

## Thermogravimetric analysis and Kinetic study of poplar wood pyrolysis

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### Abstract

A kinetic study of the pyrolysis process of poplar wood (*populus L.*) was investigated using a thermogravimetric analyzer. The weight loss was measured in nitrogen atmosphere. The samples were heated over a range of temperature from 298 K to 973 K with four different heating rates of 2, 5, 10, 15 K min<sup>-1</sup>. The results obtained from thermal decomposition process indicate that there are three main stages such as dehydration, active and passive pyrolysis. In the DTG thermograms the temperature peaks at maximum weight loss rate changed with increasing heating rate. The kinetic parameters such as activation energy and pre-exponential factor were obtained by model free methods proposed by FWO, KAS and Kissinger. The activation energy and pre-exponential factor obtained by Kissinger method are 153.92 kJ/mol and  $2.14 \times 10^{12} \text{ min}^{-1}$ , while, the same average parameters calculated from FWO and KAS methods are 158.58 and 157.27 kJ mol<sup>-1</sup> and  $7.96 \times 10^{13}$  and  $1.69 \times 10^{13} \text{ min}^{-1}$ , respectively. The results obtained from the first method represented actual values of kinetic parameters which are the same for the whole pyrolysis process, while the second method presented apparent values of kinetic parameters, because they are the sum of the parameters of the physical processes and chemical reaction that occur simultaneously during pyrolysis. Experimental results showed that values of kinetic parameters from both method are in good agreement and can be successfully used to understand the degradation mechanism of solid-state reaction. It is planned on using the results from TGA in computer softwares for simulating pyrolysis to achieve a better understanding of the devolatilization process of different type of biomass.

### Keywords

TGA, kinetics, biomass, model-free methods

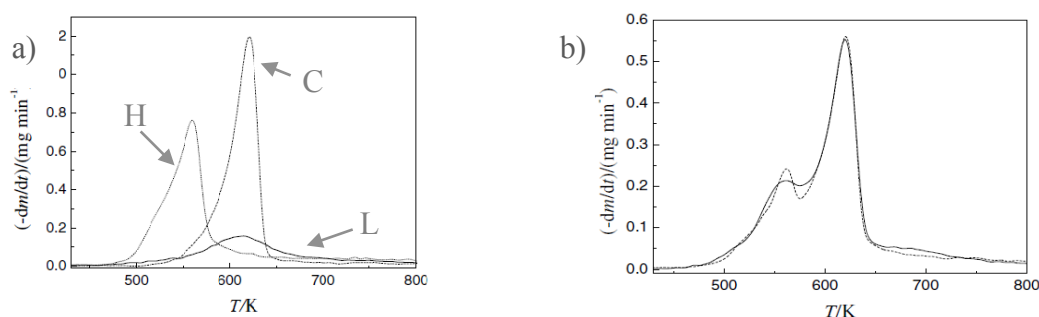
### 1 Introduction

Biomass is a renewable source of energy which is programmable through storage. Pyrolysis in particular converts biomass into high energy content biofuels provided that the adequate temperature and heating rate are reached and may be used to fuel internal combustion engines and gas turbines after an intermediate process that converts the feedstock into a liquid or gaseous biofuel [1,2]. Pyrolysis is one of the first step of all thermochemical processes occurring in an inert atmosphere [3]. It is a thermal decomposition process based on a series of complex reaction that are influenced by many factors, such as heating rate, temperature, pressure, residence time, moisture, composition of biomass material and size of particles. Adequate models to forecast pyrolysis products are also necessary for power plant optimisation and to better understand the behaviour of engines fuelled by pyrolysis products [4,5]. For a

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better understanding of pyrolysis process, many researchers studied thermal decomposition of biomass by TGA. Thermogravimetric analysis (TGA) is the most common technique used for kinetic analysis of devolatilization process. In the Literature numerous works describe TGA analysis and behaviours of different materials such as plastic [6], rubber-derivative [7], water evaporation [8], natural fibers [9], various types of biomass [10,11] during thermal degradation. Usually biomass devolatilization is referred to in terms of its three main components namely lignin, cellulose and hemicelluloses [12]. Gasparovic et al. [13] examined the pyrolysis of wood and main wood compounds by thermogravimetry and revealed that thermal decomposition of wood by TGA proceeds in three stages: water evaporation, active and passive pyrolysis, and that the decomposition process of wood depends on the composition and concentration of the main components. The decomposition of hemicelluloses and cellulose take place in active pyrolysis in the temperature from 473-653 K and 523-653 K, respectively. Whereas lignin is decomposed in both stages: active and passive pyrolysis in range from 453-1173 K without characteristic peaks, shown in Figure 1. Kumar et al. [14] investigated the thermal decomposition of corn stoves by TGA in nitrogen and air atmospheres and concluded that there are three distinct stages of weight loss in both condition and that kinetic parameters were similar only at slow heating rates. At higher heating rates, the second stage occurred very rapidly and activation energy was higher than activation energy in nitrogen atmosphere. Also Lv et al. [15] studied the thermal decomposition characteristics of hemicelluloses extracted from corn stalk and examined several different sugar units by  $C^{13}$ NMR spectra to show the presence of species of hemicellulose. Gronli et al. [16] compared the thermogravimetric curves of several hardwoods and softwoods. A comparison between both type of wood shows that the decomposition of softwood starts at lower temperatures and the hemicellulose and cellulose zone are wider.

There are many methods for analyzing non-isothermal solid-state kinetic data from TGA [17, 18]. These methods can be divided into two types: model-fitting and model-free (isoconversional) methods, both presented in Table 1 [19]. Model fitting methods consist in fitting different models to the data so that a model is chosen when it gives the best statistical fit as the model from which the kinetic parameters are calculated. The second isoconversional methods require several kinetic curves to perform the analysis. Calculations from several curves at different heating rates are performed on the same value of conversion, which allows to calculate the activation energy for each conversion point.



**Figure 1: Pyrolytic decomposition at the heating rate  $5\ K\ min^{-1}$ : a) hemicelluloses (H) cellulose (C) and lignin (L); b) wood chips (solid line) and main compounds: hemicelluloses, cellulose, lignin (dashed line) [13].**

Historically, model-fitting methods were widely used for solid-state reaction because of their ability to directly determine the kinetic parameters from a single TGA measurement. However, these methods suffer from several problems among which is their inability to uniquely determine the reaction model [20], especially for non-isothermal data; several models can be

found as statistically equivalent, whereas the fitted kinetic parameters may differ by an order of magnitude and therefore selection of an appropriate model can be difficult. Application of model-fitting methods for non-isothermal data gives higher values for kinetic parameters [19]. This method has recently declined in favor of isoconversional methods. The advantage of the model-free analysis is founded on its simplicity and on the avoidance of errors connected with the choice of a kinetic model [21]. These methods allow estimates of the activation energy,  $E_a$ , at specific extent of conversion,  $\alpha_i$ , for an independent model. Repeating this procedure at different conversion values, we obtain a profile of the activation energy as a function of  $\alpha_i$ . The underlying assumption is that the reaction model,  $f(\alpha)$ , is identical at a given  $\alpha_i$  for a given reaction under different conditions [22]. Disadvantage of these methods are a series of measurements at different heating rate which must be made for the same samples mass and the same volume flow of inert gas and their fluctuation can cause of errors.

Not all model-free methods are isoconversional: the Kissinger method is one of these exceptions because it does not calculate  $E_a$  values at progressive  $\alpha$  values but assumes a constant activation energy [19].

The purpose of this work is to investigate the kinetics of thermal decomposition of poplar wood (populus L.) The pyrolysis process was performed by TGA and the thermal analysis curves were recorded at several linear heating rates. The three model-free non-isothermal methods were used to calculate activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ). The effect of heating rate on decomposition was also studied.

Model-fitting		Model-free	
Isothermal	Non-isothermal	Isothermal	Non-isothermal
-Conventional	-Differential -Freeman-Carroll -Coats-Redfern	-Standard -Friedman -AIC	-Kissinger -Flynn-Wall and Ozawa -Vyazovkin and AIC -Kissinger-Akahira-Sonuse

**Table 1: Methods for studying solid-state kinetics [19].**

## 2 Materials and methodology

### 2.1 Experimental

The experiments were performed using thermogravimetric analyzer Leco TGA-701 at the Biomass Research Center of the University of Perugia [23]. To maintain pyrolysis conditions, high purity nitrogen was used as the carrier gas. The volume flow of  $N_2$  was  $3.5 \text{ l min}^{-1}$ . Thermogravimetric analysis for dehydration step had an heating rate of  $10 \text{ K min}^{-1}$  for all analysis, while devolatilization step were performed at four different heating rates: 2, 5, 10 and  $15 \text{ K min}^{-1}$ . For experimental tests we used fine powder size (about 0.20 mm) of density  $0.2872 \text{ g/cm}^3$  of poplar wood (populus L.) obtained from a cutting mill Retsch SM 2000. Weight of the wood samples was 1.5 g. The composition based on proximate and ultimate analyses are shown in Table 2. The sample was put in a ceramic crucible each time and first dried from laboratory temperature to 378 K and then heated from 378 K to 973 K. During the heating, the mass of the wood sample and furnace temperature were recorded.

Proximate analysis (wt %)		Ultimate analysis (wt %)	
Moisture	9.60	C	45.5
Volatile	75.54	H	6.26
Fixed carbon	11.15	N	1.04
Ash	3.70	O*	47.2

\*calculate by difference

**Table 2: Characteristic of poplar wood.**

## 2.2 Kinetic theory

The kinetics of reactions in solid-state are described by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Conversion,  $\alpha$ , is normalized form of weight loss data of decomposed sample and is defined as follows:

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad (2)$$

where  $m_i$  is the initial mass of the sample,  $m_a$  is the actual mass and  $m_f$  is the mass after pyrolysis.

According to Arrhenius equation, the temperature dependence of the rate constant  $k$  is given by:

$$k = A e^{-\frac{E_a}{RT}} \quad (3)$$

where  $E_a$  is the activation energy ( $\text{kJ mol}^{-1}$ ),  $T$  is the absolute temperature (K),  $R$  is the gas constant ( $8,314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $A$  is the pre-exponential factor ( $\text{min}^{-1}$ ). Combination of the two equations (1) and (3) gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of TGA results.

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot e^{-E_a/RT} \quad (4)$$

The expression of the function  $f(\alpha)$  and its derivative  $f'(\alpha) = -1$  are used for describing solid-state first order reaction, hence many authors restrict the mathematical function  $f(\alpha)$  to the following expression:

$$f(\alpha) = (1 - \alpha)^n \quad (5)$$

where  $n$  is the reaction order. Substituting expression (5) into equation (4) gives the expression of reaction rate in the form:

$$\frac{d\alpha}{dt} = A \cdot (1 - \alpha)^n \cdot e^{-E_a/RT} \quad (6)$$

For non-isothermal TGA experiments at linear heating rate  $\beta = dT/dt$ , equation (6) can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot (1 - \alpha)^n \cdot e^{-E_a/RT} \quad (7)$$

This equation expresses the fraction of material consumed in the time. In this work the activation energy was obtained from non-isothermal TGA. The methods used to calculate kinetic parameters are called model-free non-isothermal methods and require a set of experimental tests at different heating rates.

## 2.2 Model-free methods

### 2.2.1. Kissinger method

These methods allow to obtain the kinetic parameters of a solid-state reaction without knowing the reaction mechanism. Kissinger [24] developed a model-free non isothermal method where is no need to calculate  $E_a$  for each conversion value in order to evaluate kinetic parameters. This method allows to obtain the value of activation energy from a plot of  $\ln(\beta/T_m^2)$  against

$1000/T_m$  for a series of experiments at different heating rates ( $\beta$ ), where  $T_m$  is the temperature peak of the DTG curve (shown in Figure 4). The equation is the following:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (8)$$

The activation energy  $E_a$  can be calculated from the slope of the plot, which is equal to  $-E_a/R$ .

### 2.2.2. Flynn-Wall-Ozawa method

The FWO method [25, 26] allows to obtain apparent activation energy ( $E_{a\alpha}$ ) from a plot of natural logarithm of heating rates,  $\ln\beta_i$ , versus  $1000/T_{\alpha i}$ , which represents the linear relation with a given value of conversion at different heating rates.

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E_\alpha}{RT_{\alpha i}} \quad (9)$$

where  $g(\alpha)$  is constant at a given value of conversion. The subscripts  $i$  and  $\alpha$  denotes given value of heating rate and given value of conversion, respectively. The activation energy  $E_a$  is calculated from the slope  $-1.052E_a/R$ .

### 2.2.3. Kissinger-Akahira-Sunose

The KAS method [24, 27] is based on the following expression:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_{\alpha i}} \quad (10)$$

The apparent activation energy can be obtained from a plot of  $\ln(\beta_i/T_{\alpha i}^2)$  versus  $1000/T_{\alpha i}$  for a given value of conversion,  $\alpha$ , where the slope is equal  $-E_a/R$ .

## 3 Results and discussion

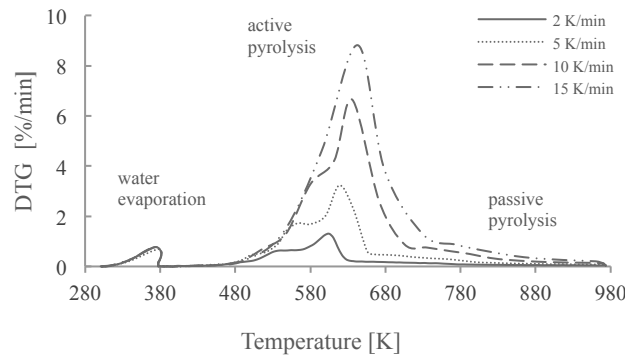
### 3.1 Thermogravimetric analysis

Differential mass loss (DTG) thermograms of thermal decomposition of poplar wood pyrolysis, at four heating rates 2, 5, 10, 15 K min<sup>-1</sup> under nitrogen atmosphere, are shown in Figure 2. As expected three regions are evident which correspond to water evaporation, active and passive pyrolysis. The first region from 330 K to 380 K is related to the extraction of moisture and adsorbed water in the wood sample. The main pyrolysis process proceeds in a range from approximately 450 K to 650 K for low heating rate and 740 K for high heating rate. In this region (active pyrolysis), there are two peaks which the Literature [13, 28] shows to be related to hemicellulose and cellulose decomposition, while lignin is decomposed in both regions of active and passive pyrolysis without characteristic peaks.

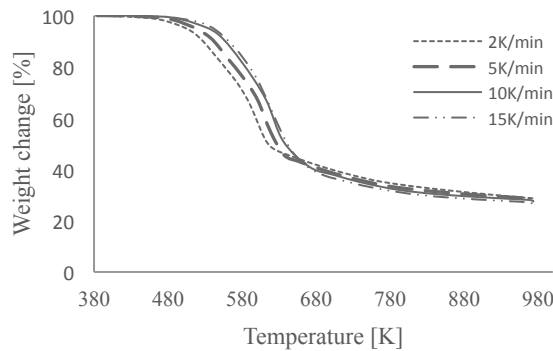
The weight loss curve (TG) in Figure 3 shows the loss of mass with temperature at different heating rates for poplar wood. As can be seen from the plot, the devolatilization process begins at about 450 K and proceeds rapidly with increasing temperature until about 660 K and then the weight loss decreases slowly to the final temperature. The solid residue yields are about 28 % for poplar wood.

The effect of heating rate is shown in Figures 2, 3 and 4. Heating rate affects TG curve positions, maximum decomposition rate and location of maximum  $T_m$  peaks. Figure 4 shows DTG curves of poplar wood (*populus L.*). When heating rate increases, starting and final temperature of active and passive pyrolysis region (Figure 2 and 4) also increase. The water evaporation region does not vary because the heating rate used for dehydration was identical for each analysis (Figure 2). Maximum points of TG and minimum points of DTG curves are shifted towards higher temperature. This data are coherent with the Literature [16] for woods with similar cellulose and hemicelluloses content to poplar such as beech wood. This

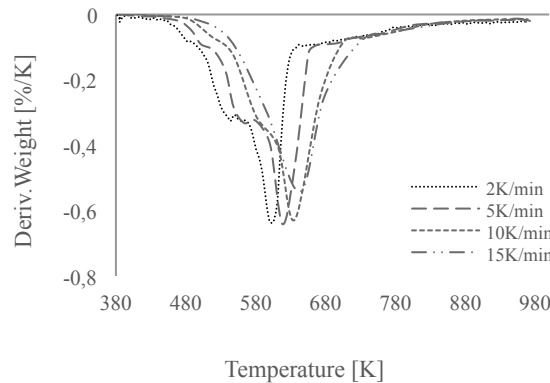
phenomena can be explained on the basis of heat transfer limitation. During the analysis, at low heating rate, a larger instantaneous thermal energy is provided in the system and a longer time may be required for the purge gas to reach equilibrium with the temperature of the furnace or the sample. While at the same time and in the same temperature region, higher heating rate has a short reaction time and the temperature needed for the sample to decompose is also higher. This causes the maximum rate curve to shift to the right [29]. To verify if the same heating rate causes a shift in the curves, we performed experiment to compare of time derivatives curves at  $5\text{K min}^{-1}$  for 1.5 g of poplar and beech wood samples. This test concluded does not any shift for the same heating rate, as shown in Figure 5.



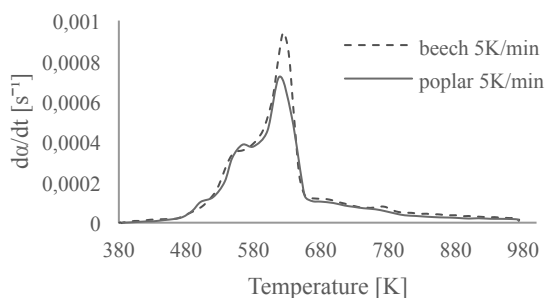
**Figure 2: DTG of a poplar wood recorded in nitrogen at different heating rates. There are three stages: dehydration, active and passive pyrolysis.**



**Figure 3: TG of weight loss curves of poplar wood recorded in nitrogen at four heating rates.**



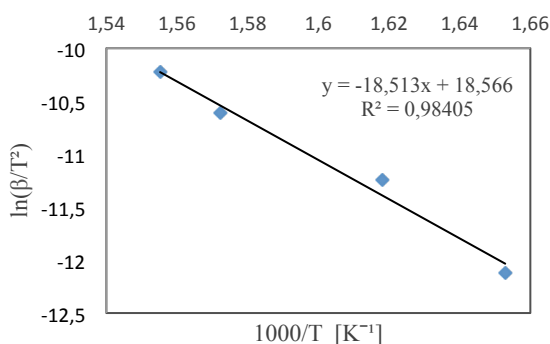
**Figure 4: DTG curves of poplar wood recorded in nitrogen at different heating rates.**



**Figure 5: Comparison of DTG curves of the mass fraction as functions of temperature for beech and poplar wood recorded in nitrogen at heating rates of 5 K min<sup>-1</sup>.**

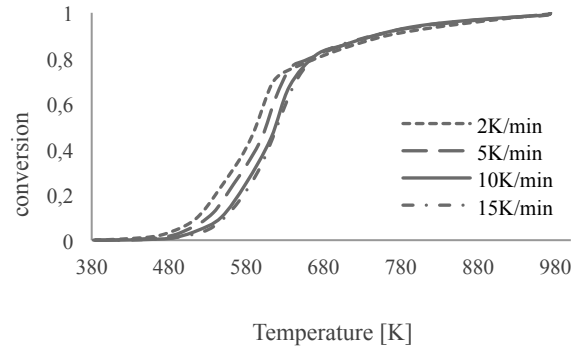
### 3.2 Kinetic analysis

The results obtained from thermogravimetric analysis were elaborated according to model-free methods to calculate the kinetic parameters. The activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) were obtained using Kissinger, KAS and FWO methods. In the first method the activation energy and pre-exponential factor were calculated from Eq. (8), where  $T_m$  is a temperature which corresponds to the maximum weight loss peaks. The peak temperatures were obtained from Figure 4. Kissinger plot of  $\ln(\beta/T_m^2)$  versus  $1000/T$  K<sup>-1</sup> of decomposition process for poplar wood is shown in Figure 6. The regression equations and the square of the correlation coefficient ( $R^2$ ) is also presented. The activation energies ( $E_a$ ) and pre-exponential factor ( $A$ ) were derived from the slope and intercept of plotting regression line, respectively. The results obtained from Kissinger methods are 153.92 kJ/mol and  $2.14 \times 10^{12}$  min<sup>-1</sup> for activation energy and pre-exponential factor, respectively.

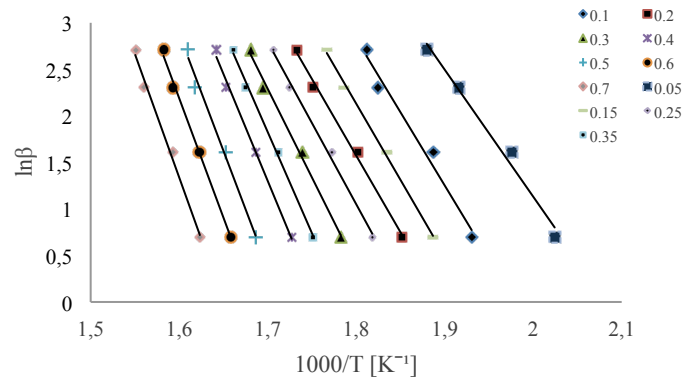


**Figure 6: Kissinger plot of poplar wood.**

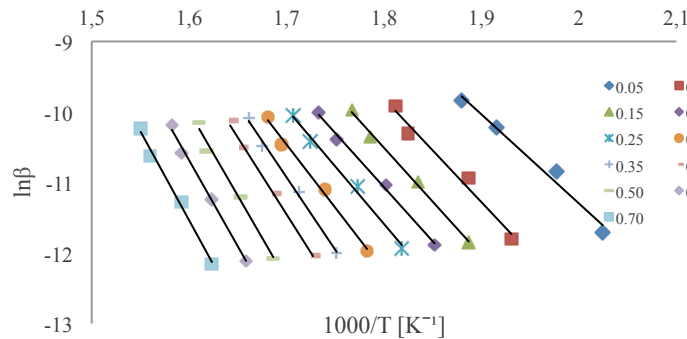
The kinetic parameters obtained by FWO and KAS methods were calculated according to eq. (9) and (10), respectively, for a given value of conversion,  $\alpha$ . Figure 7 shows the change of the conversion with temperature of the poplar wood samples at any moment at different heating rate. To determine the kinetic parameters, we chose the same value of  $\alpha$  from range 0.05 to 0.7 for all curves at different heating rate and we found the corresponding temperature. The FWO plots of  $\ln(\beta_i)$  versus  $1000/T_{\alpha i}$  K<sup>-1</sup> for different values of conversion are shown in Figure 8. The KAS plots of  $\ln(\beta_i/T_{\alpha i}^2)$  versus  $1000/T_{\alpha i}$  K<sup>-1</sup> for different values of conversion are shown in Figure 9. The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of regression line and are given in Table 3. The calculated squares of the correlation coefficients,  $R^2$ , correspond to linear fittings in Figure 8 and 9, were higher for all cases and were in range from 0.975 to 0.996.



**Figure 7: Extent of conversion curves for the devolatilization process of poplar wood at different heating rate.**



**Figure 8: FWO plot of poplar wood for different values of conversion.**



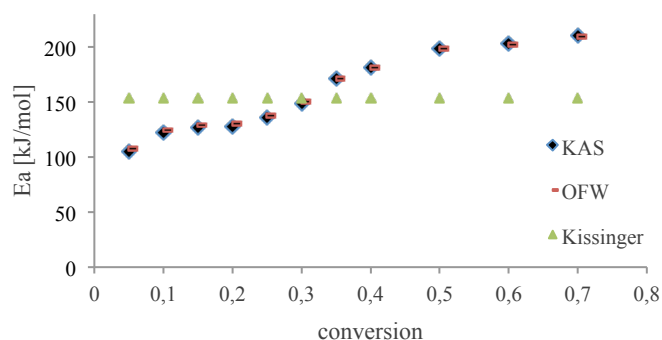
**Figure 9: KAS plot of poplar wood for different values of conversion.**

$\alpha$	FWO			KAS		
	Ea kJ/mol	A [ $\text{min}^{-1}$ ]	$R^2$	Ea kJ/mol	A [ $\text{min}^{-1}$ ]	$R^2$
0.05	107.86	$1.71 \times 10^8$	0.982	104.95	$1.44 \times 10^7$	0.979
0.10	124.40	$2.28 \times 10^9$	0.978	121.97	$2.36 \times 10^8$	0.975
0.15	129.27	$3.43 \times 10^9$	0.996	127.04	$3.67 \times 10^8$	0.996
0.20	130.08	$2.27 \times 10^9$	0.995	127.56	$2.36 \times 10^8$	0.994
0.25	137.88	$1.35 \times 10^9$	0.993	135.61	$8.51 \times 10^8$	0.992
0.30	150.77	$6.63 \times 10^{10}$	0.993	149.00	$8.73 \times 10^9$	0.993
0.35	171.88	$3.43 \times 10^{12}$	0.996	171.08	$5.75 \times 10^{11}$	0.995
0.40	181.54	$1.53 \times 10^{13}$	0.994	181.10	$2.80 \times 10^{12}$	0.994
0.50	198.53	$2.13 \times 10^{14}$	0.988	198.76	$4.47 \times 10^{13}$	0.987



0.60	202.73	$2.45 \times 10^{14}$	0.995	203.01	$5.18 \times 10^{13}$	0.994
0.70	209.49	$3.98 \times 10^{14}$	0.992	209.90	$8.62 \times 10^{13}$	0.991
Average	158.58	$7.96 \times 10^{13}$		157.27	$1.69 \times 10^{13}$	
Kissinger		153.92 kJ/mol		$2.14 \times 10^{12} [\text{min}^{-1}]$		

**Table 3: The results of  $E_a$  and  $A$  for a poplar wood obtained by FWO, KAS and Kissinger methods.  $R^2$  corresponding to linear fittings in Figure 8 and 9.**



**Figure 9: The activation energy as a function of conversion.**

In Figure 9, we can observe that apparent activation energy for the pyrolysis of poplar wood was not similar for all conversion indicates the existence of a complex multistep mechanism that occurs in the solid state. The apparent value of activation energy is about 107.86 - 209.49  $\text{kJ mol}^{-1}$  and 104.95 - 209.90  $\text{kJ/mol}$  for FWO and KAS, respectively. This means that the reaction mechanism is not the same in the whole decomposition process and that activation energy is dependent on conversion.

The model-free methods allow to estimate activation energy as a function of conversion without previous assumption on the reaction model and allows nearly unmistakably detecting multi-step kinetics as a dependence of activation energy on conversion in contradistinction to Kissinger method which producing a single value of the  $E_a$  for the whole process and complexity may not be revealed [30]. The values of activation energy obtained from the Kissinger method are consistent with the range of values obtained by the FWO and KAS methods and is very near to their average values, which are equal 158.58 and 157.27  $\text{kJ mol}^{-1}$ ; the value of the pre-exponential factor is also contained in a region of average value. The Arrhenius parameters for poplar wood found in the Literature was calculated from different methods and at different conditions. Vecchio et al. [11] examined thermal degradation of poplar wood by DSC-TG in air and applied the Kissinger method to calculate the kinetic parameters and obtained activation energies for two peaks in active pyrolysis region: 146  $\text{kJ mol}^{-1}$  for the first peak and 188  $\text{kJ mol}^{-1}$  for the second peak. As described in Kumar et. al [14], the activation energy in air is higher than  $E_a$  in nitrogen atmosphere. Biagini et al [31] applied traditional isoconversional method (Friedman) within TGA in nitrogen atmosphere and obtained activation energy and pre-exponential factor for poplar wood 168.9  $\text{kJ mol}^{-1}$  and 28.1 (lnA). The differences in kinetic parameters can be attribute to complicated nature of wood constituted by a mixture of cellulose, hemicelluloses, lignin and extractives, with proportion, reactivity and chemistry affected by variety. Moreover, use the different experimental conditions and various procedures for calculations causes that the derived kinetic parameters (even if it were calculated with the same method) may differ for the same type of biomass.

#### 4 Conclusion

In this work, an experimental kinetic study of poplar wood pyrolysis is presented. Thermogravimetric analysis was investigated under nitrogen atmosphere at different heating rates of 2, 5, 10 and 15 K mol<sup>-1</sup>. Thermal decomposition of poplar wood proceeds in three steps: water evaporation, passive and active pyrolysis. It was found that the mainly pyrolysis process occurred at about 450 to 740 K. Effect of heating rate on TG and DTG curves was also presented. Activation energy and pre-exponential factor were obtained by the model-free methods. The kinetic parameters calculated by Kissinger method were the same for the whole pyrolysis process, whereas in the FWO and KAS methods apparent activation energy and apparent preexponential factor vary with conversion and revealed the complex mechanism of reaction that occur during the pyrolysis process. The values of activation energy obtained from the Kissinger method are consistent with the range of values obtained by the FWO and KAS methods and is very near to their average values which are equal 158.58 and 157.27 kJ mol<sup>-1</sup>; the value of the pre-exponential factor is also contained in a region of average value. Experimental results showed that values of kinetic parameters are in good agreement and that the model-free methods satisfactorily described the complexity of devolatilization process, but to better understand this phenomena, to learn which chemical compounds are formed and which chemical and physical process occur during pyrolysis, further analysis is needed. It has been planned on using the results from TGA in computer softwares for simulating pyrolysis to achieve a better understanding of the devolatilization process.

#### Nomenclature

TGA: Thermogravimetry analysis

DTG: Differential thermogravimetry

E<sub>a</sub>: Activation energy [kJ mol<sup>-1</sup>]

A: Preexponential factor [s<sup>-1</sup>]

α: conversion [1]

m<sub>i</sub>: initial mass [kg]

m<sub>a</sub>: actual mass [kg]

m<sub>f</sub>: final mass [kg]

k: reaction rate constant [s<sup>-1</sup>]

n: reaction order [1]

R: gas constant [J mol<sup>-1</sup> K<sup>-1</sup>]

R<sup>2</sup>: correlation coefficient

T: Temperature [K]

T<sub>m</sub>: Maximum temperature peak [K]

β: Heating rate [K min<sup>-1</sup>]

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