KINETIC STUDY OF DIFFERENT BIOMASS PYROLYSIS AND OXYGEN-ENRICHED COMBUSTION

by

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Global warming and the GHG effect have forced the reduction of the energetic dependence on fossil fuels. Because of that, research focusing on biomass properties, characteristics and energetic conversion has increased in the last decades. The present study was carried out in terms of determination of kinetic parameters, focusing on two different energetic conversion processes: pyrolysis, carried out under nitrogen atmosphere, and oxygen-enriched combustion, using an atmosphere of air enriched with 30% oxygen. Three different lignocellulosic biomass samples were used. Thermogravimetric analysis was performed using four different heating rates in order to carry out a kinetic analysis using model free methods (Friedman, Kissinger-Akahira-Sunose, and Flynn-Wall-Ozawa). The results showed that oxygen-enriched combustion produced a more complete reaction with low char values and activation energy values greater than pyrolysis values. Among the kinetic methods, Friedman reported the most different values, acceptable for pyrolysis process but not so much for oxygen-enriched combustion.

Key words: *reaction kinetics, biomass, pyrolysis, oxy-combustion, thermogravimetric analysis, Friedman, Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa*

Introduction

In the last decades, mitigation of the problems associated to the climate change have become one of the main challenges of society. In this scenario, the use of renewable energy has significantly increased together with research on its use and efficiency so dependence on fossil fuels can be reduced [1]. In this context, biomass becomes an important energetic resource due to their advantages, such as climate non-dependence, availability, waste valorisation, *etc.* [2].

Biomass can produce energy by direct conversion processes, or can undergo previous treatments in other to improve its characteristics and energetic properties before energy conversion [3]. Most common pre-treatments are torrefaction, which reduces moisture content

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(and hygroscopicity) and increases lignin content so heating value increases too [4], and aerobic or anaerobic digestion, which uses bacteria to produce biogas [5]. There are some other common pre-treatments that modifies biomass physical properties such as milling, chipping, briquetting or pelleting [6].

On the other hand, among the different biomass energetic conversion processes, combustion, gasification, and pyrolysis are found to be the most commonly used. Furthermore, liquefaction technology can be applied, however, it is a relatively novel method therefore its use is not as extended as other processes [7]. Differences between combustion, gasification and pyrolysis lie on the amount of oxygen required, as pyrolysis is produced under no oxidizing conditions, gasification under sub-stoichiometric oxidizing conditions, and combustion under oxidizing conditions [8]. However, there are some other processes whose use have attracted attention to the scientific community in the last years, such as oxygen-enriched combustion, which is produced under oxygen-rich atmospheres [9]. From those processes, combustion is found to be the less efficient process although it is the simplest one and the more traditional one, whose only requirement is moisture content lower than 50% [10]. Gasification is the most effective converting method as it produces synthesis gas and char [11], and achieves the highest conversion rate if compared with pyrolysis or combustion [12]. However, gasification is a complex process that involves several stages and complex equipment [13]. Because of that, the present study focuses on biomass pyrolysis and oxygen-enriched combustion.

Oxygen-enriched combustion is an energetic conversion process using oxygen enriched atmosphere which leads to a more efficient combustion [9]. Furthermore, oxygen-enriched combustion atmosphere can be produced using CO_2 and oxygen, which benefits CO_2 sequestration and utilization [14]. In the last decade, the number of research focused on oxygen-enriched combustion process for solid fuels has increased. Several studies focus on process kinetics obtained from thermogravimetric analysis (TGA) for coals together with other techniques such as aerodynamic levitator particle reactor [15] or Fourier transform infrared spectroscopy [16]. On the other hand, biomass oxygen-enriched combustion has not been so widely studied, and researches that focus on this topic are less common than the ones studying coal oxygen-enriched combustion. Most of those studies approach kinetic comparison between different biomass samples [17] and different samples pre-treatment conditions [18]. Nevertheless, studies that focus on biomass oxygen-enriched combustion kinetics are a minority, as when approaching biomass oxygen-enriched combustion, studies focus on particle behavior [19], coal and biomass blends [20, 21], emissions [22], or conditions and requirements [14].

On the other hand, biomass pyrolysis is a thermochemical process that heats biomass at temperatures greater than 400 ºC using inert atmospheres (absent of oxygen) [23] typically using nitrogen as inert gas [24]. Through pyrolysis, volatile matter is degraded, and the generated products present higher heating values than raw biomass. The main pyrolysis products are bio-char (solid), bio-oils (liquid), and non-condensable gases [25]. Biomass pyrolysis was found to be one of the most useful methods to convert biomass waste into fuels [26]. Pyrolysis process can be divided in three main stages: moisture release, that takes place at the beginning of the process, primary decomposition, and secondary reactions in which repolymerization takes place [27]. Pyrolysis process has been widely studied in the last decades, therefore several studies have focused on biomass pyrolysis from the kinetic perspective. Some studies considered different types of biomass finding out that biomass obtained from shell wastes behave different than typical woody biomass, *i.e.* they present greater activation energies [28]. Other authors focus on different biomass from crop residues pyrolysis, comparing their kinetic results [29]. Furthermore, some authors have studied pyrolysis processes together with pre-treatments such as torrefaction which importantly enhances pyrolysis results [30].

The process characterization is typically carried out using TGA, as changes in mass loss rate and devolatilization are clearly seen when applying this technique. Furthermore, TGA allows the simulation of those processes since atmosphere and heating rate can be controlled.

Moreover, to properly understand the reactions that take place during those processes, kinetic studies were found to be really useful as they provide information about the activation energy, preexponential factor, order reactions, *etc.* There are several kinetic methods that can be classified into two different groups: model fitting methods and model free methods. Model fitting methods provides models that fit to the experimental data, so the best statistical fit is chosen to model the reaction. On the other hand, model free methods calculate kinetic parameters without making reaction assumptions. Coats-Redfern [31] and Freeman-Carroll [32] are the most common model fitting methods, while Friedman [33], Kissinger-Akahira-Sunose (KAS) [34], Vyazovkin [35], Flynn-Wall-Ozawa (FWO) [36], and distributed activation energy model (DAEM) [37] are the most used model free methods. Some studies have focus on pyrolysis kinetic comparison between model-fitting and model-free methods, finding out that model-free methods provide more reliable results [38]. Because of that, model-free methods to determine pyrolysis kinetic parameters have been widely studied, providing information regarding influence of composition in kinetic parameters [39] and identifying pyrolysis process of each biomass component [40]. In the past years, DAEM method use has increased as it can simulate each component behaviour using gaussian distributions [41], however, material decomposition using DAEM is not accurately described [42].

Biomass pyrolysis has been widely studied, while oxygen-enriched combustion research is beginning. Pyrolysis kinetics for different biomass types and different conditions has been studied for years, however, oxygen-enriched combustion kinetic parameters are not so common in previously published literature. Nevertheless, some authors have already compared both methods using model-fitting methods [43] finding out that oxygen-enriched combustion processes require greater activation energies than pyrolysis. Moreover, few studies compared both processes using model-free methods at high heating rates noticing that, again, oxygen-enriched combustion requires higher activation energy than pyrolysis [44, 45].

The aim of this study is to simulate pyrolysis and oxygen-enriched combustion reactions using TGA, so a kinetic study can be carried out and kinetic parameters can be compared between both processes. To do so, FWO, KAS and Friedman isoconversional (model free) kinetic methods were used to obtain reaction’s activation energy and preexponential factor. Furthermore, three different samples of lignocellulosic biomass were selected, so a comparison between biomass types can be carried out together with the kinetic study, and relation between composition and kinetic parameters can be preliminary assessed.

Materials and methods

Samples

In the present study three different biomass samples were used: almond shells (AS), oil palm wastes (OP), and wood pellets (WP). Almond shells come from Castellon (Spain) as a fine dust, whose average particle size, d50, is 45 μm. Oil palm wastes, are Elaes Oleifera empty fruit bunches from palm fields in Johor (Malaysia). The OP sample presented a fibrous shape, and it was milled and sieved through 180 μm light sieve, obtaining 145 μm average particle size. Wood pellets are commercially available as pellets and were milled and sieved through 180 μm light sieve, obtaining 150 μm average particle size. The samples were selected according to previous literature: shells were found to present higher lignin content [46] which should be noticed when carrying out TGA [47], oil palm wastes have been widely studied due to their potential as an energetic source [48], and woody biomass is the oldest biomass and, therefore, the most commonly investigated.

Each sample was characterized through proximate analysis, determining moisture, M, volatile matter, V, ashes, A_c, and fixed carbon content, FC. Those results are reported as dry basis in tab. 1.

Table 1. Samples proximate analysis -moisture, volatile, ash and fixed carbon values

Sample	M [%]	V [%] d.b.	A_c [%] d.b.	FC [%] d.b.
AS	6.15	66.79	14.13	19.08
OP	6.21	81.88	2.92	15.19
WP	6.23	79.14	2.91	17.95

Thermogravimetric analysis

The TGA was carried out using a Mettler Toledo TG-DSC T50 apparatus. To carry out the test, 20 ± 1.5 mg of sample is inserted into a 70 μL alumina crucible. Initial temperature was set at 30 ºC and final temperature at 800 ºC using four different heating rates, β: 5, 10, 15 and 20 K per minute. Pyrolysis atmosphere inside the oven was carried out using a 50 mLpm nitrogen flow, while oxygen-enriched combustion atmosphere was simulated using two gas flows: 22 mLpm of oxygen and 28 mLpm of nitrogen. Those flows allowed to simulate an atmosphere approximately 30% oxygen enriched. Some parameters can be obtained immediately from TGA, such as moisture content or differential thermogravimetric curve (DTG) which is the thermogravimetric curve first derivative and provides information regarding mass loss rate and temperature at which this rate reaches its maximum (maximum weight loss temperature, MWLT).

Kinetic models

As previously mentioned, to characterize both pyrolysis and oxygen-enriched combustion reactions, three iso-conversional model-free kinetic methods have been used, as they provide more accurate results than model-fitting methods. Those methods were Friedman, KAS, and FWO. Iso-conversional methods allow the determination of kinetic parameters without assumptions of the reaction mechanism, considering that thermochemical conversion rate is defined:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(t) f(\alpha) \tag{1}$$

where α represents the dimensionless conversion degree defined as eq. (2), t – the time, $k(t)$ – the reaction rate constant defined using Arrhenius eq. (3), and $f(\alpha)$ – the reaction model.

$$\alpha = \frac{m_0 - m_\mathrm{t}}{m_0 - m_\mathrm{f}} \tag{2}$$

$$k(t) = A\exp\left(-\frac{Ea}{\mathrm{R}T}\right) \tag{3}$$

where m_0 [mg] is the initial mass, m_t [mg] – the mass at a certain time t, m_f [mg] – the final mass, A [min^{-1}] – the preexponential factor, Ea [kJmol^{-1}] – the activation energy, R [mg] – the universal gas constant (= 8.314 J/Kmol), and T [K] – the temperature.

Considering that heating rate can be defined as $\beta = \mathrm{d}T/\mathrm{d}t$, eq. (1) can be rewritten:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{Ea}{\mathrm{R}T}\right)f(\alpha) \tag{4}$$

Friedman method

Friedman method is a differential method that assumes that the reaction model remains constant, so the degradation depends on the mass loss rate. Friedman method equation is shown in eq. (5) and can be obtained applying logarithms to eq. (4):

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln[A\,f(\alpha)] - \frac{Ea}{\mathrm{R}T} \tag{5}$$

When plotting ln(dα/dt) *vs.* $1/T$ for each heating rate, a straight line is obtained whose slope is proportional to the activation energy.

The KAS method

The KAS method is an integral method, that applies approximation of $P(x) = x^{-2}\mathrm{e}^{-x}$ to the rate equation. If the integral form of eq. (4) is expressed as shown in eq. (6), where $g(\alpha)$ is the integral form of the reaction model, then eq. (7) that represent KAS method is:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \mathrm{e}^{-\frac{Ea}{\mathrm{R}T}}\,\mathrm{d}T = \frac{AE}{\beta\mathrm{R}}P(x) \tag{6}$$

$$\ln\beta = \ln\frac{AEa}{\mathrm{R}g(\alpha)} - \frac{Ea}{\mathrm{R}T} \tag{7}$$

When plotting $\ln(\beta/T^2)$ *vs.* $1/T$, a straight line for each α is obtained, whose slope is proportional to the activation energy.

The FWO method

The FWO method is similar to KAS, however the approximation to the rate equation differs, leading to the following equation:

$$\ln\beta = \ln\frac{AEa}{\mathrm{R}g(\alpha)} - 5.331 - 1.052\frac{Ea}{\mathrm{R}T} \tag{8}$$

When plotting $\ln(\beta)$ *vs.* $1/T$, a straight line for each α is obtained, whose slope is proportional to the activation energy.

Results and discussion

The TGA results for each sample and process are plotted in fig. 1. When considering pyrolysis TGA, at the very beginning (from 30 ºC to 120 ºC) a mass loss is produced due to the moisture release, that is quite similar for every sample (as they present similar moisture contents according to tab. 1) and each single rate, as this parameter does not affect moisture release. After that, steady process takes place followed by mass loss acceleration that produces a drastic mass loss. The maximum mass loss rate is produced when DTG curve reaches its minimum (MWLT).

When considering oxygen-enriched combustion, hemicellulose, cellulose, and lignin decomposition are not so clearly seen as the mass drop takes place in a shorter temperature interval than pyrolysis. Indeed, when oxygen-enriched combustion is carried out, the following stages take place: again, at the very beginning moisture release is produced and followed by a steady process, after that, a fast oxidation of the volatile matter takes place in a short temperature interval (between 250 ºC and 400 ºC), at the end, it can be noticed that after the main oxygen-enriched combustion reaction is fulfilled, a char oxidation takes place up to 500 ºC.

On the other hand, as noticed in previous studies [43], the pyrolysis process is slower as its atmosphere does not interfere with the sample. Decomposition takes place in a wider range of temperature, however, the greatest degradation begins around 250 ºC, and reduces mass progressively up to 400 ºC. This fact is related to the three main components of lignocellulosic biomass decomposition, as hemicellulose degradation begins around 200 ºC and mass significantly decreases when cellulose degradation adds to this process at 250-300 ºC. Finally, lignin, which exhibits the strongest molecular structure, presents the wider degradation range (from 200 ºC up to 900 ºC) so the mass loss after hemicellulose and cellulose degradation processes is produced to lignin decomposition [49]. After that, a char-forming stage takes place, mainly from the non-degraded lignin content, leading to a greater solid residue after pyrolysis.

The MWLT for each sample, heating rate, β, and process are shown in tab. 2, together with final residue.

Table 2. The TGA final residue and decomposition peak (MWLT) for each sample and process

		5 K per minute		10 K per minute		15 K per minute		20 K per minute	
		MWLT [ºC]	Final residue [%]	MWLT [ºC]	Final residue [%]	MWLT [ºC]	Final residue [%]	MWLT [ºC]	Final residue [%]
AS	Pyrolysis	298.02	16.18	314.93	33.54	311.92	28.15	318.02	35.21
	Oxygen-enriched combustion	279.16	11.11	278.86	13.21	279.20	12.83	287.46	14.00
OP	Pyrolysis	291.50	6.19	299.87	11.29	313.32	20.09	318.93	22.35
	Oxygen-enriched combustion	277.98	0.59	282.90	0.19	287.77	2.40	295.78	2.47
WP	Pyrolysis	336.27	12.64	339.22	6.73	350.56	22.14	340.34	2.51
	Oxygen-enriched combustion	317.95	0.55	318.14	0.95	319.54	1.33	323.28	2.01

If both processes are compared, it can be noticed that oxygen-enriched combustion produces a drastic mass drop around 300 ºC, as the main reaction is a fast oxidation whose main product is ash. On the other hand, pyrolysis is a slower process, and degradation is produced in a wider range of temperatures, which means that not only temperature at which reaction accelerates is greater for pyrolysis, but that DTG peak will be wider. Furthermore, the sooner the reaction accelerates, the lower the temperature at which maximum weight loss is produced, in other words, the maximum mass loss rate is produced at lower temperatures when considering oxygen-enriched combustion. Indeed, the greater the oxygen concentration, the higher the reaction rates [45]. Each of those results leads to the same conclusion: oxygen-enriched combustion is a faster process that degrades matter at lower temperatures than pyrolysis due to the oxidant atmosphere. Comparing samples, WP show greater MWLT values both for oxygen-enriched combustion and pyrolysis than other samples, which means that the reaction's fastest mass loss requires greater temperatures.

Regarding the final residue, if oxygen-enriched combustion is considered both fig. 1 and tab. 2 show that the oxidant atmosphere produces almost no residue besides almond shell samples, that presented the greater ash content, as shown in tab. 1, and so their residue after oxygen-enriched combustion process is greater. As pyrolysis subproducts are gases, bio-oils and bio-char [50], the residue after this process should be significant. Indeed, if final residues after pyrolysis and oxygen-enriched combustion are compared, it is noticed that pyrolysis produces higher amounts of residue. Bio-char quality depends on temperature and heating rate among other parameters [51], therefore, not only quantity should be considered. Nevertheless, from the present results, it can be noticed that usually the higher the heating rate, the greater the bio-char amount. However, if together with those results, volatile matter is considered, it can be assumed that when high heating rates are applied, volatile matter does not completely decompose, so the bio-char produced might include some volatiles. On the other hand, oxygen-enriched combustion completely devolatilizes the samples, but no bio-char is produced, as its main result are ashes.

When curve shapes were considered, it was noticed that after oxygen-enriched combustion reaction, sample temperature slightly reduces, probably due to fast devolatilization, so the curve slightly shifts to the right. After that, the final mass loss is produced, which corresponds to char oxidation, and leads to almost zero residue. Regarding pyrolysis curves shape, WP and AS samples present a left shoulder due to hemicellulose and cellulose decomposition. When those components are clearly differentiated, two peaks are produced, however, when samples present low hemicellulose content, hemicellulose peak joins cellulose peak and a shoulder is produced [39, 52]. However, OP samples do not present neither a peak with a shoulder nor two differentiated peaks. Previous studies have noticed that among different oil palm wastes, empty fruit bunches present a small shoulder [53] or none at all [54] due to hemicellulose devolatilization.

Shells present higher lignin content than other lignocellulosic biomasses as it plays an important role regarding structure bonding and strengthening [55] and it is related to mechanical strength, seal grade and shell thickness [56]. As previously mentioned, lignin presents the wider degradation temperature interval, so high lignin contents will be noticed after hemicellulose and cellulose volatilize. Indeed, when considering AS pyrolysis results, not only a left shoulder but a right shoulder is produced due to lignin degradation. When applying slow heating rates, lignin degradation is clearly seen as happens in 5 K per minute DTG curve where the right shoulder is easily noticed, however, as heating rate increases, and processes do not properly differentiate lignin decomposition, the shoulder disappears. Indeed, when ap-

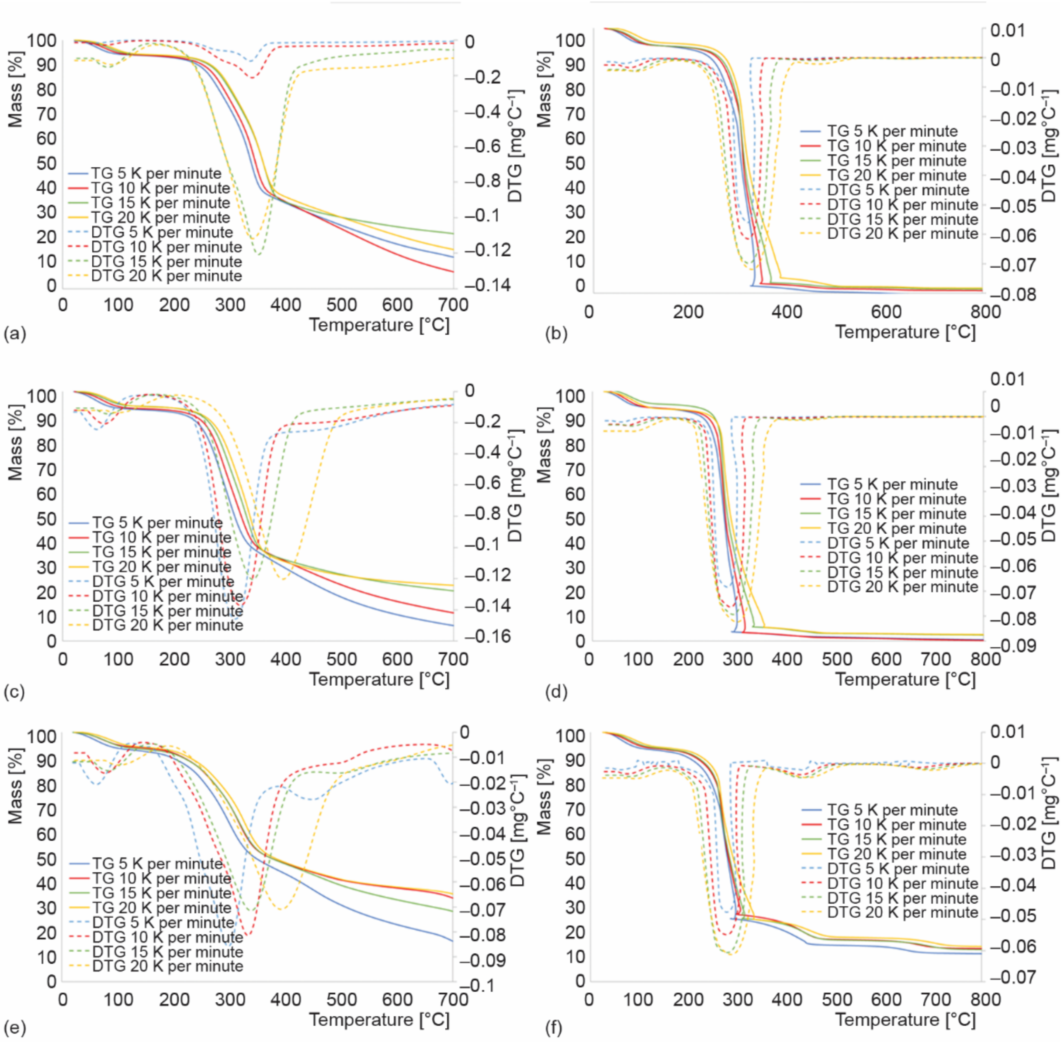

Figure 1. The TG and DTG plots for each sample and process; (a) WP pyrolysis, (b) WP oxygen-enriched combustion, (c) OP pyrolysis, (d) OP oxygen-enriched combustion, (e) AS pyrolysis, and (f) AS oxygen-enriched combustion

plying 20 K per minute DTG the obtained curve is the widest curve, as it represents hemicellulose, cellulose, and lignin decomposition altogether.

Low heating rates lead to lower induction temperatures, in other words, reaction begins at lower temperatures. It can be seen clearly that oxygen-enriched combustion curves follow the same order for each sample, in which curves with lower heating rates begin at lower temperatures. This fact can also be noticed in some pyrolysis curves, especially when considering 5 K per minute heating rate, as it reduces the thermal lag [57]. If DTG curves are considered, when heating rates increase, MWLT increases too (DTG peak shifts to the right), which means that reaction acceleration does not only require temperature but time to adjust temperature effect in order to break the molecular bonds and fasten degradation [58]. As previous authors pointed out, heating rate affects pyrolysis stages temperature range [53].

Furthermore, when considering heating rate effect on DTG some authors have pointed out that the greater the heating rate, the greater the DTG curve intensity [59] as at higher heating rates there is more energy available to heat transfer between sample and surroundings [53]. This effect is clearly noticed under oxygen-enriched combustion processes, but not so obvious when considering pyrolysis. Indeed, some samples present greater intensity for lower heating rates (OP and AS). When considering WP pyrolysis DTG curves, the higher the heating rates, the greater the intensity, even producing a significant difference between 5-10 K per minute DTG curves and 15-20 K per minute. This fact has already been noticed in previously published results by other authors [60, 61]. As Gašparovič *et al.* [62] pointed out, when heating rate increases, conversion values are reached at higher temperatures, due to a mass transfer limitation. When applying high heating rates furnace temperature might be greater than samples temperature, therefore devolatilization rate is higher than volatile release.

For each curve, the dimensionless conversion factor or degree, α, was calculated, in order to calculate activation energy and preexponential factor for each value of α. Figure 2 shows the activation energy obtained values for each kinetic model, and for conversion degree values from 0.2 up to 0.8, as between those values the reaction takes place (before 0.2 moisture release is produced, and after 0.8 char-formation/oxidation takes place). Furthermore, activation energy typically increases up to 0.5-0.6 and, after that, decreases, as noticed in previous studies [63]. This phenomenon is produced as, after that point, most part of the reaction is completed, thus, activation energy reduces. Indeed, from pyrolysis activation energy values, two different stages can be noticed: devolatilization and bio-char production. Devolatilization process takes place with a steadier activation energy, and after volatiles are released, Ea, decreases as bio-char formation does not produce significant mass changes therefore, reaction stabilizes. On the other hand, when oxygen-enriched combustion is considered, the first stage correspond to a fast oxidation in which volatile matter is completely released, and char oxidation. These stages have been previously noticed by other authors [64]. As Jaroenkhasemmeesuk and Tippayawong [44] pointed out, maximum activation energies for pyrolysis are found when conversion is approximately 50%, while oxygen-enriched combustion activation energy peak is produced earlier in the process. Indeed, pyrolysis activation energies showed a peak between 50-60% conversion while oxygen-enriched combustion shifts this peak to 30-40% conversion as the mass drop is more intense, and the peak takes place at lower conversion rates.

If pyrolysis and oxygen-enriched combustion activation energy progression is considered, it can be noticed that oxygen-enriched combustion presents more steady values among the different conversion degrees. Furthermore, if average activation energy and preexponential values, shown in tab. 3, are considered, oxygen-enriched combustion presents the greatest values for each sample and kinetic model, which means that oxygen-enriched combustion requires greater energies than pyrolysis, as previously noticed by Maitlo *et al.* [43]. Actually, Chen *et al.* [45] already pointed out that, activation energy increases with oxygen concentration.

Considering the kinetic models applied to each process and sample, it was noticed that KAS and FWO provided similar results while Friedman differs significantly. Friedman method applies conversion rate data, which might produce numerical instability [35] as the method avoids the problem of integral approximation but amplifies the noise produced due to the experimental conditions [65]. For pyrolysis processes this difference is not so great, how-

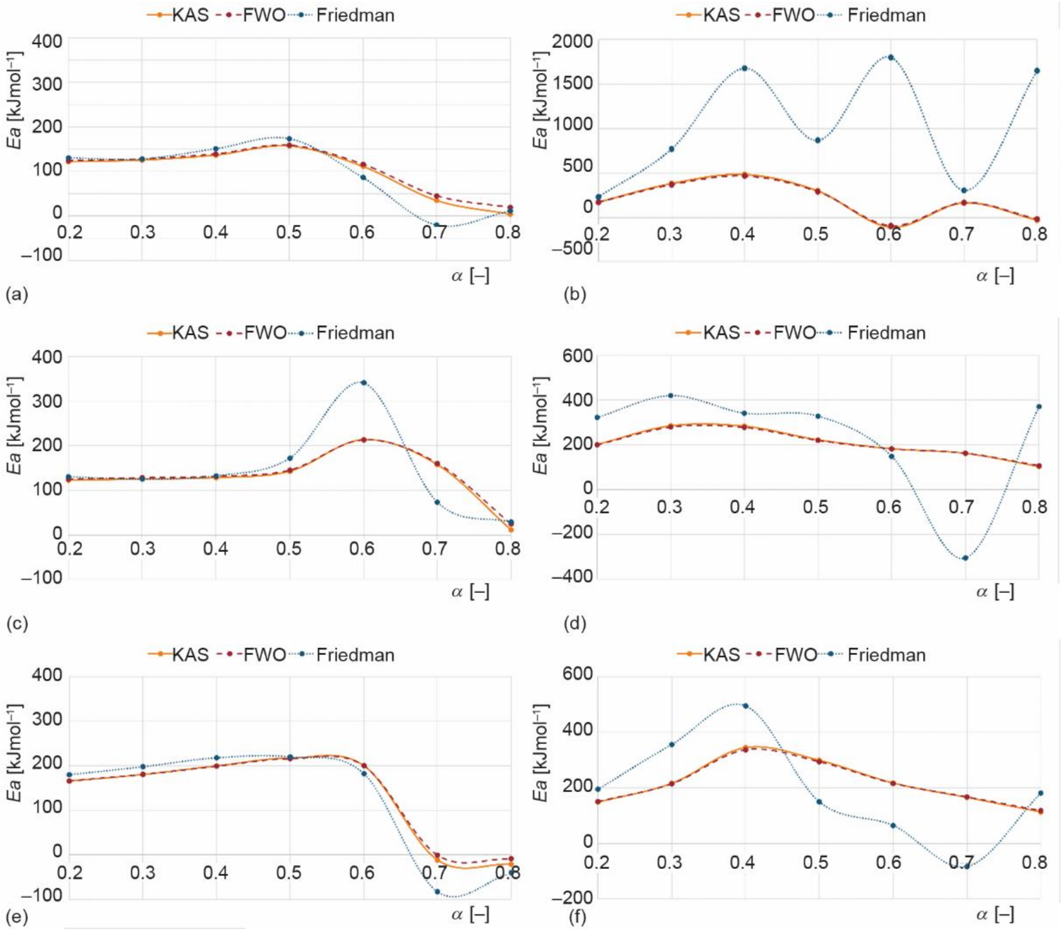

Figure 2. Activation energy results for each sample and process calculated using KAS, FWO and Friedman methods; (a) AS pyrolysis, (b) AS oxygen-enriched combustion, (c) OP pyrolysis, (d) OP oxygen-enriched combustion, (e) WP pyrolysis, and (f) WP oxygen-enriched combustion

ever for oxygen-enriched combustion Friedman values are not consistent with KAS and FWO. Barzegar *et al.* [18] studied kinetic parameters under different oxygen atmospheres and pointed out that Friedman might provide results out of the tendency due to the complex reaction nature of biomass combustion, which amplifies together with the conversion degree. Indeed, Friedman results present a similar tendency at the beginning of the reaction but change immediately after. Same fact, was observed by Fernandez-Lopez *et al.* [64] when comparing pyrolysis and combustion kinetic. In this study, oxygen enriched atmosphere was used, so high oxygen concentration was produced, which means that complex combustion mechanisms take place and Friedman cannot properly estimate kinetic parameters, as the noise is significantly magnified. Besides the Friedman discrepancies, KAS and FWO similarities provide consistent results, which means that a correct approach can be carried out by using those methods, as previously pointed out Apaydin-Varol *et al.* [66].

Table 3. Activation energy and preexponential factor mean values for each sample and process calculated using KAS, FWO and Friedman methods

		Ea [kJmol^{-1}]			A [minutes^{-1}]		
		KAS	FWO	Friedman	KAS	FWO	Friedman
AS	Pyrolysis	98.66	104.29	94.29	$1.49 \cdot 10^{12}$	$2.36 \cdot 10^{12}$	$1.11 \cdot 10^{13}$
	Oxygen-enriched combustion	192.36	191.62	1042.40	$3.29 \cdot 10^{45}$	$4.81 \cdot 10^{44}$	$1.26 \cdot 10^{167}$
OP	Pyrolysis	129.00	132.70	143.36	$7.81 \cdot 10^{16}$	$6.75 \cdot 10^{16}$	$2.32 \cdot 10^{27}$
	Oxygen-enriched combustion	205.47	204.03	232.50	$8.49 \cdot 10^{26}$	$3.28 \cdot 10^{26}$	$5.86 \cdot 10^{39}$
WP	Pyrolysis	132.71	136.00	124.85	$1.46 \cdot 10^{17}$	$1.26 \cdot 10^{17}$	$2.35 \cdot 10^{17}$
	Oxygen-enriched combustion	215.06	213.66	193.82	$1.90 \cdot 10^{30}$	$5.76 \cdot 10^{29}$	$4.20 \cdot 10^{43}$

Friedman discrepancies can be noticed not only considering average values, but also when assessing activation energy curves for conversion degree, fig. 2, as for pyrolysis processes Friedman curves present a similar tendency. However, this fact does not take place when assessing oxygen-enriched combustion curves. As a conclusion, it might be assumed that Friedman method does not properly work for that process.

If samples are compared, it can be noticed that AS samples require lower activation energy values than OP and WP (which present similar values). The fact that shells present lower activation energies than other samples has already been noticed in previous literature [67]. The Ea depends not only on the process, but on the sample, which means that AS composition is different from OP and WP composition. As shells present higher lignin content, lignin oxidation plays an important role regarding activation energy.

Conclusion

After reviewing existing literature, it was noticed that most of the published studies focus on biomass pyrolysis, as it is one of the most effective biomass conversion processes. Works that study oxygen-enriched combustion and comparison between it and pyrolysis are less common. Nevertheless, there is a lack of information regarding biomass kinetic comparison between both processes, as only few studies focus on this topic.

From the results obtained, a significant difference between oxygen-enriched combustion and pyrolysis process could be noticed. Oxygen-enriched combustion required greater activation energies and preexponential factors, producing almost a complete reaction with low residue composed mainly by ashes. On the other hand, pyrolysis process can be carried out with lower activation energies producing a great amount of residue that is mainly constitute by bio-char, which is a carbon enriched solid product that can be used for energy production. However, it was noticed that pyrolysis process required greater temperatures, as the complete reaction only takes place after 500 ºC while oxygen-enriched combustion completely ends devolatilization around 300 ºC. Furthermore, it was noticed that high heating rates produce DTG changes due to heat transfer limitations, modifying process stages.

Regarding kinetic methods, as KAS and FWO methods depend both on temperature and heating rate, the results are consistent, and both models provide similar kinetic values.

However, Friedman shows great differences, as the method considers conversion degree and amplifies experimental noise. Nevertheless, Friedman pyrolysis results show similar tendencies to KAS and FWO, which leads to think that Friedman can be used for pyrolysis assessment. However, it should not be used for oxygen-enriched combustion processes, as the higher the oxygen concentration, the more complex the reaction mechanisms and the worst the results are when using Friedman method. Furthermore, if samples are compared, it was noticed that AS samples showed lower activation energy values both processes than WP and OP, as AS presents greater lignin content.

Further research lines should consider carrying out ultimate analysis and/or biochemical analysis, in order to properly define how thermal degradation, affect hemicellulose, cellulose and lignin content and the relation between process kinetic and composition. Moreover, non-linear heating rates or other model-free methods could be used, such as distributed activation energy method that could provide kinetic parameters for each component.

Nomenclature

A_c – ash content, [%] d.b.
A – preexponential factor, [minutes^{-1}]
DTG – thermogravimetric curve first derivative [mg^{o}C^{-1}]
Ea – activation energy, [kJmol^{-1}]
FC – fixed carbon, [%] d.b.
$f(\alpha)$ – reaction model, [–]
$g(\alpha)$ – integral form of $f(\alpha)$, [–]
$k(t)$ – reaction rate constant [minutes^{-1}]
M – moisture content, [%]
MWLT – maximum weight loss temperature [^{o}C]
m_f – final mass, [mg]
m_t – mass at certain time, [mg]
m_0 – initial mass, [mg]
R – universal gas constant (= 8.314 kJK^{-1}mol^{-1})
T – temperature, [^{o}C]
t – time [minutes]
V – volatile matter, [%] d.b.

Greek symbols

α – dimensionless conversion degree, [–]
β – heating rate, [Kmin^{-1}]

Acronyms

FWO – Flynn-Wall-Ozawa
KAS – Kissinger-Akahira-Sunose
TGA – thermogravimetric analysis

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