A COMPLETE KINETIC MODEL FOR BIOMASS TORREFACTION BASED ON AN ISOCONVERSIONAL APPROACH

M. BRIGHENTI, M. GRIGIANTE[*], M. CARLESSO and D. ANTOLINI

Department of Civil, Environmental and Mechanical Engineering,

University of Trento, Via Mesiano 77, 38123, Trento, Italy.

[*]Corresponding author: maurizio.grigiante@unitn.it; phone: +39 0461 282653

Keywords: kinetics, isoconversional, torrefaction, model.

Abstract

The *aim* of this work consists in proposing an extended kinetic analysis dedicated to torrefaction process and applied to three different type of biomasses: *ash-wood*, *beech-wood* and *hornbeam*. As specific object this study investigates the reliability of the isoconversional *"model free"* methods in determining the kinetic triplet of the global torrefaction kinetics: the activation energy E_a, the $f(a)$ model function and the pre-exponential factor A.

The *methods* adopted in this investigation are based on the utilization of suitable TGA experimental measurements integrated on an innovative modelling scheme based on isoconversional approaches applied to both integral and differential methods.

The obtained *results* confirm the high reliability of the adopted methods in determining, in particular, the activation energy E_a of the torrefaction reaction. The introduced computational procedure allows to extend the good accuracy level in describing the global kinetics of the biomasses decomposition within the torrefaction ranges.

As *main conclusions* this investigation confirms that the proposed *"model free"* approach, integrated with the proposed extended procedure, represents an improved alternative to traditional kinetics methodology of significant impact to improve the kinetics of torrefaction process.

1- INTRODUCTION

The torrefaction process, a thermochemical process that subjects biomasses to a relative low thermal treatment in the range of 200-300°C, is expected to play a relevant role in upgrading the quality of raw biomasses in view of many major end-use applications as co-combustion, gasification and pyrolysis [1-4]. This process appears particularly suitable to enhance the homogeneity degree of raw biomasses as agro-forestry, agricultural crops and woody-waste industrial residues that, through torrefaction, could be upgraded in view of their use as renewable solid biofuels. The perspectives of biomass utilization could therefore be enhanced by incorporating this process within the global biomass chain value [5-8]. Actually, the industrial applications of torrefaction are yet very limited in particular for the reduced availability of consolidated plants. The industrial performances are far to be well understood in particular for those aspects regarding the energy requirements and the economic costs of the delivered torrefied biomass [9,10]. Within this scenario, improvements on the process kinetics knowledge have a strategic impact. Recent studies [11,12] have identified the role of mass and energy yield as important indicators on the final quality of the final product. Only recently kinetics studies have emerged with increasing importance and have been carried out by importing in this area some modelling schemes applied as well on biomass pyrolysis [13-18]. Usually they consist in describing this complex process by assuming only a single reaction step. The reaction rate is expressed as product of two functions, one depending solely on the temperature T, the other solely on the transformed fraction α:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \tag{1}$$

The conversion fraction α is defined as the fraction of the total mass loss at a certain step of the process:

$$\alpha = \frac{m_o - m_T}{m_o - m_\infty} \tag{2}$$

where m_o is the initial mass of the sample while m_∞ the final one. For the case of non isothermal procedures as those of this study, m_T refers to the sample weight at temperature *T*. The temperature dependent function *K(T)* is assumed to follow an Arrhenius form:

$$K(T) = A \cdot \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where *A* and E_a are, respectively, the pre-exponential factor and the activation energy, while *R* is the universal gas constant. The dependence form of the extent of conversion α is included on suitable *f(a)* model functions. Through this approach a single reaction is assumed as representative of the progress of the global transformation. The resulting kinetics parameters have to be therefore identified as "*global*" or "*apparent*" parameters, to stress the fact that their could deviate from those effectively pertaining to the single steps of a hypothetical multiple reactions scheme. Looking at Eqs. 1 and 3, a complete kinetic model is defined when the terms of the kinetic triplet: E_a, *A* and *f(a)* are determined. The adoption of iso-conversional methods introduces some significant advantages. The main consists in evaluating the E_a quantity without assuming any particular form of the reaction model. Furthermore, the selection of a suitable *f(a)* function allows to derive the corresponding *A* parameter. The selection of the *f(a)* term is yet a debate question. In this study it is proposed to adopt the Coats-Redfern (CR) method that assumes a constrain based on the evaluation of the best linear fit of a suitable equation. The resulting *A* quantity is therefore strongly dependent on the *f(a)* selected function and on the reliability of the adopted CR method. The aim of this work consists in verifying this modelling scheme when applied to thermal degradation of biomasses limited to torrefaction temperature range.

2- MATERIALS AND METHODS

2.1. Material characterization, preparation and equipment

One of the most extensively technique used to study the kinetics of biomass has proved to be thermogravimetric analysis (TGA) carried out at non-isothermal conditions. For sake of brevity, reference is made to the following papers [19-21] for a detailed description of this type of measurements procedure. This study examines three types of biomasses, all belonging to the hardwood family: *ash-wood*, *beech-wood* and *hornbeam*. For each species, about 600g have been selected in terms of defect, bark and knots free, brought to the laboratory, oven-dried and sieved by means of a 600 μm trapezoidal mesh before storing in a desiccator. The moisture content was determined in triplicate according to AOAC standard method 930.15 [22]. Samples have been preliminary characterized in terms of ultimate analysis (UA), higher heating value (HHV) and fibres composition comprehensive of ash content. The Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) amount was determined by using the Elemental Analyzer Mod. Vario Macro Cube-Elementar (Elementar Analysen Systeme GmbH, Hanau, D) while the oxygen content was calculated by subtracting the ash and the CHNS amount from the total. The ash content was determined according to the standard method DD CEN/TS 14775:2004 [23]. The HHV was measured by using the Oxigen Bomb Calorimeter Mod. IKA C5000 (Isoperibolic Calorimeter). These quantities are summarized on Table 1.

Biomass	Ultimate analysis [wt.%db]					Chemical components analysis [wt.%db]					HHVdb
	C	H	N	S	Oa	hemicel.	cellul.	lignin	extr.	ash	[MJ/kg]
beech-wood	49.13	6.21	0.11	0.10	43.70	24.85	54.12	15.87	4.41	0.75	19.178
ash-wood	48.58	5.81	0.40	0.07	44.53	20.45	59.08	15.02	4.84	0.61	18.808
hornbeam	48.40	6.36	0.08	0.01	44.53	21.28	55.48	15.73	6.89	0.62	18.550

db: dry basis. *a*: oxygen content calculated by difference. *c*: as received.

Table 1: Chemical analyses and Higher Heating Value (HHV) of the raw biomasses.

The TGA analysis were performed by a thermogravimetric analyser Labsys Setaram by using approximately 20 mg of specimen for each runs placed in the aluminium oxide crucible of the furnace microbalance. A total of 5 replicates have been performed for each of the specified runs. Reference is made to [24] for a detailed description of the adopted apparatus.

2.2. Kinetics methods

2.2.1 Isoconversional methods applied to the E_a determination

The basic assumption of the iso-conversional methods states that, for a given extent of the conversion, the reaction rate depends only on temperature, while the reaction mechanism is independent on the heating rate.

If the logarithmic derivative of the reaction rate, expressed by Eq. 1, is computed, it comes:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T}\right]_\alpha = \left[\frac{\partial \ln K(T)}{\partial T}\right]_a + \left[\frac{\partial \ln f(\alpha)}{\partial T}\right]_\alpha \qquad (4)$$

where each term is assumed at a defined (constant) α value. If α is constant, *f(a)* is also constant and, considering the Arrhenius *K(T)* function, Eq. 3, the previous Eq. 4 reduces to:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T}\right]_\alpha = \frac{E_a}{R} \qquad (5)$$

This equation states that at a fixed extent of conversion (α=const.), the temperature dependence of the reaction rate $d\alpha/dt$ can be exploited to determine the activation energy E_a without any particular assumption of the reaction model. Further, as explained on the following sections, the E_a calculation procedure is implemented step by step at the same defined α value, thus the name isoconversional or multi-curve methods [25, 26].

Considering the non-isothermal mode adopted in this study, the temperature increment is imposed to follow a linear heating rate program:

$$T = T_0 + \beta \cdot T \tag{6}$$

where T_0 indicates the starting temperature while $\beta = \dfrac{dT}{dt}$ the constant heating rate (C°/min.).

Considering the following relation:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT} \tag{7}$$

Eq. 1 can be substituted into Eq. 7 to obtain the differential form of the non-isothermal law:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \tag{8}$$

This equation lays the basis for a significant number of computational approaches normally classified into two main categories: differential and integral methods.

2.2.2. Differential isoconversional methods

By applying the logarithmic derivative of the fundamental form, Eq. 8, the following relationship, indicated as Friedman method [27,28], can be easily derived:

$$\ln\left(\beta \cdot \frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \tag{9}$$

An alternative approach, based on a rearrangement of Eq. 9, identifies the Flynn method [29]:

$$\ln(\beta) = \ln\left[A \cdot \frac{f(\alpha)}{d\alpha/dT}\right] - \frac{E_a}{RT} \tag{10}$$

By plotting the term $\ln\left(\beta \cdot \dfrac{d\alpha}{dT}\right)$ or $\ln(\beta)$ against 1/T respectively for the two methods, the

E_a/R quantity can be determined by the slope of the straight line. For a deep investigations of this approach reference is made to [28-30].

2.2.3. Integral isoconversional methods

For a constant heating rate procedure, the general isoconversional form, Eq. 8, can be rearranged to give:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot dT \tag{11}$$

Considering the position: $y = E_a/RT$, Eq. 11 can be re-written in its integral form:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \int_0^T \exp\left(-\frac{E_a}{RT}\right) \cdot dT = \frac{A \cdot E_a}{\beta \cdot R} \int_\infty^y \frac{\exp(-y)}{y^2} dy \tag{12}$$

where T is the temperature at an equivalent (fixed) state of transformation. The final integral $\int_\infty^y \dfrac{\exp(-y)}{y^2} dy$ is traditionally named the temperature integral or Arrhenius integral and is placed equal to $g(\alpha)$. This integral does not present an analytical solution so that a variety of approximate solutions give rise to approximate integral forms that can be represented by the

following generalized equation:

$$\ln\left(\frac{\beta}{T^e}\right) = +F\frac{E_a}{RT} + const \tag{13}$$

For sake of brevity, reference is made to the following papers [31-41] for a detailed description and applications of these methods.

Through Eq. 13, the activation energy can be determined from the slope resulting by plotting $\ln\left(\frac{\beta}{T^e}\right)$ Vs. $\frac{1}{T}$ once the parameters e and F are assigned.

Integral Method	e	F	Equation form
KAS (Kissinger-Akahira-Sunose)	2	-1	$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E_a}{RT} + const$
FWO (Flynn-Wall-Ozawa) (Doyle model)	0	-1,0518	$\ln\beta = -1.0518 \cdot \frac{E_a}{RT} + const$
Starink-1	1,95	-1	$\ln\left(\frac{\beta}{T^{1.95}}\right) = -\frac{E_a}{RT} + const$
Starink-2	1,92	-1,0008	$\ln\left(\frac{\beta}{T^{1.92}}\right) = -1.0008\frac{E_a}{RT} + const$

Table 2: Parameters and equations form of the adopted integral isoconversional methods.

Four integral isoconversional methods have been considered: KAS (Kissinger-Akahira-Sunose), FWO (Flynn-Wall-Ozawa, mod. Doyle), Starink-1 and Starink-2. These methods originate from Eq. 13 by assigning suitable values for the e and F parameters summarized on Table 2. It is to note that the FWO equation reported on Table 2 is indicated as *Doyle method*.

2.2.4. Activation Energy determination

The activation energy determination by means of iso-conversional methods requires several kinetics curves at different heating rates. For each of the three biomasses, four experimental kinetics curves have been performed at the selected heating rates: β= 3, 5, 10 and 20 °C/min.
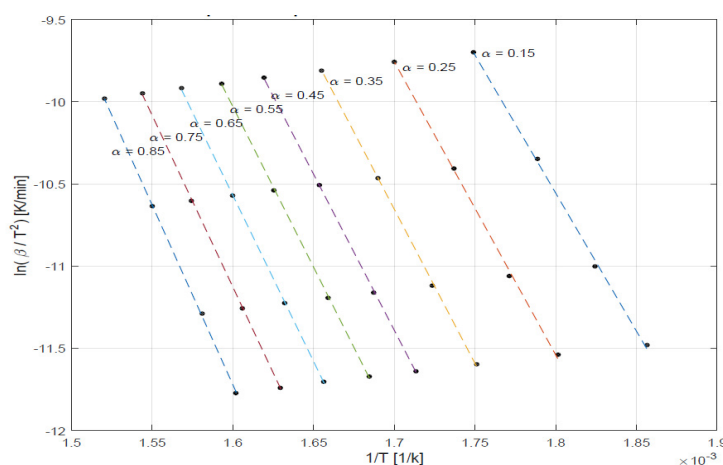

Figure 1: Arrhenius–like plot referred to isoconversional KAS method at selected α values.

As example of application, the introduced Fig.1 reports, in the range $0.15 < \alpha < 0.85$, the lines resulting by plotting $\ln\left(\dfrac{\beta}{T^2}\right)$ Vs. 1/T for the case of KAS method.

2.2.5. Order of reaction and pre-exponential factor A determination

To define the order of reaction, reference is made to the Coast and Redfern (CR) method [42]. The fundamentals of this approach move from a rearrangement of Eq. 12. By introducing an asymptotic series expansion for the temperature integral, the CR method is defined by the following equation:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\frac{A \cdot R}{\beta \cdot E_a}\left(1 - \frac{2R\overline{T}}{E_a}\right)\right] - \frac{E_a}{RT} \tag{14}$$

Since the $2R\overline{T}/E_a$ term exhibits a small variation with T and, usually, it reaches values significantly lower that 1, the term $2R\overline{T}/E_a$ is assumed as constant and the term $(1 - 2R\overline{T}/E_a)$ equal to unity [43]. If the activation energy is obtained from independent procedures as those previously investigated, this equation can be utilized to test different equations models by selecting different g(α) functional forms.

The basic assumption of the CR approach states that, plotting $\ln[g(\alpha)/T^2]$ Vs. 1/T for different g(α) functional form, the g(α) model that reaches the best linear fit is assumed as the most suitable to represent the investigated kinetic data. Further, the corresponding intercept terms allows to determine the pre-exponential factor *A*. In the present work the possibility to use non-integers orders of reaction has not been considered and the final best function that satisfies the CR constrains corresponds to a first order form:

$$f(\alpha) = 1 - \alpha \tag{15}$$

3- RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis

The initial and final samples weights have been identified in the range where torrefaction decomposition occurs. Usually this corresponds to a maximum temperature close to 330°C and, considering that hemicellulose degradation is substantially complete at temperature below 350°C (it decomposes around 220°C<t<280°C [44,45]), the torrefaction process usually leads to a nearly complete degradation of this fiber. In this investigation, the experimental TGA measurements have been extended up to 400 °C considering that a partial and simultaneous degradation of cellulose occurs. Regarding lignin degradation, this fiber is thermally more stable so that its degradation slowly happens under a wide temperature range from 100 to 900 °C. To consolidate the experimental results, a number of 5 replicates have been carried out to which refer the average values.

The effects of different heating rates on the TGA and DTG curves, as well known, are confirmed in this investigation too. In Fig. 2, the higher is the heating rate, the lower is the weight loss; on Fig. 3, an increase of the heating rate entails a shift toward right of the curves and a corresponding shift toward higher temperatures of the DTG peaks. These trends reflect the general behavior of thermal decompositions of biomasses as emerged also on recent studies on different biomasses [46-49]. These results, reported for *ash-wood*, can be drawn out for *hornbeam* and *beech-wood* as well. It is important to evidence the high superimposition degree of the TGA curves, Fig. 4, for the three investigated biomasses.
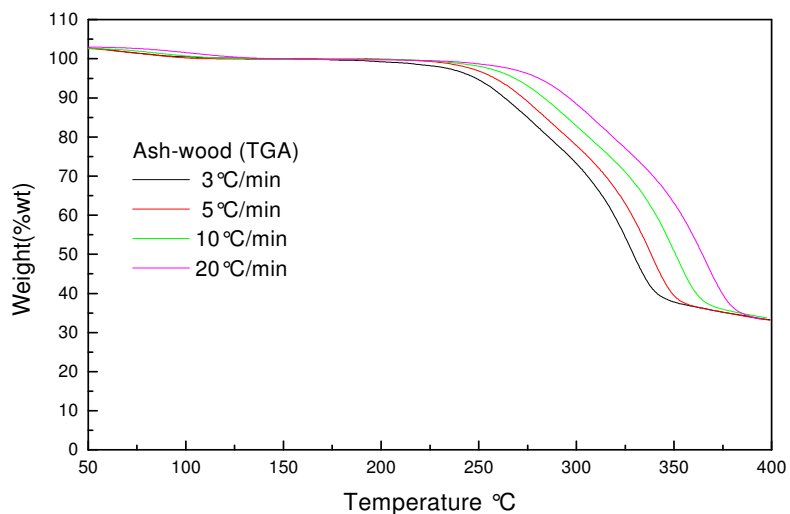
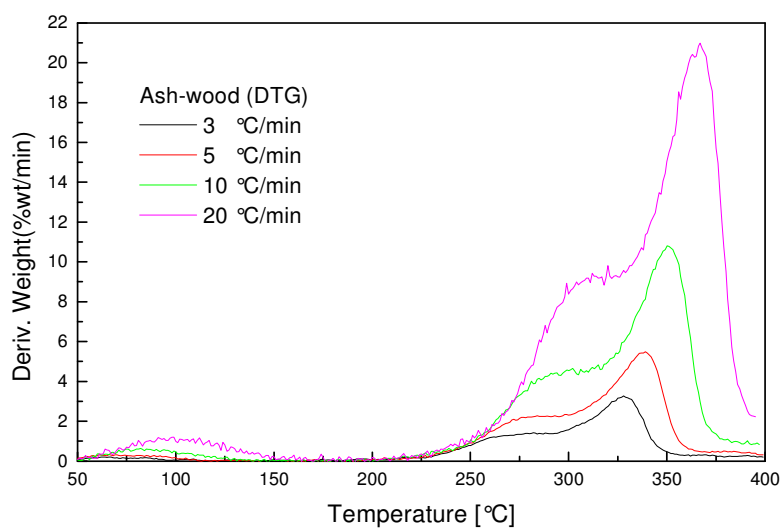*Figure 2: Ash-wood TGA curves at the selected heating rates: β =3, 5, 10, 20 °C/min.*

Figure 3: Ash-wood DTG curves at the selected heating rates: β =3, 5, 10, 20 °C/min.
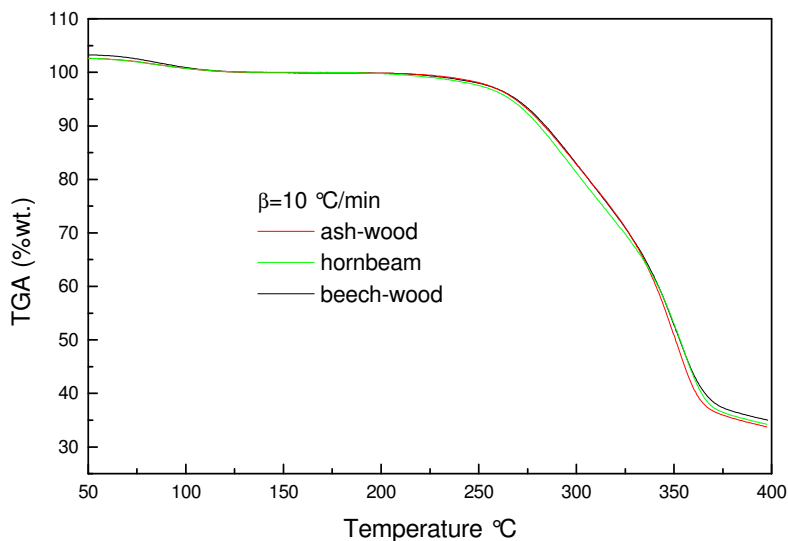
Figure 4: TGA curves for ash-wood, hornbeam and beech-wood at 10 °C/min.

3.2 Models analysis

3.2.1 Models results for the activation energy determination
A direct application of the procedure introduced on paragraph 2.2 is evidenced on the following Figs. 5 and 6 that depict the evolution of the activation energy E_a Vs. α for the temperature range selected for torrefaction. A global view of the results achieved by the application of all the proposed methods to *hornbeam* as case test, are depicted on Fig. 5. The performances of the integral methods, applied to *beech-wood* as case test, are reported on Fig.6. Very similar trends are observed for the other biomasses.
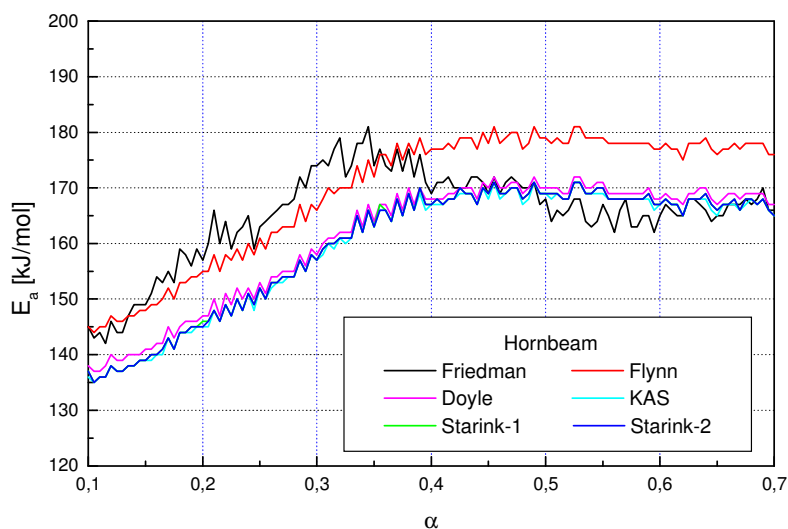

Figure 5: E_a [kJ/mol] Vs. α for hornbeam resulting from the proposed models.
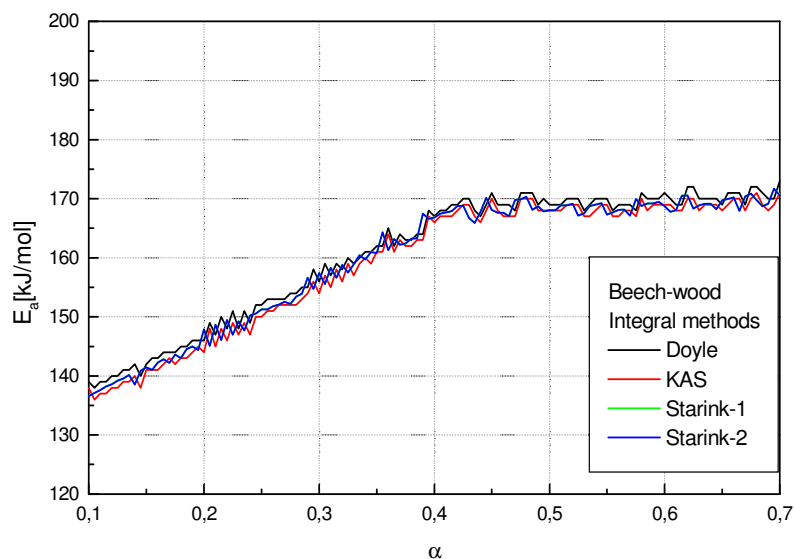
Figure 6: Ea [kJ/mol] Vs. α for beech-wood resulting from the integral methods.

From a general point of view, the results emerged on Figs. 5 and 6 confirm, for the analyzed biomasses, the following trend: the activation energy E_a increases when α ranges from 0.1 to 0.4, while a plateau can be observed from 0.4 up to 0.7. This confirms the results of recent studies referred to different types of biomasses as *rice husks* [48], *Nigerian lignocellulosic resources* [50] and *olive pomace* [46]. Despite the discrepancies among the models, in the α range: 0.1<α<0.4, the $E_a(α)$ reaches values normally encountered for hemicellulose decomposition (137-196 kJ/mol), also confirmed by Lopez-Velazquez et al. [51] and Wang et al.[52]. This reflects, in particular, the presence of multiple and competitive reactions involving multi-step mechanisms like the two-steps model proposed by Prins et al.[53]. Looking at Fig. 5, Friedman model confirms an unstable trend as highlighted by Vyazovkin [54] and Golikeri and Luss [57]. The more regular trend of the Flynn method is confirmed also for all the other integral methods. Despite the introduction of the crude temperature integral approximations, this study evidences that, for the three investigated biomasses, all the adopted integral methods perform at a quite similar accuracy level. Among the models, E_a values are significantly lower to 10%, the conventionally higher accepted limit for activation energy accuracy level [19]. As evidenced on Fig. 6, the E_a differences cannot be appreciated for the Starink-1 and Starink-2 methods. Considering the very similar trends observed for the E_a quantity of three biomasses, a generalized equation form is proposed to represent the E_a as function of only the conversion fraction α. Considering the Doyle method, two equations have been obtained:

-for the first step: α in the range 0.1 <α<0.35-0.4

$$E_a = -242.94 \cdot α^2 + 227.45 \cdot α + 112.8 \qquad (16)$$

-for the second step: α in the range 0.35-0.4 <α<0.7

$$E_a = -80.447 \cdot α^2 + 100.86 \cdot α + 139.08 \qquad (17)$$

Their accuracies are reported on the following Table 3 in terms of the AAD % (Absolute Average Deviation,%), and the Maximum Error (%) for the three biomasses.

Biomass	range 0.1 <α<0.35-0.4 (Eq. 22)		range 0.35-0.4 <α< 0.7 (Eq. 23)	
	AAD%	Max. Error %	AAD%	Max. Error %
Beech-wood	1.07	2.47	0.63	1.58
Hornbeam	0.93	-2.77	1.03	2.62
Ash-wood	2.77	4.83	4.21	6.46

Table 3: AAD and Max. Error % of the E_a values calculated from Eqs. 16 and 17.

3.2.2 Models results for the pre-exponential factor determination

The following Fig.7 depicts the obtained pre-exponential trends as result of the described CR by adopting the integral methods and selecting *hornbeam* as case test. Similar trends are obtained for the other biomasses.
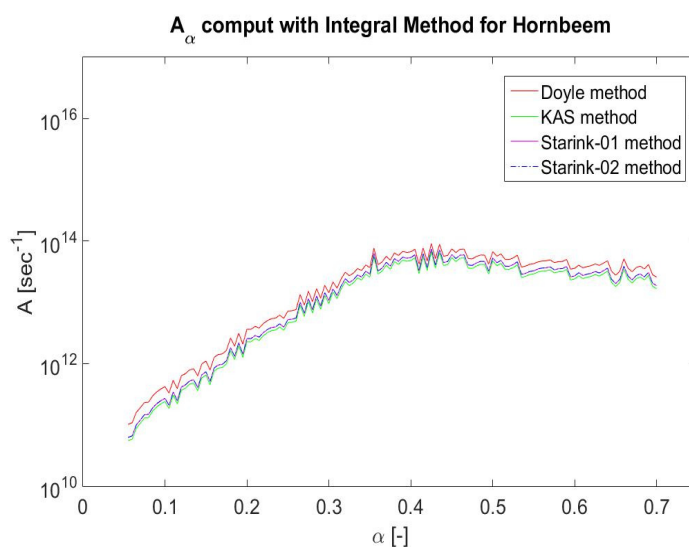

Figure 7: Pre-exponential factor A[sec^{-1}] Vs. α for hornbeam as result of integral methods.

3.2.3 Model validations of the complete kinetic model

An example of the performances of the proposed model is depicted on the following Fig. 8. The model curves have been obtained by implementing the Doyle model by following the procedures previously described and applied to *beech-wood*, for *β*=3 and 5°C/min, as case test. Considering the iso-conversional approach of this study, both the E_α and A_α parameters are not constant but they vary with the extent of the conversion fraction α. It emerges that the calculated residual mass presents lower values with respect to the indicated experimental TGA measurements. Besides, the higher is the temperature, the error increases. To improve the performances of the involving model, an innovative procedure, based on an adjustment of the kinetics parameters, has been introduced. For sake of brevity it is not possible to present all the details within this paper as it is also part of a work in progress. Synthetically, the base concept consists in defining, preliminary, the confidential range of the E_α and A_α parameters that is conditioned by the corresponding range of variation of the TGA experimental data. For a selected *β* value and within the confidential range, a suitable grid of E_α and A_α parameters is

determined and the couple that allows to reach the lower standard deviation is therefore chosen.
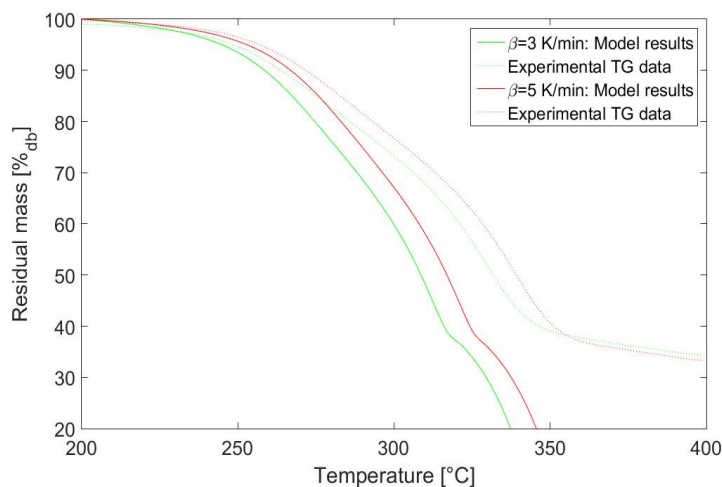

Figure 8: Comparison of the Experimental TGA and Doyle Model trends for the degradation of beech-wood at two different heating rate.

The optimized E_α and A_α values obtained for β=5 °C/min have been maintained also to calculate the degradation curves for the other heating rate values. The results are depicted on the following Fig. 9 for the case of Doyle model applied to *beech-wood* as example. The maximum error values set below 5% and the error trend curves present a similar accuracy level for all the investigated heating rates. As final result, the proposed procedure presents an effective predictive character particularly useful to be applied and extended to torrefaction process design calculations.
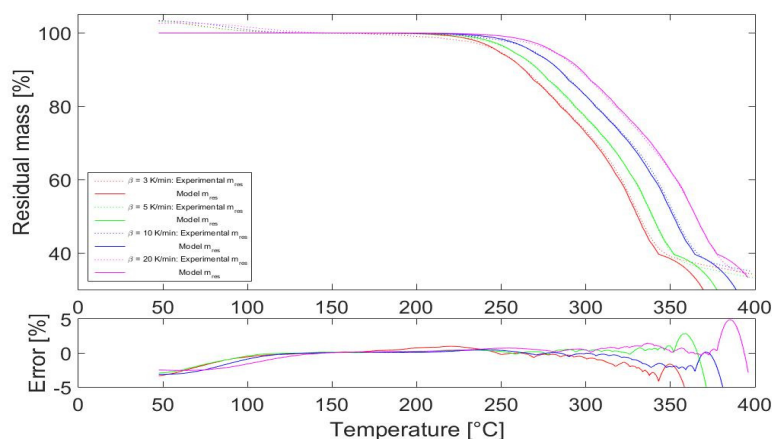

Figure 9: Experimental and Doyle Model TGA trend and Error bar as result of the new optimization procedure applied to beech-wood.

4- CONCLUSIONS

Thermogravimetric analysis (TGA) of three biomasses, *ash-wood*, *beech-wood* and *hornbeam*, all belonging to the hardwood family, has been conducted at four heating rate: 3, 5, 10 and 20 °C/min. The investigated temperature range limits to the torrefaction condition, thus setting the upper limit to 330 °C. The proposed modeling analysis focuses on the determination of the activation energy (E_a) by adopting several isoconversional methods. The

results of the proposed models in determining the E_a parameter confirm the reliability of the proposed approach. Due to the very close trends observed for the investigated biomasses, a generalizing approach for E_a has been proposed in terms of suitable equations requiring only the knowledge of the α parameter. By adopting the Coast and Redfern approach the pre-exponential factor A can consequently be determined. A complete kinetic model is therefore proposed by improving its accuracy by the introduction of a suitable optimization procedure. The final performances reach a maximum error below 5% and are maintained when the model works in a predictive mode to calculate the TGA data sets within the torrefaction range.

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