Pyrolytic Degradation of Olive Waste Residue (OWR) by TGA: Thermal Decomposition Behavior and Kinetic Study

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Abstract: Olive oil is an important food industry product in Mediterranean countries. Large quantities of OWR (olive waste residue) are generated during a two- or three-phase separation process. This represents a major pollution problem for the industry and oil farms. The OWR is a source of substances of high value and can be used as a low-cost renewable energy. This work studied the behaviour of OWRs during the thermal decomposition process. The experiments of the slow pyrolysis process of three different waste olive products as olive pomace, olive tree pruning and olive kernels were performed under a nitrogen atmosphere at different heating rates, using a thermogravimetric balance. The samples were heated to a maximum temperature of 1,023 K, with four different heating rates of 2, 5, 10, 15 K/min. A comparison of different isoconversional (Flynn-Wall-Ozawa), not-isoconversional (Kissinger) model-free and model-fitting (Freeman-Carroll) methods to calculate the activation energy and pre-exponential factor is presented. In the Kissinger method the kinetic parameters were invariant for the whole pyrolysis process. While, in the case of Freeman-Carroll, it differs with change of the heating rate. The Flynn-Wall-Ozawa technique revealed the "not one-step" mechanism of reaction that occurs during the slow pyrolysis process. The kinetic data obtained in nitrogen atmosphere may provide more useful information for engineers for a better and complete description of the pyrolysis process and can be helpful to predict the kinetic model.

Key words: Thermogravimetry, kinetics, biomass, isoconversional methods, OWR, model-fitting methods, model-free methods.

Nomenclature

DTG	Differential thermogravimetry
FC	Freeman-Carroll
FWO	Flynn-Wall-Ozawa
TGA	Thermogravimetric analysis
OWR	Olive waste residue
A	Pre-exponential factor (s^{-1})
β	Heating rate (K/min)
α	Conversion
E_a	Activation energy (kJ/mol)
K	Reaction rate constant (s^{-1})

m_a	Actual mass (kg)
m_f	Final mass (kg)
m_i	Initial mass (kg)
n	Reaction order
T_m	Maximum temperature peak (K)
T	Temperature (K)
R	Gas constant (J/mol·K)
R^2	Correlation coefficient

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1. Introduction

The irreversible effects of pollution of the natural environment caused by rapid outgrowth of population and urbanization are an important issue [1]. The searches for new sources of energy are now steadily

increasing. Renewable energy derived from biomass has the potential to reduce our dependence on fossil fuels. Biomass offers several advantages compared to fossil fuels. It is renewable, does not add new CO_2 to the atmosphere and its exploitation can promote the development of rural areas [2].

Italy occupies the second position in the world in the production of olive oil [3]. The solid waste residue from oil production industry (olive kernels and olive pomace) and olive tree plantation (olive tree pruning) are produced annually in large quantity. All of these waste products can be used mainly for the production of heat and power. Olive kernels are used as a low-cost solid biofuel also in the form of pellet destined to use for gasification plants, thermal power station and biomass boilers [4]. Wet olive pomace is used in anaerobic digestion, while drying pomace is used for pyrolysis, combustion or gasification. Also olive pruning could be used for energy production, but often is unexploited and left to natural decomposition or burt in fields [4].

Biomass is defined as any biological material and can be divided into three general categories: wastes, standing forests, energy crops which can be converted into energy through many conversion processes.

Pyrolysis is the first chemical step of thermochemical conversion methods as gasification, combustion [5-11]. This process relies on thermal decomposition of biomass by heating in an inert atmosphere and leads to the formation of solid residue, tar, water and combustible gases. Different pyrolysis types exist: slow, fast and flash, depending mainly on temperature, heating rates, residence times and type of biomass [12]. Modification of these parameters allows

controlling the process to decrease or increase the product yields. Slow pyrolysis occurs at a low reactor temperature (400-700 °C) and long residence times with lower heating rate. Increasing the temperature decreases the yield of char and increases the volatile substances, while the tar is subjected to the secondary reactions, which results in a lower production of liquids in favour of the gaseous phase.

Thermochemical decomposition of biomass has a very complex mechanism and many chemical reactions coupled with mass transfer and heat processes. Full understanding of biofuel properties and its thermochemical behaviour are essential for the proper design of thermochemical conversion systems [13].

TGA (thermogravimetric analysis) is commonly used to study thermochemical degradation of different biomass samples [14, 15]. In order to simulate the pyrolysis, obtain the data necessary for its modelling and for a better understanding of the process, many researchers studied the kinetics of thermal degradation of the biomass sample by thermogravimetric balance. The TGA results are used to determine the kinetic parameters of devolatilization process. Non-isothermal solid state kinetic analysis can be obtained by several methods divided into two types: model-free and model-fitting methods. The comparison of the non-isothermal methods is given in Table 1. The model-fitting methods are considered to be approximate, because a single TGA curve was used and performed at one heating rate. The kinetic parameters are obtained from fitting different models to the TGA data which give in the plots a straight line. The model is chosen when giving the beast linearization with experimental data. However,

Table 1   Comparison of models for non-isothermal experiments.

Model-fitting	Model-free
e.g. Freeman-Carroll, Coats-Redfern	e.g. KAS, FWO, Kissinger
Advantages	
Single TGA measurement at one heating rate	Several kinetic curves at different heating rates
"Fitting" of the data of the TGA	Kinetic parameters related to the different conversion (α) of biomass
Chosen the model when giving better statistical fit	Avoidance of the errors associated with the "fitting" of data
Disadvantages	
Several statistical models equivalent	The same mass of the samples and the same gas flow for all tests to avoid errors

because more than one kinetic model can give the best statistical fit with the same experimental data curves the simply choosing of the reaction model is difficult. In the model-free methods the multiple TGA experiments at different heating rates are performed. The apparent kinetic parameters are calculated in progressive degree of conversion (α) without evaluating the reaction model $f(α)$. The Kissinger method is model-free, but not isoconversional method, because the activation energy is not calculated at progressive conversion degree, but assumes a constant value of the activation energy [16].

In the present paper the slow pyrolysis of three OWR (olive waste residues) performed by thermogravimetric analyser with heating rate 2, 5, 10, 15 K/min in nitrogen atmosphere is discussed. Numerous studies on the thermal decomposition of the mixed olive residue have been carried out. Many scientific papers describe the devolatilization behaviour during degradation of mixed olive residue in air atmosphere or co-pyrolysis with other materials [1, 13, 17, 18] without giving precise details of the proportions that were used to experiment. Also, use of air for TGA test results in an increase of the value of the activation energy [19]. For engineers who occupied the preliminary analysis and simulation of pyrolysis process this fact is unacceptable. The difference in values of Arrhenius parameters is caused not only by the fact of different experimental conditions, as inert or oxidative atmosphere, but also by different methods of calculation and different physical and chemical properties of biomass.

In literature there is a little information about slow pyrolysis of non-mixed OWR based on model free methods.

The objective of this work is to study the slow pyrolysis of olive pomace, olive tree pruning and olive kernels by isoconversional model-free (Flynn-Wall-Ozawa), not isoconversional model-free (Kissinger) and model-fitting (Freeman-Carroll) methods and to provide clues about their decomposition mechanism. Also the thermal behaviour of samples and effect of heating rate were described. The experiments performed in nitrogen atmosphere may provide more useful information to predict the kinetic model of the waste biomass sample compared to those available for oxidizing atmosphere. Besides, it may help optimize pyrolysis parameters and understand how the process proceeds.

2. Materials and Instrumentation

2.1 Materials and Instrumentation

Olive waste samples were received from the company Iraci Borgia in Bevagna, an Umbria region, Italy in Fig 1. All the analyses of the samples were performed in the Biomass Research Centre of the University of Perugia [20]. Before performing TGA the samples were first dried and later grounded in the cutting mill Retsch SM 2000, to obtain a uniform material with average particle size of about 2 mm. Moisture, volatile matter and ash content of olive waste samples were analyzed using thermogravimetric balance Leco TGA-701, according to CEN/TS 14774-14775. Ultimate analysis was performed using a Leco TruSpec CHN analyzer, according to ASTM

Fig. 1 Types of raw samples: olive pruning, dry olive kernels, dry olive pomace, respectively.

Table 2   Characterization of olive waste samples.

	Olive tree pruning	Dry olive kernels	Dry olive pomace
Moisture (%)	8.12	4.53	4.52
Ash (db%)	6.77	0.49	5.81
Volatile (db%)	90.38	87.06	86.71
Fixed carbon (db%)	2.85	12.45	7.48
HHV (MJ/kg)	18.21	19.21	19.88
Carbon (%)	45.3	50.0	51.8
Hydrogen (%)	6.49	6.17	6.76
Nitrogen (%)	1.65	0.42	1.32
Oxygen[a] (%)	46.56	43.41	40.12

a: calculate by difference.

D5373. The calorific value of raw materials was determined with a Leco AC-350 analyzer, with isoperibolic method. Characterization of olive waste products is shown in Table 2.

3. Methodology

3.1 TGA Experiments

Pyrolysis tests of OWRs were carried out by thermogravimetric analyzer TGA-701, Leco. All experiment runs were performed with a flow of nitrogen of 3.5 L/min, to reproduce the conditions of the pyrolysis process. Thermogravimetric curves were obtained at four different heating rates: 2, 5, 10, 15 K/min. The sample was put in a ceramic crucible covered from top and heated from ambient temperature to 1,023 K. The amount of the sample used in this study was 0.5 g. The experimental data as mass and furnace temperature of each olive waste product were recorded.

3.2 Determination of Kinetic Parameters

3.2.1 Kinetic Theory

The devolatilization is the first step of all thermochemical processes and consists in the release of volatiles (light gases and condensable), during continuous heating of the solid fuel due to thermal cleavage of chemical bonds of natural polymers (hemicellulose, cellulose and lignin). Therefore, this process has a very complex mechanism, because in a very narrow range of temperatures consecutive and parallel chemical reactions occur. To simplify the

process of pyrolysis many researchers used a "one-step" model, which assumes that the phenomenon of devolatilization takes place in a single reaction:

$$biomass \xrightarrow{k} volatiles + char \qquad (1)$$

Volatile represents the sum of the fractions of gas and tar, and k is defined as the kinetic constant of the reaction whose temperature dependence is expressed by Arrhenius equation.

$$k(T) = A \cdot e^{\frac{-E_a}{RT}} \qquad (2)$$

The fundamental rate equation which is used in all kinetic studies is expressed as:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \qquad (3)$$

where $f(\alpha)$ is the reaction model. This equation expresses the degree of conversion, $d\alpha/dt$ at a constant temperature. The degree of conversion, α represents the decomposed amount of the sample at time t, and is described as:

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \qquad (4)$$

where m_a, m_i and m_f are the actual, initial and final mass of the sample during the experiments. Biomass devolatilization reaction (1) can be described also by Eq. (5).

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot e^{-E_a/RT} \qquad (5)$$

Assuming solid state reactions are of the first order $f(\alpha) = (1-\alpha)^{n=1}$, for non-isothermal TGA experiments with linear heating rate $\beta = dT/dt$, Eq. (5) is

described with the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot (1-\alpha)^n \cdot e^{-E_\alpha/RT} \qquad (6)$$

where A, E_α, R, T, α, t, $k(T)$, $f(\alpha)$ are respectively: frequency factor (s^{-1}), activation energy (J/mol), gas constant (8.314 J/mol·K), temperature (K), conversion, time (s), rate constant and the reaction model.

3.2.2 Mathematical Methods

In literature many different methods exist for studying the kinetics of the degradation of solid materials. In this study, we used some of the model-free and model-fitting methods.

(1) Kissinger method

One of the simplest model-free non-isoconversional methods, which allow obtaining kinetic parameters without knowledge of the reaction mechanism, is the Kissinger method [21]. This method allows obtaining the value of the activation energy (E) by plotting $\ln(\beta/T_{2m})$ versus $1{,}000/T_m$ for a series of experiments at different heating rates (β), where T_m is the temperature peak of the DTG curve. The equation is as following:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \qquad (7)$$

(2) FWO (Flynn-Wall-Ozawa) method

Another model-free but isoconversional is the Flynn-Wall-Ozawa method [22, 23]. This method allows obtaining apparent activation energy (E_α) from a plot of natural logarithm of heating rates, $\ln\beta_i$, versus $1{,}000/T_{\alpha i}$.

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_\alpha}{RT_{\alpha i}} \qquad (8)$$

The subscripts i and α denote given value of heating rate and given value of conversion (change of weight), respectively. The activation energy (E_α) is calculated from the slope and the pre-exponential factor (A_α) can be calculated from the intercept of the plot. The activation energy is calculated directly from the linear equation while, pre-exponential factor requires a modelistic assumption for its estimation.

(3) FC (Freeman-Carroll)

The FC method [24] needs only one heating rate experiment. This method is based on the Eq. (9):

$$\frac{\Delta\left[\ln\left(\frac{d\alpha}{dt}\right)\right]}{\Delta\left[\ln(1-\alpha)\right]} = n - \frac{E}{R}\left[\frac{\Delta\left(\frac{1}{T}\right)}{\Delta\left[\ln(1-\alpha)\right]}\right] \qquad (9)$$

The plot of $Y' = \dfrac{\Delta\left[\ln\left(\dfrac{d\alpha}{dt}\right)\right]}{\Delta\left[\ln(1-\alpha)\right]}$ versus

$X' = \dfrac{\Delta\left(\dfrac{1}{T}\right)}{\Delta\left[\ln(1-\alpha)\right]}$ gives a straight line where from the slope we can calculate the activation energy and from the intercept order of reaction.

4. Results

4.1 Thermal Decomposition Behaviour

The TGA and DTG experiments data were performed in a nitrogen atmosphere from ambient temperature to 1,023 K at four different heating rates 2, 5, 10, 15 K/min. Fig. 2 shows the percentage loss of mass vs. temperature. The temperature-dependence curves were recorded during thermal decomposition for three different OWRs as olive kernel, olive pomace and tree pruning. Initially the pyrolysis process began slowly and we can observe a slight loss of mass. With increasing temperature, the mass loss of the sample radically increases. The increased sample mass loss is associated with chemical reaction which releases tar and volatile products. As it can be seen from Fig. 2, solid residue yields vary from about 23% to 25% for waste olive products.

In the DTG curves of the analyzed samples there are three distinct areas known as water evaporation, active region and passive region. Desiccation step starts from ambient temperature to about 450 K for lower heating rate and is associated with the evaporation of water present in the sample. The area of the active region is located in the range of about 450 to 650 K for lower heating rate and 740 K for high heating rate. This range is a particularly important step of pyrolysis, here the
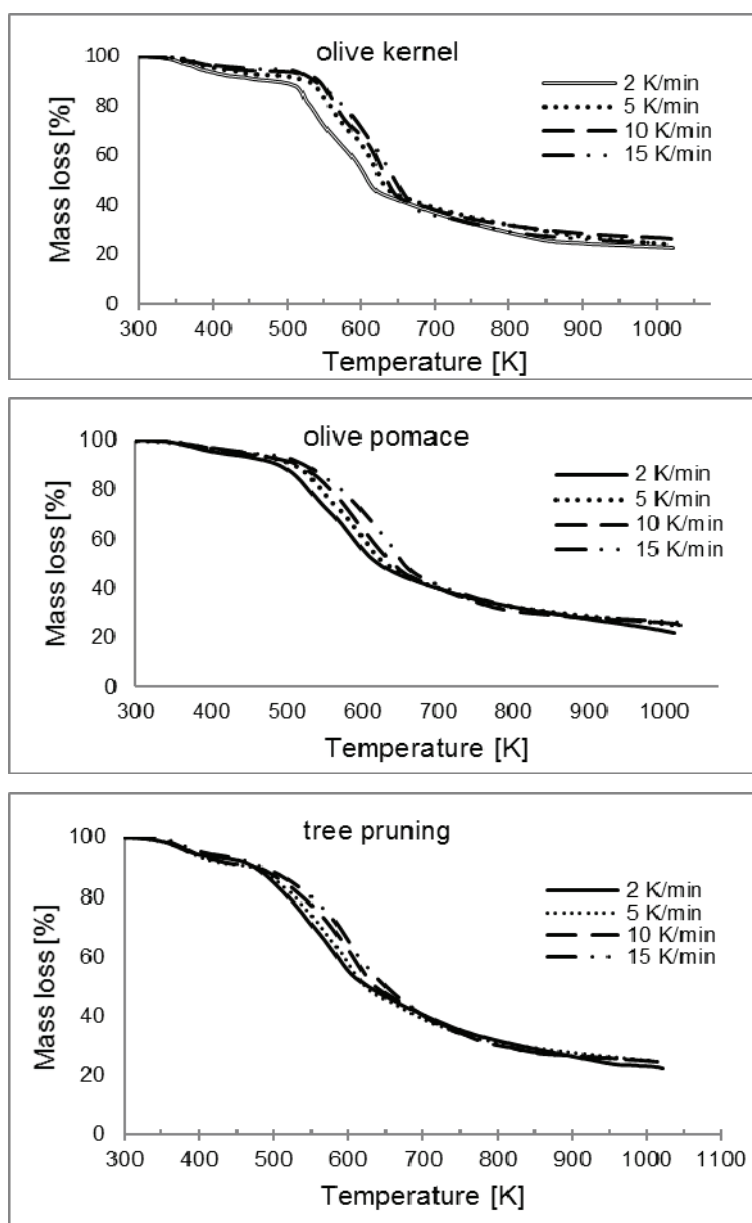
Fig. 2   TG diagrams at different heating rates in nitrogen atmosphere.

devolatilization process takes place. In this area most volatile components are generated as it can be seen from the overlapping peaks of DTG curves. Frequently, in the active pyrolysis region of DTG curves, two distinct peaks are visible, which in Ref. [25] are related to hemicellulose and cellulose decomposition. Tree pruning has a different behavior and shows only one visible peak. Otherness may be related to the fact that the sample contained leaves and branches mixed together. Separately, the olive leaves contain lower

yield of hemicellulose and high yield of lignin. While, olive wood includes an inverse amount of these polymers. Our sample was predominantly leaves and it is possible that the decomposition peak of hemicellulose is partly mixed with the peak of cellulose.

Hemicellulose decomposes at low temperature, between 430 and 630 K, releasing lighter volatiles. Cellulose begins to break down at high temperature range between 513 and 663 K [26]. Lignin, which is

more thermally stable, is decomposed in both regions of active and passive regions and corresponds to heavier volatile decomposition. In the DTG for lower heating rate the lignin decomposition occurs without characteristic peaks forming a long tail. From the DTG profiles, it is difficult to identify the separate peaks of hemicellulose, cellulose and lignin because of overlapping on each other [27].

In the temperature range of about 573-623 K

reactivity index varies from 4.9-7.5%·min^{-1} for tree pruning to 7.5%·min^{-1} for olive kernel, this means that each sample contains a different amount of lignin which overlaps the peak of cellulose. It is worth noting that the production of ash depends on the content of lignin in the sample.

The effect of heating rate is shown in Fig. 3. As can be seen, the increasing value of heating rate for the same sample causes a shift of the peaks on DTG/TG
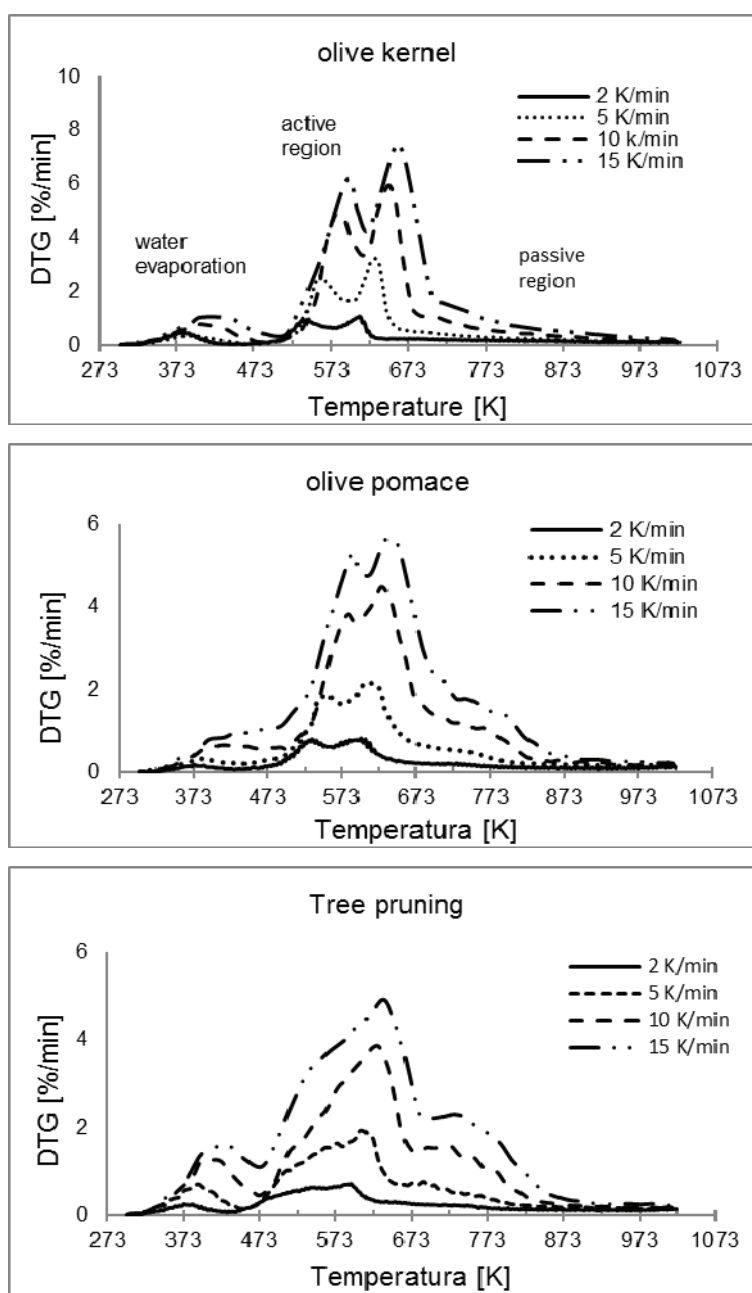

Fig. 3   DTG diagrams at different heating rates in nitrogen atmosphere.

plots in direction of higher temperatures. This fact can be explained on the basis of heat transfer limitation [27, 28] described also in the previous article [20]. On the other hand N. Yub Harun et al. [29] suggested that biomass structure is initially constrained and, at high heating rate, a finite time is required for the structure to relax and respond to the thermal input. This induction period may be responsible for pushing volatile evolution to a higher temperature.

4.2 Kinetic Analysis

The TG/DTG experimental data were used to perform the kinetic analysis. The kinetic parameters were determined using isoconversional (FWO), not-isoconversional (Kissinger) model-free methods and model-fitting (FC) method. The Kissinger plot of $\ln(\beta/T^2)$ versus $1,000/TK^{-1}$ and corresponding regression equations and the square of the correlation coefficient (R^2) are shown in Fig. 4. The kinetic parameters were found from the slope and intercept of a regression line. The activation energy and pre-exponential factor obtained from Kissinger methods are 145.54 kJ/mol and 8.84×10^{11} min^{-1}, 149.87 kJ/mol and 3.32×10^{12} min^{-1}, 130.03 kJ/mol
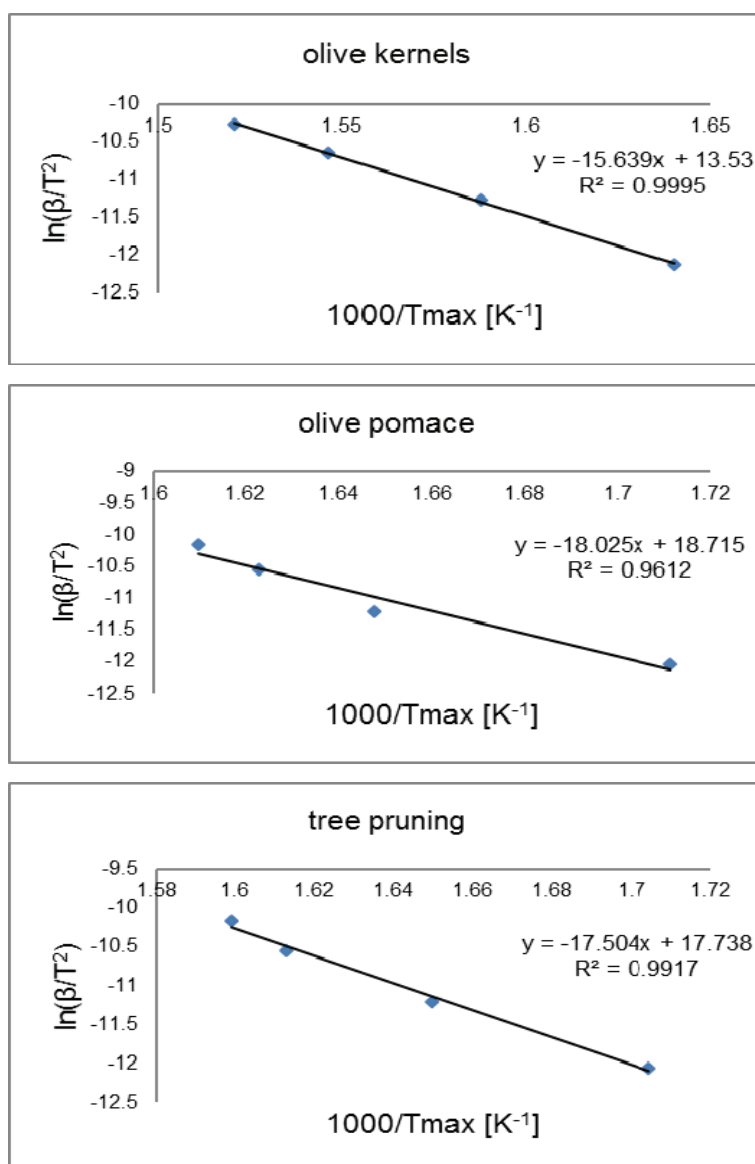
Fig. 4   Kissinger plots OWRs.

and 1.18×10^{10} min^{-1} for tree pruning, olive pomace and olive kernels, respectively.

In the model-free isoconversional method the kinetic parameters were calculated for a known value of the conversion, α. The change of the conversion with temperature for different heating rates is shown in Fig. 5. The kinetic parameters were calculated for different ranges of conversion contained in the interval from 0.1 to 0.7. The plots of FWO method for olive waste samples are shown in Fig. 6. From the regression lines of the plots the apparent kinetic parameters were

found. The pre-exponential factors were calculated from the intercept and activation energies from the slope of the line. The values of estimated kinetic parameters and correlation coefficients for FWO method are listed in Table 3.

The apparent activation energy calculated by FWO method was comprised between 26.58-214.94 kJ/mol for olive kernels 116.40-207.99 kJ/mol for olive pomace and 17.10-214.13 kJ/mol for tree pruning. As we can observe from Table 3, the apparent activation energy changes with different value of the conversion.
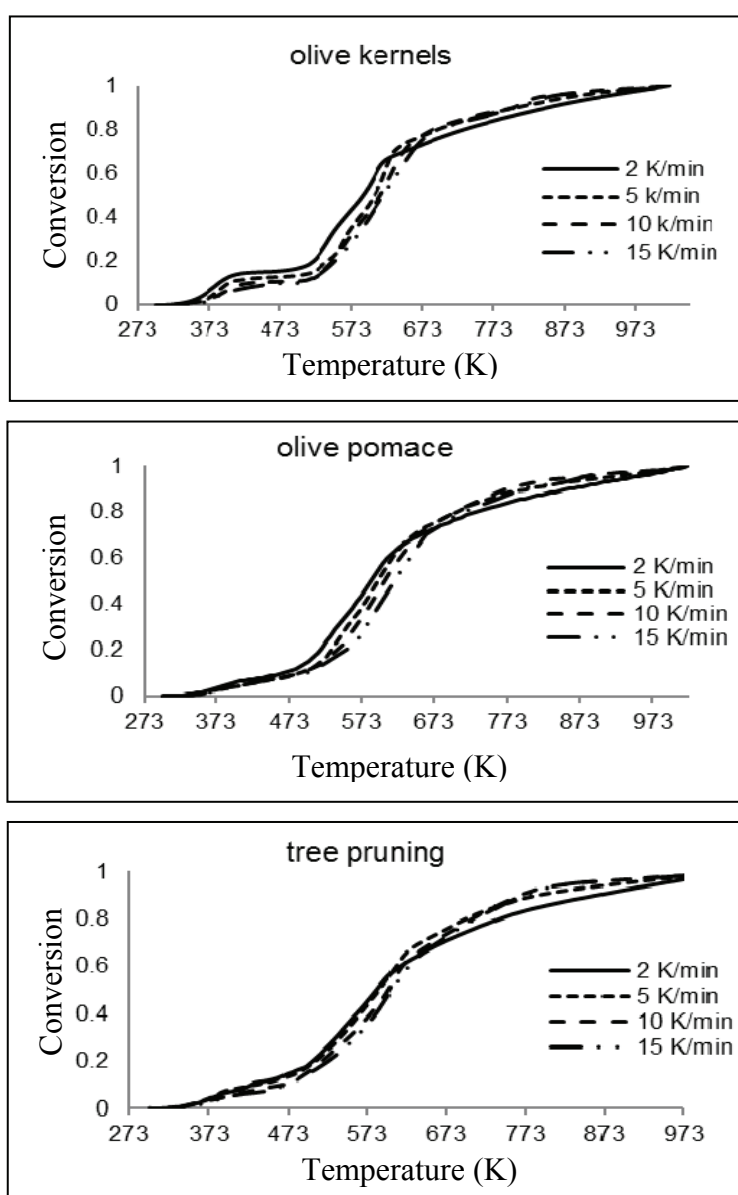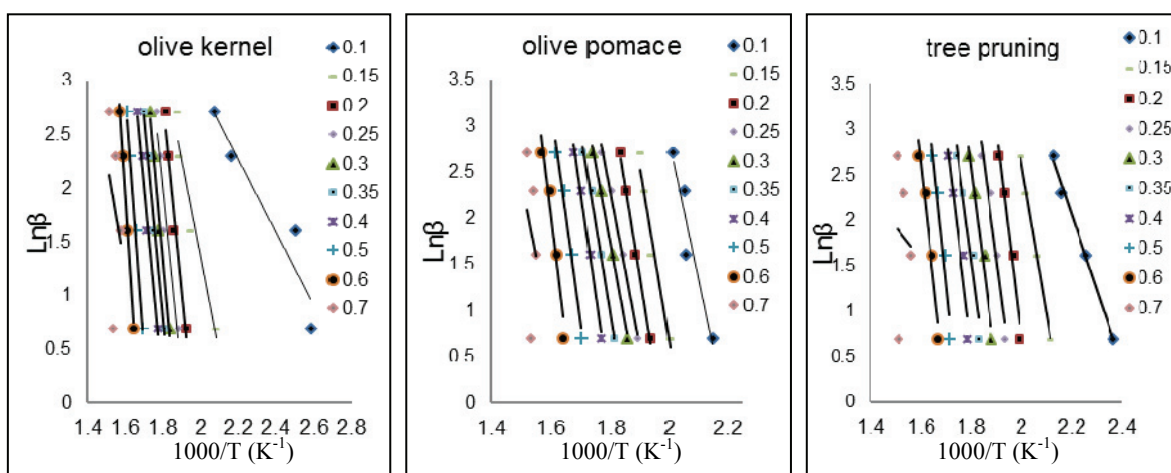

Fig. 5   Extent of conversion curves of OWR at different heating rates.

Fig. 6　FWO plots for different values of conversion.

Table 3　Kinetic parameters and correlation coefficient calculated by FWO method.

α	Olive tree pruning			Olive pomace			Olive kernels		
	E_α (kJ/mol)	A (min^{-1})	R^2	E_α (kJ/mol)	A (min^{-1})	R^2	E_α (kJ/mol)	A (min^{-1})	R^2
0.1	65.26	7.70E+04	0.9953	116.40	7.21E+09	0.9043	26.58	4.92E+00	0.9086
0.15	13259	3.21E+11	0.9985	153.48	7.30E+12	0.9504	70.25	2.40E+04	0.9369
0.2	185.38	2.08E+16	0.9626	153.28	2.18E+12	0.9932	137.48	3.75E+10	0.9616
0.25	177.50	7.63E+14	0.9456	128.01	2.87E+09	0.9888	136.86	1.53E+10	0.9038
0.3	171.88	6.31E+13	0.9734	135.41	8.31E+09	0.9909	152.29	2.33E+11	0.9720
0.35	168.31	1.01E+13	0.9400	149.29	8.96E+10	0.9939	146.20	3.62E+10	0.9770
0.4	183.04	1.06E+14	0.9326	169.80	4.02E+12	0.9873	146.44	2.11E+10	0.9862
0.5	212.97	1.10E+16	0.9267	187.91	3.66E+13	0.9696	188.33	3.3E+13	0.9947
0.6	200.66	2.38E+14	0.9372	207.99	5.59E+14	0.9157	214.94	2.3E+15	0.9927
0.7	26.57	3.30E-01	0.0087	119.78	5.44E+06	0.0603	82.5	6.1E+03	0.0887

This fact confirms that multi-step mechanisms with complex chemical reactions exist during the pyrolysis process.

In the model-fitting (FC) method to calculate the activation energy we need only one experiment performed at one heating rate. The plots of

$$Y' = \frac{\Delta\left[\log\left(\frac{d\alpha}{dt}\right)\right]}{\Delta\left[\log\left(1-\alpha\right)\right]} \quad \text{versus} \quad X' = \frac{\Delta\left(\frac{1}{T}\right)}{\Delta\left[\log\left(1-\alpha\right)\right]} \quad \text{for}$$

the three samples are given in Fig. 7.

The mathematical treatment of the experimental data was difficult. The main issue was selecting the appropriate straight line which best fits the points from TGA experiments. We note that the activation energy and reaction order calculated from different heating rates were significantly different from each other. The differences between various heating rates for the same sample are given in Fig. 8. For this reason we chose experiments performed at 10 K/min where calculated activation energy was similar to those of the other methods presented before. The activation energy obtained from Freeman-Carroll method is 158.54 kJ/mol, 143.31 kJ/mol, 123.95 kJ/mol for tree pruning, olive pomace and olive kernels, respectively.

The dependence of the activation energy on conversion of three olive waste samples is shown in Fig. 9. The activation energy for Kissinger method does not change with extent of conversion. The behavior is different in the case of the FWO method. Initially, the activation energy at low conversion value rises for all the examined samples. For the sample of olive kernel
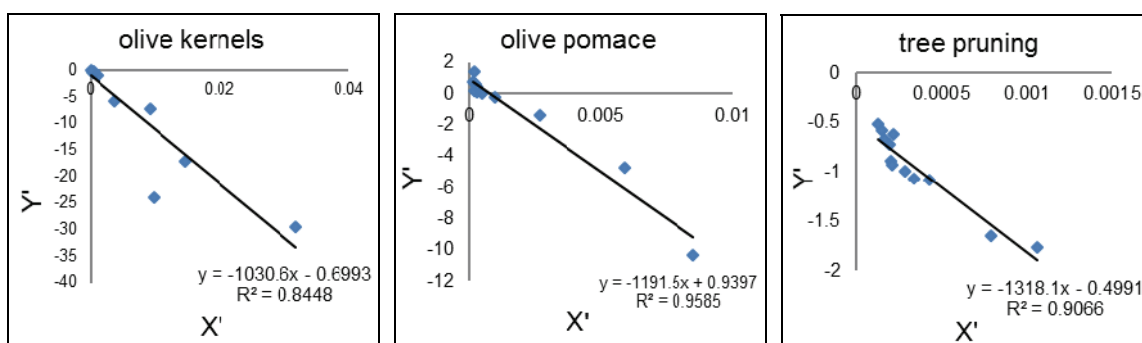
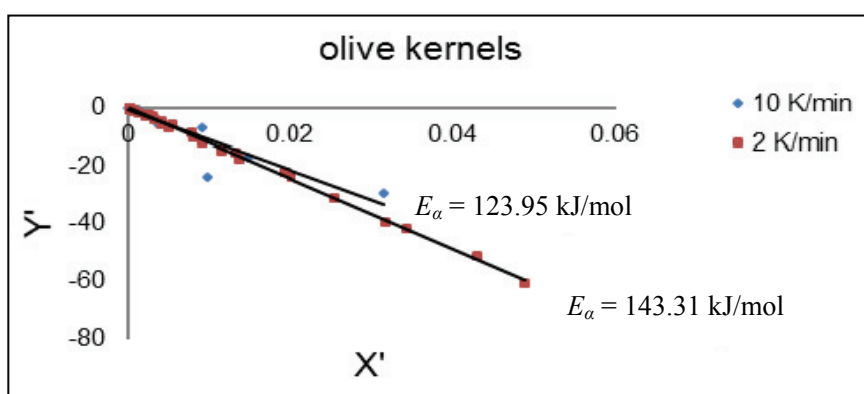**Fig. 7   Freeman-Carroll plots for different samples at heating rate 10 K/min.**

$E_\alpha = 123.95$ kJ/mol

$E_\alpha = 143.31$ kJ/mol

Fig. 8   Difference of activation energy between various heating rates in FC method for the same sample.
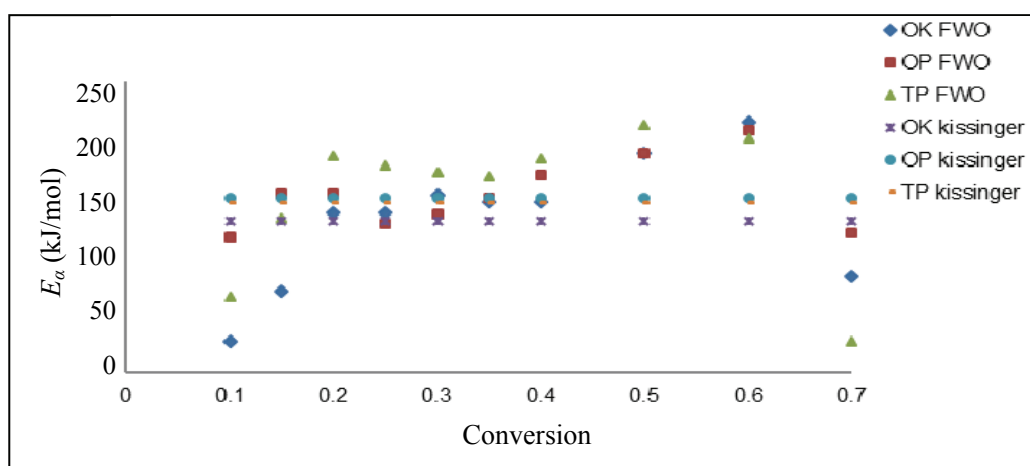

Fig. 9   Dependence of activation energy on conversion. Samples: OK-olive kernels, OP-olive pomace and TP-tree pruning.

we can note that three levels exist. In the first level the activation energy starts from about 26 kJ/mol to 137 kJ/mol, subsequently, in the second levels from 136 kJ/mol to 152 kJ/mol and in the third from 146 kJ/mol to 214 kJ/mol. Near the end of devolatilization process, activation energy drops to about 82 kJ/mol. In the case of olive pomace and tree pruning samples we have only two clearly visible levels. For olive pomace sample the

activation energy first increases from 116 kJ/mol to 153 kJ/mol then slightly decreases to value about 128 kJ/mol and again grows to about 209 kJ/mol ending with a decrease in activation energy at high value of conversion. Olive pomace sample was a similar course. At the start of the pyrolysis process, a low activation energy growth may indicate cleavage of weak chemical bonds. In this point, formations of some light volatile

Table. 4   Comparison of activation energy calculated by different model-free and model-fitting methods.

Sample	Kissinger		Flynn-wall-Ozawa (average value)		Freeman-Carroll	
	E_α (kJ/mol)	A (min^{-1})	E_α (J/mol)	A (min^{-1})	E_α (kJ/mol)	n
Olive kernels	130.03	1.18×10^{10}	130.21	2.06×10^{14}	123.95	0.7
Olive pomace	149.87	3.32×10^{12}	152.13	6.10×10^{13}	143.31	0.9
Tree pruning	145.54	8.84×10^{11}	152.41	3.30×10^{15}	158.54	0.5

Table 5   Comparison of activation energy with literature data.

	Sample	Condition	Method	Activation energy (kJ/mol)
	Olive kernel			130.2
Our work	Olive pomace	Nitrogen	FWO	152.1
	Tree pruning			151.2
Ounas [29]	No specified olive residue	Nitrogen	FWO	178.0
Aboulkas [16]	Olive residues (mixture of solid components)	Nitrogen	FWO	188.5

compounds occurs. With the progress of decomposition more activation energy is required by the system to break more stable molecules which contained covalent linkages and in Fig. 9 we can observe higher values of activation energy. When the pyrolysis is near the end more chemical bonds are broken. In the system the energy barrier is low because less stable molecules are present and we can observe a rapid decrease of activation energy.

The isoconversional methods are commonly used to calculate the activation energy and pre-exponential factor. The values obtained in our paper from different not-isoconversional, isoconversional model-free and model-fitting methods are in good agreement, see Table 4. The comparison of activation energy with those found in the literature for waste olive residues was slightly different, see Table 5.

In literature we found the kinetic parameters obtained from different methods and different experimental conditions. Above mentioned authors used different substrates input as mixed solid components or no specific olive residues. This difference causes that the kinetic parameters even calculated according to the same method and under the same condition may be significantly different from each other.

The not-isoconversional (Kissinger), isoconversional (FWO) model-free and model-fitting (FC) methods

allow estimating the kinetic parameters without knowing the reaction model. Furthermore, the isoconversional FWO method allows revealing the complexity of the pyrolysis process.

5. Conclusions

Thermal degradation experiments of OWR were investigated under a nitrogen atmosphere at different heating rates of 2, 5, 10 and 15 K/mol in temperature range from 298 to 1,023 K. From the thermal degradation results we can observe that the pyrolysis process occurs in three steps as evaporation, active and passive range. The mainly devolatilization range is enclosed in the region about 450-630 and 740 K for low and high heating rate. The increased values of heating rate for the same sample cause a shift of the peaks on DTG/TG plots in direction of higher temperatures.

The kinetic parameters were obtained by not-isoconversional (Kissinger), isoconversional (FWO) model-free and model-fitting (FC) methods. The activation energy and pre-exponential factor obtained by Kissinger method were invariant for the whole pyrolysis experiment. In the case of FC the activation energy differs with changes of the heating rate. In the case of FWO method the apparent kinetic parameters change with the extent of conversion. The isoconversional FWO technique revealed the "not

one-step" mechanism of reaction that occurs during the slow pyrolysis process compared to the not-isoconversional model-free and model-fitting method. Experimental results showed that the values of activation energy and pre-exponential factor are in good agreement.

There is little information about slow pyrolysis of non-mixed OWR based on model free and model-fitting methods in the literature. The isoconversional methods allow revealing the complexity of the pyrolysis process. The results obtained in nitrogen atmosphere may provide more useful information for engineers with a better and complete description of the pyrolysis process and can be helpful to predict the kinetic model.

Acknowledgements

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