.09	42.86	14.88	32.00	-	3.18
EP	10	7.75	42.53	45.84	0.11	-	3.77
	20	6.61	40.39	49.29	0.47	-	3.24
	50	7.44	46.17	16.75	26.46	-	3.19
	100	8.00	53.26	13.34	24.01	-	5.03
EC	10	8.68	12.57	36.93	38.94	-	2.89
	20	11.78	11.89	35.05	39.05	-	2.22
	50	10.09	21.41	27.22	38.70	-	2.57
	100	11.62	13.31	41.06	31.64	-	2.38
EA	10	10.80	11.91	32.98	43.19	0.38	0.75
	20	10.32	15.47	41.55	32.34	-	0.33
	50	11.01	19.11	41.94	28.05	-	0.00
	100	8.91	21.95	38.34	30.36	-	0.44
AP	10	8.36	51.03	-	34.38	2.33	3.90
	20	8.00	49.51	-	39.21	-	3.28
	50	7.48	27.13	25.45	36.99	-	2.95
	100	7.60	23.25	34.29	23.21	-	11.66

Table 6. Fractions of biomass components during combustion.

Sample	HR	W water (%)	W1 (%)	W2 (%)	W3 (%)	W4 (%)	W Ash (%)
ER	10	6.94	44.26	13.14	15.13	17.71	2.81
	20	9.39	24.64	16.33	11.85	32.06	5.72
	50	10.13	20.81	19.99	15.17	29.05	4.84
	100	8.78	20.67	20.75	19.71	10.31	19.77
EP	10	7.51	18.43	26.02	16.76	21.20	10.07
	20	7.43	18.79	24.63	16.79	25.16	7.20
	50	6.89	20.44	23.92	15.36	12.33	21.06
	100	6.21	22.97	23.55	16.22	9.22	21.83
EC	10	8.89	9.56	36.51	39.40	-	5.65
	20	11.05	17.74	32.60	21.35	-	17.26
	50	11.24	16.02	36.98	13.75	-	22.01
	100	10.59	16.48	41.86	11.00	-	20.07
EA	10	9.21	14.80	40.14	22.38	-	13.47
	20	10.41	13.19	41.02	31.25	-	4.14
	50	9.62	18.70	46.16	12.03	-	13.49
	100	9.36	15.74	48.65	17.06	-	9.18
AP	10	8.53	15.86	33.07	28.66	-	13.88
	20	7.77	30.35	20.65	27.73	-	13.50
	50	7.86	24.43	27.76	21.41	-	18.53
	100	7.34	21.84	34.73	20.79	-	15.30

Table 7. Fractions of biomass components during pyrolysis.

Table 6 and table 7 summarizes the data that was obtained. The symbol "-" indicates the fourth component reaction was not added.

Water:

It can be seen from the tables that the water content is low, less than 12% for all samples. The samples with the highest water content are Eucalyptus bark (EB) and Eucalyptus splinters (EA) with an average water content of 10.50% and 9.95% respectively, which agrees with the research carried out by Chen [10].

The samples with lower water content are the Eucalyptus branches (EB) with 7.35% of average content, Eucalyptus pellets (EP) with 7.23% and acacia pellets (AP) with 7.87%. The water content is consistent with what is expected since the pellets are designed to be compact and have a low water content.

Hemicellulose:

The sample with the lowest amount of hemicellulose is the Eucalyptus Bark (EC) with an average value of 12% taking into account the data obtained in both pyrolysis and combustion tests. The next sample with a slightly higher content of hemicellulose is the Eucalyptus splinters (EA) with a value around 16%. The samples with the highest hemicellulose content, around 30%, are the Eucalyptus pellets (EP) and acacia pellets (AP), and lastly the highest percentage of hemicellulose, around 35%, appear in the Eucalyptus branch (ER).

Cellulose:

Cellulose content was higher in the samples of eucalyptus bark (EC) and splinters (EA), with an average content of 36.03% and 41.35% respectively, both data with a coefficient of variation of 13% and 11%, which means that the data are reliable. The samples of acacia pellets (AP) also shown a high content of cellulose, around 29.32%, their coefficient variation is in the acceptable range.

The samples of eucalyptus pellets (EP) show a content around 27.92%, and finally, the sample with the lowest cellulose content is the eucalyptus branch (ER) with a value around 17.71%, these data show great variation, therefore they are not reliable.

Lignin:

Lignin content is highly variable since lignin decomposes over a wide temperature range, and it is the last of the three main pseudocomponents of biomass to degrade. As the temperature in the process increases, the heating rate begins to affect the heat and mass transfer processes, which causes the last stage to advance through different reaction mechanisms.

What can be deduced from the data is that at lower heating rates, there is a more efficient heat transfer, which leads to more efficient degradation of the pseudocomponents and less residue formation.

4. Conclusion

Based on the mass loss profile, it can be determined that the thermal degradation of the samples can be well described by three independent first order reactions, that would correspond to the individual thermal degradation of cellulose, hemicellulose and lignin as the pseudo-components of lignocellulosic biomass, since the experimental results shown a very good correlation ($r^2 > 0.99$) for both combustion and pyrolysis tests.

The evolution of weight loss shown that at higher heating rates the temperature range of the different process stages widen causing the overlapping of the stages. Lower heating rates improve the heat transport and avoid temperature gradients along the particle. As a consequence, the cracking stage is more efficient because more matter is reacting to form volatiles and less residue is generated.

At low heating rates, generally two peaks can be seen, the first peak represents the combustion of volatiles, and the second peak represents the char combustion.

At higher heating rates, the peaks tend to approach each other so the heat flow profiles start to smooth out.

Concerning kinetic parameters, the data obtained in the first stage of hemicellulose degradation show great variability, this stage can be affected by the sensitivity of the model during the dehydration stage due to the low amount of water in the samples.

The apparent activation energies of cellulose obtained by the model show a quite reliable coefficients of variation (<10%). The apparent activation energies have been slightly higher in the combustion tests than in the pyrolysis tests.

Results indicate that cellulose has a higher activation energy than hemicellulose and lignin. During combustion, the rate constant of hemicellulose decomposition tends to decrease at higher heating rates, while the rate constant of lignin degradation increase at higher heating rates. This occurs due to the heat flow, since there is an endothermic first stage up to a temperature of 250 °C, and then the whole process is exothermic. This was also noticed during pyrolysis test. DSC profile during pyrolysis at low heating rate shows a completely endothermic process, but at higher heating rate part of the process shows an exothermic behaviour. This might be due to the fact that high heating rates promotes the appearance of secondary cracking reactions of primary products.

Regarding to sample characterization, the water content is low, less than 12% for all samples, this causes a minor sensitivity of the model which might results in a deviation of the data. The samples with the highest water content are Eucalyptus bark (EB) and Eucalyptus splinters (EA). The samples with the highest hemicellulose content, around 30%, are the Eucalyptus pellets (EP) and acacia pellets (AP), and lastly the highest percentage of hemicellulose, around 35%, appear in the Eucalyptus branch (ER). Cellulose content was higher in the samples of eucalyptus bark (EC) and splinters (EA), with an average content of 36% and 41% respectively.

The average value obtained from lignin in all samples is about 20% during pyrolysis and 30% during the combustion. Eucalyptus pellets (EP) and eucalyptus branches (ER) are the samples that shown the least amount of lignin with an average of 16% during the pyrolysis. Lignin content is highly variable since lignin decomposes over a wide temperature range.

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