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## Thermal characterization of agro-industrial waste for its use in energy valorization processes

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### ABSTRACT

The aim of this work is to define, develop and evaluate a methodology for an improved and more sustainable management of waste, in particular, agricultural residues, turning them into a new source of energy and added-value products. Specific attention is paid to the use of cotton seed (CS) for energy generation. The recovery of energy was carried out through the pyrolysis of this biomass in a fixed bed reactor. An initial definition of the main physico-chemical and thermal properties of the feed was performed. The design and operational parameters of the reactor were set according to the characteristics of the biomass. The thermo-chemical process of pyrolysis was simulated in the first stage by multi-rate linear non-isothermal thermogravimetric (TGA) experiments using argon (Ar) as carrier gas. The thermogravimetric analysis is a widely used technique to assess the thermal stability and decomposition kinetics of biomass. From the kinetic analysis, valuable parameters related to the thermo-chemical process were obtained, such as the activation energy and the pre-exponential factor, both highly dependent on the temperature of reaction. Furthermore, the composition of the raw material was also provided by thermal studies, through the quantification of the different processes of mass loss observed during the heating process. The results were obtained from the TGA measurements, by applying a kinetic methodology based on the combination of the Friedman, Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose iso-conversional methods and the use of Master Plots permitted to describe mathematically the thermochemical reactions. These results will help define the further use of CS as feedstock in energy recovery processes.

**Keywords:** Cotton seed, pyrolysis, thermal decomposition, thermogravimetric analysis, kinetics

### 1. Introduction

The cotton plant (*Gossypium hirsutum*) is a warm climate plant that does not support the cold, their growing season ranges from five to seven months, depending on the amount of incoming heat, and requires long, hot and quite humid summers for growth. The world's largest cotton producers are China, India, USA, Pakistan and Brazil. (Liu, He, Shankle, Tewolde 2016)

The cultivation of cotton is mainly directed to the production of fiber, which has innumerable industrial applications, being the raw material for manufacturing various types of fabrics, threads, shoelaces, ropes, etc. After the cotton processing process, which separates the fiber (plume) from the seed, various by-products can be obtained from the seed and, besides the plume and seeds, the main product on scale of importance is the edible oil. (Apaydin-Varol, et al., 2014; Moletta 1999)

After the plume is removed, the cotton seed is opened, releasing the grain, which is pressed for the extraction of the oil, the process carried out by hydraulic pressing or chemical extractors.

The oil obtained from the cotton seeds is dark-colored, caused by the formation of derivatives and complexes of gossypol with substances that accompany it inside the glands, where at least 15% are phenolic and alkaloid.

The presence of these compounds, which are toxic, leads to the need to refine the oil for elimination through heat, because once they are thermo-labile, and during refining, they are degraded. (Deng, Li, et al., 2010; Primaz 2018; Moletta 1999) After refining, an edible oil of excellent nutritional quality can be obtained due to the presence of essential fatty acids and vitamin E. However, particularly low rates of oil content from the seed (around 14 - 26%) lead to a limited production of edible oil from this seed. (Liu, He, Shankle, Tewolde 2016)

The “cotton cake”, obtained after the extraction of the oil, can be used as fertilizer and in the dye industry; however, its current application lies in the elaboration of animal feed due to its high protein value. Ruminant animals have the ability to detoxify gossypol, but the seed “in nature” is highly toxic and should not be used as feed for monogastric animals, mainly birds and swine. However, the high fat content (20%) and the presence of gossypol (1.2-2.4%) impose limitations on the use of cotton seed as animal feed and even for the ruminant animals have a daily tolerance, which is around 24 g/day which makes this residue less attractive for animal feed and suggests a different alternative for its use. (Risco, Holmberg, Kutches 1992; Moletta 1999)

Recently, different types of biomass have been used to perform rapid pyrolysis, each biomass has its own ideal pyrolysis condition and it is suggested that the cotton seed is a passable and abundant residue for the performance of thermochemical degradation processes for generation liquid and solid biofuels. (Wang, et al., 2017; Liu, et al., 2016; McKendry 2002)

The characterization of the thermo-chemical behavior of the biomass and the further study of their kinetics was carried out by Thermogravimetric Analysis (TGA), this technique is a widely used to assess the thermal stability and decomposition kinetics of biomass and bio-based materials. (Moliner, et al., 2016; Moliner, et al., 2018; Moliner, et al., 2018(1); Greenhalf, et al., 2012; Bove, et al., 2016)

The composition of the material can be determined by thermal studies as a result of the quantification of the different processes of mass loss observed during the heating process, the profiles of decomposition were obtained and a kinetic analysis was performed to obtain the characteristic parameters during the degradation process. All the studies were carried out following an accurate methodology defined by Badia et al in previous works (Badia, et al., 2013; Badia, et al., 2012; Badia, et al., 2010).

## 2. Materials and methods

### 2.1 Experimental procedure

The cotton seed was donated by Fazenda Planalto, Costa Rica, Mato Grosso do Sul, Brazil. The seed is the residue from the processing of cotton for the production of fiber for the textile industry. Prior to analysis, the seeds were mechanically pressed to remove excess oil.

The thermogravimetric analyses were performed with a Mettler Toledo TGA/SDTA 851 (Columbus OH) modulus at the “Funcionalización, Degradación y Reciclaje de Materiales Polimero” (DREMAP) facilities at the Universitat Politècnica de València (UPV). The samples weighing around 7 mg were heated in an alumina holder with the capacity of 70  $\mu$ L. Experiments were performed from 25°C to 800°C at different heating rates ( $\beta$ = 5, 10, 15, 20°C/min) under a constant flow of 50 ml/min of gas of analysis. All samples were analyzed under inert argon (Ar) to characterize the thermal processes. Assessment was performed with the aid of the software *Star<sup>e</sup> 9.10* from Mettler Toledo.

### 2.2 Proximate and Elemental Analysis

The determination of moisture, volatile compounds and ashes of the cotton seed were performed according to the Spanish standard methods UNE-EN ISO (18134-1/18134-2/18134-3:2015), UNE-ISO

18123:2015, UNE-EN ISO 18122:2015 respectively and the fixed carbon was determined by difference (Primaz 2018).

The elemental analyzes were performed for the cotton seed and an equipment CE Instruments CHNS1100 was used. The purpose of this analysis was to determine the percentage of Carbon, Nitrogen, Hydrogen and Sulfur in the samples.

### 2.3 Analysis of the TGA experimental results

Significant information about the different stages of mass loss was obtained including: the onset temperature ( $T_0$ ), indicator of the start of the decomposition process, the temperature of maximum decomposition rate ( $T_{peak}$ ), corresponds to the inflexion point in the TG curve and the endset temperature ( $T_{endset}$ ), temperature at which the process is considered finished, the mass loss ( $\Delta m$ ) is the amount of sample that it is degraded in the decomposition step, the fraction of sample that remains non reacted after the experiment finishes is the residue.

The presence of shoulders in the curve indicates that more than one decomposition process is occurring and, in order to describe the individual contributions of each component of the sample, the DTG curve was fitted to a sum of contributions by means of the tool *Advance Fitting Tool* from the Origin Lab Software. The results were fitted to a sum of Gaussian contributions as shown in Eq (1).

$$y = \sum_{i=1}^n A_i \cdot \exp\left(-0.5 \cdot \frac{(x - x_{ci})^2}{w_i^2}\right) \quad (1)$$

with  $A$ ,  $x_{ci}$  and  $w_i$  being the fitting parameters.

#### 2.3.1 Application of Kinetic analysis methodology

The behavior of the biomass during the thermal decompositions was studied through the calculation of their related kinetic expressions. It is widely known that the decomposition of any solid material can be described as:  $A_{solid} \rightarrow B_{solid} + C_{gas}$

In the case of biomass, this single degradation step can be considered as one step global model grouping all the decomposition processes taking place during the heating process. However, this methodology results in a simplified solution and becomes unsuitable to predict the complex biomass behavior. Solutions expressed as the sum of the different processes of decomposition of the main components of the initial sample provide a more accurate description of the process.

In both cases, the kinetics of decomposition is the result of two main contributions: the reaction rate, which depends on the concentration of reactants and the dependence of the rate constants with temperature. The velocity equation that describes the degree of thermal decomposition is expressed by a mathematical function that depends on the absolute temperature ( $T$ ) and the degree of conversion ( $\alpha$ ).

$$\frac{d\alpha}{dt} = f(\alpha) \cdot k(T) \quad (2)$$

Where  $\alpha$  is defined, according to Eq (3), as the loss of mass in a time  $t$  ( $m_0 - m_t$ ), divided by the total mass loss ( $m_0 - m_\infty$ ), with the initial mass ( $m_0$ ), the final mass ( $m_\infty$ ), the function of the degree of conversion is therefore  $f(\alpha)$ .

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (3)$$

The dependence on temperature can be expressed with an Arrhenius model in the form of:

$$k(T) = A \cdot \exp(-E_a/R \cdot T) \quad (4)$$

Where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy  $R$  is the gas constant and  $T$  the absolute temperature.

Merging Eq. (4) with Eq. (2), the rate expression may be expressed as:

$$\frac{d\alpha}{dt} = f(\alpha) \cdot A \cdot \exp(-E_a/R \cdot T) \quad (5)$$

If non-isothermal analysis are carried out, the previous law can be expressed as a function of the heating rate ( $\beta$ ) as:

$$\frac{d\alpha}{dt} = \beta \cdot \frac{d\alpha}{dT} = f(\alpha) \cdot A \cdot \exp(-E_a/R \cdot T) \quad (6)$$

### 2.3.2 Obtaining of the Activation Energy

If the experimental TGA data are fitted to the previous expression (with the appropriate selection for  $f(\alpha)$ ), it is possible to calculate the kinetic parameters describing the degradation of the sample. However, since Eq.(6) cannot be directly integrated, numerical approximations are required to calculate its solution. Solid-state kinetics assume that the activation energy and pre-exponential factor remain constant all through the degradation, but it has been proved that they can vary with the degree of conversion. For this reason, iso-conversional methods were applied. These methods can be classified as integral or differential methods, depending on whether the rate expression is integrated or derived. The most used iso-conversional methods are:

- *Linear integral methods:*

$$\text{Flynn-Wall-Ozawa (FWO)} \quad [log\beta]_y = \log\left(\frac{A_\alpha}{R} \cdot \frac{E_{a\alpha}}{g(\alpha)}\right) - 2.315 - \frac{0.457 \cdot E_{a\alpha}}{R} \cdot \left[\frac{1}{T_\alpha}\right]_x \quad (7)$$

$$\text{Kissinger-Akahira-Sunose (KAS)} \quad \left[\ln\left(\frac{\beta}{T^2}\right)\right]_y = \ln\left(\frac{A_\alpha \cdot R}{E_{a\alpha} \cdot g(\alpha)}\right) - \frac{E_{a\alpha}}{R} \cdot \left[\frac{1}{T_\alpha}\right]_x \quad (8)$$

with  $g(\alpha)$  is the inverse integral kinetic model

$$g(\alpha) = \int_0^\alpha (f(\alpha))^{-1} \cdot d\alpha \quad (9)$$

- *Linear differential methods:*

$$\text{Friedman (F)} \quad \left[\ln\left(\frac{d\alpha}{dt}\right)\right]_y = \ln(A_\alpha \cdot f(\alpha)) - \frac{E_{a\alpha}}{R} \cdot \left[\frac{1}{T_\alpha}\right]_x \quad (10)$$

### 2.3.3. Obtaining of the mechanism and order of reaction

The reaction models can be classified as nucleation and nuclei growth, phase boundary conditions, diffusion or chemical reactions. A list of the expressions defining the most common models for biomass is given in Table 1. The table shows the values of the integral  $g(\alpha)$  and differential  $f(\alpha)$  function. (Gotor, et al., 2000). More detailed information about the mechanisms can be found in the work of Khawam and Flanagan (2006) that reviewed the relationship between the theoretical decomposition mechanisms and their mathematical models (Khawam and Flanagan 2006).

Master Plots (MP) are defined as the theoretical reference curves ( $MP_i$ ) dependent on the kinetic model and, generally, independent on the kinetic parameters of the process. The comparison between the experimental values ( $MP_e$ ) and theoretical curves permits the selection of the appropriate kinetic model according to the better fitting of the experimental data on the  $MP_i$ .

The three main types of  $MP_f$  are those based on the differential form ( $MP_f$ ) of the general kinetic equation as expressed in Eq.(11), the integral form ( $MP_g$ ) as in Eq. (12) and the combination of both  $MP_{fg}$ , usually reduced at  $\alpha=0.5$  for better visualization.

$$MP_f(\alpha) = \frac{d\alpha}{dt} \equiv \beta \cdot \frac{d\alpha}{dT} = A \cdot f(\alpha) \cdot k(T) = A \cdot f(\alpha) \cdot (e)^{\frac{-E_a}{R \cdot T}} \quad (11)$$

$$MP_g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A \cdot E_a}{\beta \cdot R} \cdot \int_0^\infty \frac{e^{-x}}{x^2} = \frac{A \cdot E_a}{R \cdot T} \cdot p(x), x = \frac{E_a}{R \cdot T} \quad (12)$$

The advantage of using  $MP_f$  and  $MP_g$  instead of  $MP_{fg}$  is the clear dispersion among models of the formers in the ranges  $\alpha < 0.5$  and  $\alpha > 0.5$  which permits a straightforward initial identification.

Table 1 Summary of models of description the thermal degradation processes

Model	Differential form – f(α)	Integral form – g(α)	Mechanism
<b>Chemical reaction control</b>			
<b>n = 0</b>	1	α	Being <i>m</i> the orders of reaction
<b>n = 1</b>	(1 - α)	-ln(1 - α)	
<b>n = 1.5</b>	(1 - α) <sup>1.5</sup>	2·(-1+(1 - α) <sup>-1/2</sup> )	
<b>n = 2</b>	(1 - α) <sup>2</sup>	-1+(1 - α) <sup>-1</sup>	
<b>Diffusion control</b>			
<b>D1</b>	1/2·(1 - α) <sup>-1</sup>	α <sup>2</sup>	Unidimensional diffusion (unidimensional particle shape)
<b>D2</b>	-ln(1 - α)	(1 - α)·ln(1 - α) + α	Two-dimensional diffusion (bidimensional particle shape)
<b>D3</b>	3/2·(1 - α) <sup>2/3</sup> (1 - (1 - α) <sup>1/3</sup> ) <sup>-1</sup>	(1 - (1 - α) <sup>1/3</sup> ) <sup>2</sup>	Three-dimensional diffusion (tridimensional particle shape) (Jander equation)
<b>Nucleation models</b>			
<b>n = 1.5; m = 0.5</b>	α <sup>0.5</sup> (1 - α) <sup>1.5</sup>	((1 - α)/α) <sup>-0.5</sup> (0.5 <sup>-1</sup> )	Being <i>n</i> and <i>m</i> the orders of reaction
<b>n = 1.9; m = 0.5</b>	α <sup>0.1</sup> (1 - α) <sup>1.9</sup>	((1 - α)/α) <sup>-0.9</sup> (0.9 <sup>-1</sup> )	
<b>Others</b>			
<b>R2</b>	2·(1 - α) <sup>1/2</sup>	1 - (1 - α) <sup>1/2</sup>	Phase boundary controlled reaction (contracting area, i.e., bidimensional shape)
<b>R3</b>	3·(1 - α) <sup>2/3</sup>	1 - (1 - α) <sup>1/3</sup>	Phase boundary controlled reaction (contracting volume, i.e., tridimensional shape)
<b>A2</b>	2·(1 - α)(-ln(1 - α)) <sup>1/2</sup>	(-ln(1 - α)) <sup>1/2</sup>	Nucleation and growth (Avrami 1)
<b>A3</b>	3·(1 - α)(-ln(1 - α)) <sup>2/3</sup>	(-ln(1 - α)) <sup>1/3</sup>	Nucleation and growth (Avrami 2)

<b>F1</b>	$1 - \alpha$	$-\ln(1 - \alpha)$	Random nucleation with a nucleus in the individual particle.
<b>F2</b>	$(1 - \alpha)^2$	$1/(1 - \alpha)$	Random nucleation with two nucleus in the individual particle.
<b>F3</b>	$1/2(1 - \alpha)^3$	$1/(1 - \alpha)^2$	Random nucleation with three nucleus in the individual particle.

### 3. Results and Discussion

#### 3.1 Immediate and Elemental analysis

The **Table 2** presents the results for the elemental analysis, immediate analysis, and calorific value for the biomass and biochar obtained from cottonseed.

Table 2 Results for the immediate and elemental analysis

Analysis Realized		Biomass
		Cottonseed
<b>Elemental Analysis</b>	N (%)	$6,41 \pm 0,01$
	C (%)	$44,06 \pm 0,13$
	H (%)	$7,25 \pm 0,25$
	O (%)*	$42,28 \pm 0,38$
<b>Ultimate analysis</b>	Moisture (%)	$8,43 \pm 0,09$
	Ashes (%)	$5,06 \pm 0,26$
	Volatiles (%)	$92,43 \pm 1,37$
	Fixed Carbon (%)*	$2,51 \pm 1,37$
<b>Heating Value</b>	HHV (MJ/kg)	19,34
	LHV (MJ/kg)	17,95

(\*)Obtained by difference

According the results presented in **Table 2**, it can be observed that the elemental analyzes revealed the high carbon and oxygen content for the biomass, which is indicative of its lignocellulosic structure. The high amount of volatiles in biomass indicates that it is possible to obtain a bio-oil with important constituents that can be valuable chemical for industry. During the pyrolysis process, the organic functional groups of the biomass are broken and recombine to form the volatile matter as the temperature increases and consequently the elemental composition of the biochar changes greatly in this process (Jahirul, et al., 2012; Pütün, et al., 2005). The values obtained in these analyzes demonstrated the feasibility of the use of residues in the generation of energy, since, besides presenting considerable calorific value in their natural form, they can still be submitted to thermal conversion, generating products that can be used as secondary sources of energy (McKendry 2002; Wang, et al., 2017).



### 3.2 Analysis of the TGA experimental results

The **Figure 1 (a-b)** present the TGA (a) and DTG (b) curves for the biomass from cotton seed. The mass loss values and temperatures for the main peaks of mass loss, extracted from the curves, can be visualized in the **Table 3**.

The initial mass loss (7% until  $\sim 200$  °C) is attributed to water evaporation, release of CO<sub>2</sub> and the following three peaks represent the major decomposition reactions, indicating the presence of hemicellulose, cellulose and lignin, as well as presence of a significant amount of cotton seed oil.

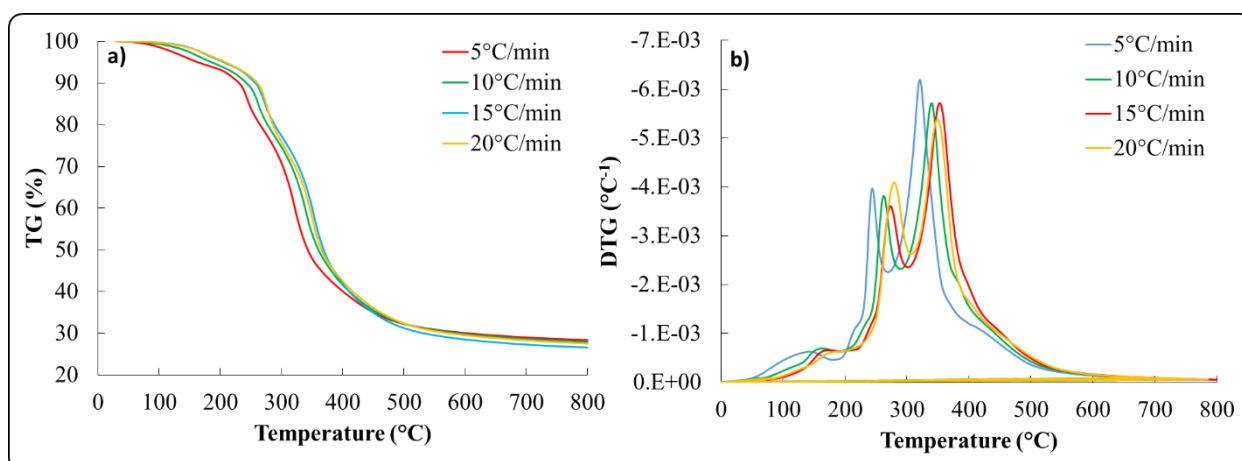


Figure 1. (a) Thermogravimetric curve (TGA) and derivative curve DTG (b) for the cotton seed in inert atmosphere at different heating speeds.

As can be seen in **Figure 1**, when the heating rate  $\beta$  increases, the thermograms shift to higher temperatures because of a delay in the degradation process and the sharp gradients of temperature obtained between the particle and surroundings that postpone the decomposition of biomass.

Table 3 Mass loss obtained in each process of decomposition for cotton seed and temperature of main peaks

$\beta$ (°C/min)	T <sub>0</sub> (°C)	T <sub>p1</sub> (°C) Moisture	T <sub>p2</sub> (°C)	T <sub>p3</sub> (°C)
5	25	146.8	276.8	324.49
10	25	161.9	272.6	323.42
15	25	162.8	272.3	352.52
20	25	176.8	270.8	351.97
$\beta$ (°C/min)	$\Delta m$ (%) Moisture	$\Delta m$ (%) Process 1	$\Delta m$ (%) Process 2	Ash (%)
5	6.1	15.1	43.5	27
10	5.9	17.0	40.4	28
15	5.5	18.8	43.7	27
20	5.9	19.2	40.3	28

Following the removal of moisture, occurs the beginning of biomass degradation. At  $\sim 150\text{-}170\text{ }^{\circ}\text{C}$ , the volatile and semi-volatile organic compounds begin to be eliminated (Stefanidis, et al., 2014; Apaydin-Varol, et al., 2014). The decomposition of hemicellulose, represented by first peak of **Figure 1** (b) occurs at low temperatures in the range of  $270\text{ to }280\text{ }^{\circ}\text{C}$ . The second peak represents the decomposition of cellulose, if occurs in the range between  $320\text{ }^{\circ}\text{C}$  and  $350\text{ }^{\circ}\text{C}$ . This well-defined decomposition temperature range is due to the homogeneous crystalline structure and non-branched d-glucose units of cellulose. Besides, hemicellulose, which is also a polysaccharide, decomposes at lower temperatures, but in some cases in a slightly higher temperature range, this difference is attributed to its structure, which is amorphous with many branched units and little activation energy. (Stefanidis et al., 2014)

The decomposition that is possibly related to the lignin structure, occurs in a wide range of temperature, superior to hemicellulose and cellulose, and comprises temperatures of decomposition in the range of  $200\text{ }^{\circ}\text{C}$  to  $550\text{ }^{\circ}\text{C}$ , and contributes to the cellulose and hemicellulose decomposition peaks. (Greenhalf, et al., 2012; Garcia-Perez, et al., 2008) This biomass component will be the main contributor to the final mass of the biochar. The residual solid is the product of continuous decomposition occurring at a very slow rate with slight weight loss due to carbon consolidation and at the end of the process  $\sim 28\%$  of char was obtained in all experiments (Kelkar, et al., 2015; Li, Strezov, Kan 2014).

The first derivative of the TG (DTG) curve with deconvolution of the components, shows that the major decomposition of the biomass components, with a weight loss of approximately 70% occurring in the range of  $200\text{ to }500\text{ }^{\circ}\text{C}$ . The cotton seed had a high content of volatile and semi-volatile matter, indicating that this biomass is a good suggestion for application in thermal degradation processes to obtain compounds of interest. According to the data obtained, temperatures between  $450\text{ and }600\text{ }^{\circ}\text{C}$  can be selected to carry out the pyrolysis process for this biomass.

### 3.3 Application of Kinetic analysis methodology to obtain the activation energy, mechanism and order of reaction

The kinetics of the main thermal decomposition processes of cotton seed has been studied following the described methodology, the temperature range for all the kinetic studies was taken from  $T-150\text{ }^{\circ}\text{C}$  because, at temperatures below this value, only moisture and absorbed water was removed and its kinetics did not exhibit differences with the change of heating rates. Thus, two principal processes of mass loss were considered for the kinetic calculations.

First, the methods that have been used are the Friedman differential method and the integral Flynn-Wall-Ozawa method. These methods let the calculation of  $E_a$  independently of the mechanism of thermal degradation followed by each decomposition process (Petrović, Zavargo 1986). In order to apply the Friedman method on each decomposition process, the previously deconvolution was applied.

Representing the derivative of the conversion as a function of time versus the inverse of temperature yields a series of straight lines that are defined for a constant degree of conversion (**Figure 2 (a,b)**). From the slopes of the straight lines, the  $E_a$  of each decomposition process are calculate.

The values of  $E_a$  calculated applied the Friedman method for the main process associated with the decomposition of the cotton seed, in a range of  $\alpha$  from 0.1 to 0.8, ranged from 90 to 146 kJ/mol in the first process and from 68 to 210 kJ/mol in second process.

Then, the Flynn-Wall-Ozawa (FWO) method is applied. The values of  $E_a$  obtained by FWO are relatively close, but below the values obtained by Friedman method for each decomposition process. These values being a range of 65-159 kJ/mol for the first and second processes. It was possible to observe that these values increase as the degree of conversion of the sample increases.

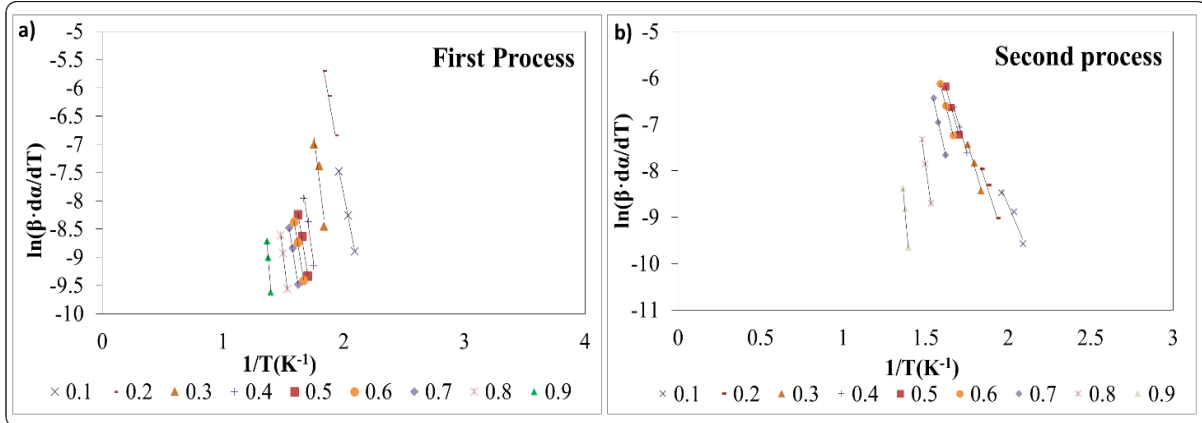


Figure 2. Representation of Friedman's method for a) first, b) second decomposition process.

The following method described in the methodology is the Kissinger Akahira-Sunose (KAS) method, which represent the neperian logarithm of the heating rate with respect to the inverse of the maximum temperature of each decomposition proces. From the slopes of these linear representations the  $E_a$  of each processes were calculated.

The values obtained by the Kissinger Akahira-Sunose method range from 52 to 101 kJ/mol for the first and second process. The  $E_a$  obtained by the method of KAS matches with the methods used previously.

The iso-conversional methods (Friedman, Flynn-Wall-Ozawa and Kissinger Akahira-Sunose) were applied to evaluate the dependence of the apparent activation energy ( $E_a$ ) with the conversion degree ( $\alpha$ ) for cotton seed, as shown in **Figure 3**.

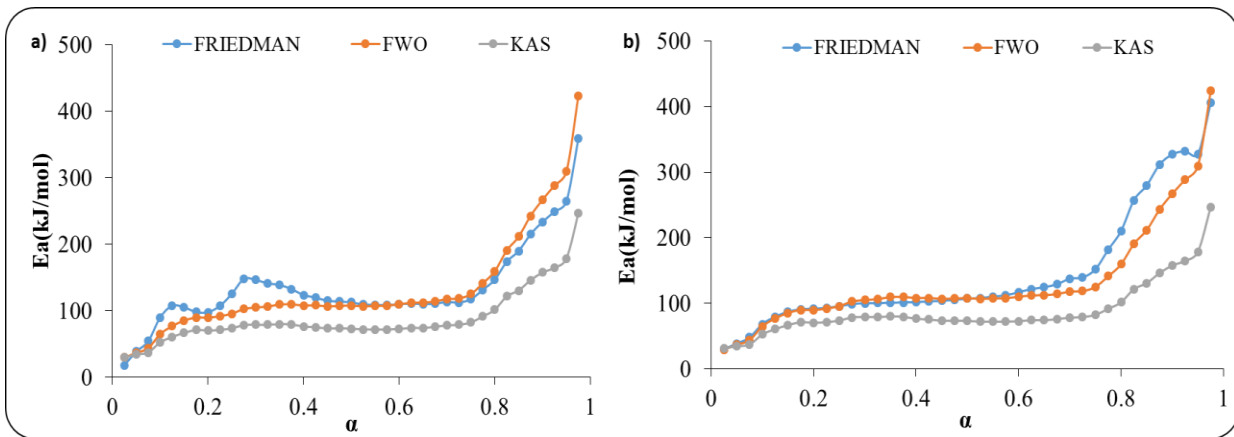


Figure 3. Evolution of  $E_{aFRIEDMAN}$ ,  $E_{aFWO}$ ,  $E_{aKAS}$  for the main decomposition process of cotton seed (range  $\alpha = 0.2-0.8$ ) at inert conditions

From a technical point of view, the apparent activation energy offers the wall of energy that the system needs to exceed in order to start and maintain the thermo-chemical reaction. The **Figure 3** shows how a definition of a constant apparent activation energy  $E_a$  might not be representative of the whole process.

The kinetic analysis were carried out in the range of  $\alpha=0.2-0.8$  due to this range comprise the main reactions, but it was observed that even within this range there is a large variation in the calculated  $E_a$ .

These values are in agreement with previous works with apparent activation energy for different agricultural residues as cotton stalk, in these studies, the results obtained are in the range of 50–180 kJ/mol (El-Sayed, Mostafa 2014; Yao, et al., 2008; Mishra, Bhaskar 2014).

### 3.4. Obtaining of the mechanism and order of reaction

The kinetic model was evaluated from the kinetic analysis of the composites and the reduced Master Plot curves (MP) as shown in **Figure 4**.

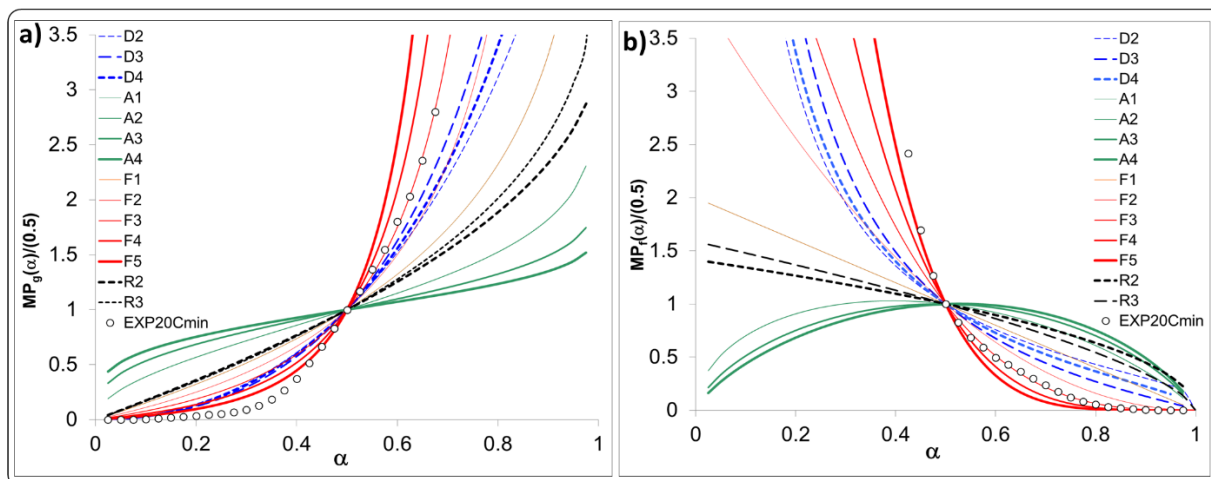


Figure 4. Example of Master plots based on the integral  $MP_g(\alpha)$  (a) and  $MP_f(\alpha)$  (b) and form of the general law compared to the experimental data obtained by the thermal process applied corresponding to first process of cotton seed at  $20^\circ\text{C}/\text{min}$  under inert atmosphere (circles).

In the **Figure 4**, the kinetic models represented are  $D_n$ : diffusion controlled, dashed blue lines,  $A_n$ : nucleation and growth, solid green lines,  $F_n$ : n-order reactor, solid red lines,  $R_n$ : reaction controlled, pointed lines. The theoretical master plots of the different kinetic models can be clearly distinguished for  $\alpha < 0.5$  (in the case of the differential curves) and  $\alpha > 0.5$  (for the integral curves) and therefore a straightforward identification can be done. The theoretical curves coincide at  $\alpha = 0.5$  and so, this point is taken as a reference and all the curves are reduced to it for a better visualization.

By comparison of the experimental data on the theoretical curves as shown in **Figure 4**, it can be suggested that the sample follows a 4th-order chemical reaction mechanism. The best fitting of the experimental data corresponds to the curve  $F_3$  on  $MP_g$  and  $MP_f$  representations, with a random nucleation with three centers in the individual particle and therefore the function defining the mechanism will be  $f(\alpha) = (1 - \alpha)^3$ .

## 4. Conclusions

The thermal behavior of cotton seed when submitted to pyrolysis reaction was studied and an accurate methodology were applied to evaluated the parameters to carry out energy valorization processes using cotton seed as feedstock. The major loss mass was obtained in the range of  $T = 200\text{--}550^\circ\text{C}$ , and the characteristic peak temperatures of the thermal decomposition process ( $T_{p1}$ ,  $T_{p2}$ ,  $T_{p3}$ ) increased when increasing the heating rate.

The total average activation energy of the process for each sample was calculated. After the kinetic analysis, it was concluded that  $E_a$  cannot be assumed as constant for the range of study ( $\alpha = 0.2\text{--}0.8$ ) for inert atmosphere, and the variations of the values for the applied methods comprise a large range of  $52\text{--}210\text{ kJ/mol}$ .

The kinetic model was evaluated with the aid of master plots, obtaining the best fitting for the 4th-order chemical reaction mechanism. Efforts will be focused then on the optimization of the working conditions with the aid of the developed model to obtain the highest efficiencies ensuring a good performance of the reactor.

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