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Kinetics of Thermal Decomposition of Egyptian Olive Tree Pruning Residues

Fatma M. Abosamra[1*]; A. M. Radwan[2]; Y. M. EL-Hadidi[1]; M. A. Hamad[2] and M. M. El kholy[3]

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[1]Agriculture Engineering Department, Faculty of Agriculture, Mansoura University
[2]Chemical Engineering and Pilot Plant Department, Engineering Research & Renewable Energy Institute, National Research Centre, El Dokki, Cairo, Egypt
[3]Agricultural Engineering Research Institute El Dokki ,Giza.

ABSTRACT

A kinetic study for the Egyptian olive tree pruning residues (OTP) was performed in a nano isothermal area and the temperature ranged from 200 to 750 ºC. The thermal behavior of OTP has been studied using a technique called (thermogravimetric analysis TGA), which measures the sample's weight loss rate as a function of temperature and time. The results of TGA showed the same results as those conducted in the proximate analysis. The study was conducted at various heating rates of 5,10 and 20 ºC/min. The TGA experiment measurement has been used to determine the kinetic parameters, including the order of reaction and activation energy. Olive tree pruning residues in this study reached the activation energy of (59.1- 62.8- 68.9) kJ/mol. A regression model square root coefficient of (0.9859, 0.9534, 0.9631) was obtained. The kinetic data obtained may provide more useful information for a better and complete description of the pyrolysis process and clarify the availability to gasify this agricultural residue.

Keywords: kinetics, olive trees pruning, agricultural residues, thermogravimetric analysis, activation energy.

INTRODUCTION

Biomass is an alternative energy source that reduces fossil fuel dependence (Wang *et al.*, 2016). Agricultural residues are considered byproducts of agricultural practices following different harvesting activities. Egypt produces 30-35 million tons of agricultural residues each year, with only 7 million tons used as animal feed and 4 million as organic manure. (Abou Hussein and Sawan, 2010).

Recycles of materials are recovered from agricultural residues by methods such as biogas technology, gasification, and composting. The utilization of field crop residues and animal wastes for non-traditional energy production is vast and provides sound theoretical knowledge and practical applications. One of the prospective energy sources for rural development with a focus on sustainability is the gasification process for the conservation of biomass. Via a high-temperature partial oxidation reaction, the thermal conversion technology known as "biomass gasification" turns biomass into a flammable gas. The syngas can be utilized to generate a wider range of outputs, including energy, heat and power, liquid fuels, and synthetic chemicals. Consequently, a variety of market demands can be satiated (Basu, 2006).

According to FAO, (2021), the amount of olives produced in Egypt in 2019 was almost 1.08 million metric tons. Martín-Lara *et al.*, (2017) mentioned that the residues resulting from pruning olive trees, which are represented by branches, leaves, and occasional fragments of the trunk, represent about 62% of the total agricultural waste.

Thermogravimetric analyses (TGA) is a powerful analytical technique for understanding the thermal properties of olive residues during pyrolysis. According to (Fernandes, 2014). TGA can be used to evaluate the thermal behavior of olive pruning, which is essential to optimize its utilization in biofuel production and other applications. TGA can provide essential information on the amount and type of organic compounds present in olive residues, their thermal stability, and degradation kinetics. Combining TGA with other techniques such as infrared spectroscopy can improve the understanding of the complex thermal behavior of olive pruning during pyrolysis, which is crucial for developing efficient pyrolysis processes for sustainable energy production.

Therefore, the main objective of this work is to determine the kinetic parameters of the pyrolysis of olive tree pruning waste in terms of reaction order, activation energy, and pre-exponential factor, which were developed from gravimetric pyrolysis measurements at heating rates of 5, 10 and 20 °C per minute.

MATERIALS AND METHODS

Materials preparation and characterization

Olive tree pruning (OTP) is an olive waste that is required for the maintenance and reshaping of olive trees. The OTP utilized in this work was taken from a plantation in Sharqia, Egypt, at Sekem Farm from a 4-year-old tree of the 'koroneikil' olive variety. Before performing TGA the raw materials were first dried using air and to homogenize the sample, it was ground using a crusher mill. In all of the experiments, 1 mm average particle size was used.

Physio-Chemical Characterization of Olive Pruning

Proximate analysis:

According to ASTM, proximate analysis is the determination of moisture, volatiles, fixed carbon, and ash

*** Corresponding author.**
E-mail address: fatmaabosamra33@gmail.com
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using standard methods as shown in Table (1) . The moisture content was determined using the oven-drying method (ASTM, 2010). It has been determined in 3 replicates with 3 crucibles whereas a crucible was weighted, then 50 g samples were placed in the crucible and the crucible and sample were weighed. Each crucible and 50 g sample were then placed in an air-forced drying oven and kept at 105°C until a constant weight was achieved. The crucible containing the dried sample was cooled to room temperature in a desiccator and then weighed. The moisture content was calculated on a wet basis as follows:

$$MC = \frac{WW - DW}{WW} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(1)}$$

Where:

MC = the moisture content (%)
WW = the wet weight of the sample and crucible (g)
DW = the dry weight of the sample and crucible (g)

According to the UNE-EN 14775 standard, which is used for solid biofuels, the ash content has been determined. The method specified in UNE-EN 15148, which is appropriate for solid biofuels, was used to determine the volatile content. It was then decided how much carbon was determined.

Table 1. Proximate analysis of olive tree pruning (%w. b).

Moisture (MC) %	Volatiles (VM) %	Fixed carbon (FC) %	Ash %
8.4	71.8	17.9	1.9

Elemental analysis:

An elemental analyzer CHNS (model: Flash 2000, Serial no: 2015.F0028) has been utilized to analyze the elemental composition (C, H, N, S, O) of samples as illustared in Table (2). It is based on organic samples flash combustion, which allows for the simultaneous determination of percent carbon, hydrogen, nitrogen, sulfur and oxygen in 15 minutes. This analysis was carried out at the Mansoura University laboratory.

Table 2. An analysis of the pruning of olive trees.

C (%)	H (%)	N (%)	S (%)	O (%)
46.52	5.94	1.35	0	46.19

Chemical analysis: Composition (%, wt.).

Table 3. Chemical analysis of olive tree pruning.

Hemicellulose	Cellulose	Lignin
19.7	36.6	20.8

Based on the ultimate analysis, the molecular formulas of the biomass wastes were calculated to be $CH_{1.5}O_{0.74}$. It is apparent from both molecular formulas that the fundamental structure of the biomass residues does not significantly vary.

The Higher Heating Value (HHV) of the chosen biomass was calculated based on the concluded analysis using the formula below, which was mentioned by Parikh *et al.* (2005).

HHV= 0.3536 FC + 0.1559 VM – 0.0078 ASH, [MJ/kg].. (2)

Table 4. The heating value of Olive tree pruning.

Biomass	Molecular formula	HHV (MJ/kg)
Olive trees pruning	CH1.5O0.74	17.320

Thermogravimetric analysis:

A method of thermal analysis known as thermogravimetric analysis allows for the observation of changes in a material's physical and chemical properties as a function of temperature. As the material is heated, weight loss is measured. The measurement yields information on the biomass's thermal stability and volatile content. (Fernandes, 2014).

Decomposition starts depending on the type of biomass, particularly its cellulose and lignin content. (Khalideh *et al*., 2017).

Thermogravimetric analysis TGA was performed on olive tree pruning residue at heating rates of 5, 10, and 20 ºC/min, with an ultimate heating temperature of 750 ºC in a nitrogen atmosphere. The kinetic parameters of the thermochemical degradation are found by implementing the TGA measurements.

Kinetic analysis

Kinetic parameters Ko and E for olive tree pruning were estimated using the TGA results and the weight observed loss over a wide temperature range. According to the equations listed by Marini *et al.* (1979), the reaction was assumed to be first order, and the parameters were estimated in accordance with them.:

$$da/dt = k(1-a)n \ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3)}$$
$$k = kioe^{-E/RT}$$

Where:

a=(V*-V/V*) is the percentage of the products of the volatile produced,
K is the Arrhenius kinetic constant,
V and V* are the initial and ultimate yield of the volatile products during the reaction,
n is the reaction order,
E is the activation energy (KJ/mol).

Temperatures ranging from 200 to 500 °C were used in the kinetic analysis, which was conducted in the non-isothermal region of the TGA curves. The analysis of the differential equation in Equation (3) usually leads to Equation (4), a linearized form from which E and Ki are calculated as follows:

$$\log\left(-\log\left(1-\frac{a}{T2}\right)\right) = -\frac{E}{2.303} * \frac{1}{T} + Log\left(\frac{KiR}{qE}\right) \mathbf{(4)}$$

The TGA diagrams demonstrate that for residuals from olive tree pruning, there are two overlapping zones where devolatilization reactions take place between 200 and 500 °C.

RESULTS AND DISCUSSION

The thermogravimetric analysis results for the Egyptian olive tree pruning residue at various heating rates of 5,10, and 20 ºC/min are listed in Tables 5 - 10 and Figures 1 - 3. These measurements were utilized to calculate the reaction kinetic parameters of OTP residue.

Table (5) provides results of the thermal degradation of olive tree pruning residue at a rate of 5 ºC/min; weight losses are plotted against the temperature increase. When the temperature reached 200 ºC, the decomposition process began, but the rate of decomposition was slow. Following the observation of a higher thermal decomposition. The olive tree pruning residuals exhibit significant thermal decomposition at temperatures over 500 ºC for the pyrolysis and gasification process, with weight loss ranging from 40.8 at 500 ºC to 33.3 at 750 ºC.

Eq. (4) was plotted for the case of first-order reaction assumption, obtaining a straight line with R^2 of 0.9859. As a result, the assumption of the first-order reaction has been demonstrated here. According to the slope of the line, the activation energy of olive tree pruning residue breakdown was 59.1 kJ/mol.

Table 5. TG analysis of OTP at a heating rate of 5 °C/min:

T, ºC	Wt, %
200	103.5
260	94.2
300	78.8
351	50.7
400	45.9
450	42.8
500	40.8
550	39.2
650	35.3
750	33.3

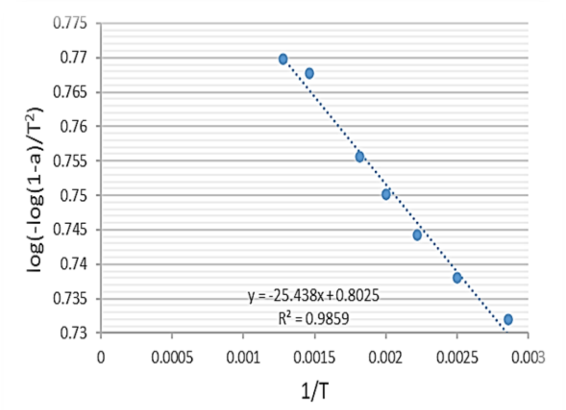

Fig. 1. The order of decomposition reaction in olive trees pruned at a heating rate of 5 °C/min.

Table 6. Kinetic parameters of olive trees pruning residues thermal decomposition reaction.

N	E (kJ/mol)	R^2
1	59.1	0.9859

Table 7. TG analysis of OTP at the heating rate of 10 °C/min:

T, ºC	Wt, %
200	92.0
250	85.7
300	70.2
350	44.1
400	34.5
450	29.5
500	26.3
550	24.6
650	21.5
750	20.0

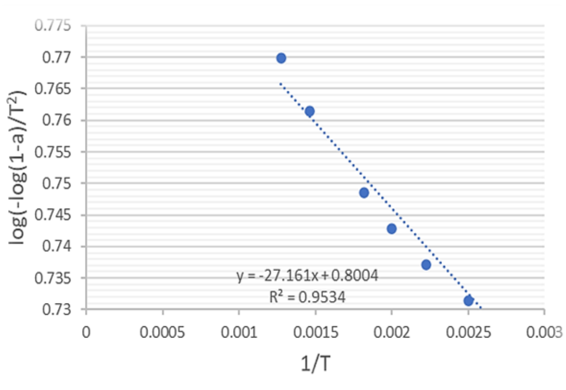

Fig. 2. The order of decomposition reaction in olive trees pruned at a heating rate of 10 °C/min.

Table 8. Kinetic parameters of olive trees pruning residues thermal decomposition reaction.

N	E (kJ/mol)	R^2
1	62.8	0.9534

Table 9. TG measurements of OTP at 20 °C/min:

T, ºC)	Wt, %
200	93.7
250	86.9
300	73.8
350	54.6
400	42.6
450	35.1
500	30.4
550	28.6
650	26.5
750	25.1

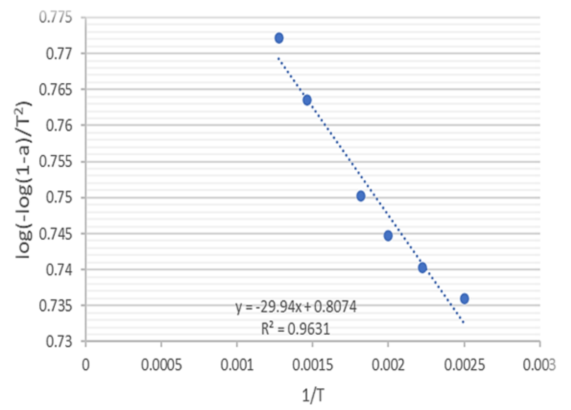

Fig. 3. The order of decomposition reaction in olive trees pruned at a heating rate of 20 °C/min.

Table10. Kinetic parameters of olive trees pruning residues thermal decomposition reaction.

n	E (kJ/mol)	R^2
1	68.8	0.9631

CONCLUSION

The results of thermogravemtric analysis TG for Olive tree pruning resiues has been investigated via a kinetic study. The thermal decomposition appears to follow the first order reaction mechanism. The attained kinetic parameters, particularly the activation energies, indicate that relatively high activation energy is needed to gasify this agricultural residue. That may be attributed to the low heating rate (5oC/min). On the other side, the heating values of this agricultural residue are reasonably high. Accordingly, OTP can be appropriate energy source via gasification process provided that high heating rates are used.

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حركية التحلل الحرارى لمخلفات تقليم الزيتون المصرى

فاطمة أبو سمره[١]، على رضوان[٢]، ياسر الحديدى[١]، محمد حمد[٢] و محمد الخولى[٣]

[١]قسم الهندسة الزراعية – كلية الزراعة – جامعة المنصوره
[٢]قسم الهندسة الكميائيه والتجارب نصف صناعيه – المركز القومى للبحوث
[٣]معهد بحوث الهندسة الزراعية - الدقى

الملخص

تم إجراء دراسة حركية تفاعل مخلفات تقليم شجر الزيتون المصرية في منطقة نانو متساوية الحرارة وتراوحت درجة الحرارة من ٢٠٠ إلى ٧٥٠ درجة مئوية. تمت دراسة السلوك الحراري للمخلف عن طريق قياس معدل فقدان الوزن للعينة كدالة للوقت ودرجة الحرارة (التحليل الحراري الوزني TGA). وكانت نفس نتيجة التحليل التقريبي. أجريت الدراسة بمعدلات تسخين مختلفة باستخدام ٥ ، ١٠ ، ٢٠ درجة مئوية / دقيقة. تم تحديد المعلمات الحركية (ترتيب التفاعل وطاقة التنشيط) من قياس تجربة التحليل الحراري الوزني (TGA). أشارت النتائج الحركية إلى أن التحلل الحراري هو تفاعل من المرتبة الأولى للتفاعلات الكيميائيه. تراوحت قيم طاقة التنشيط للتفاعل عند المعدلات الحرارية المستخدمة الى (٥٩,١-٦٢,٨-٦٨,٩) كيلوجول / مول لمخلف تقليم شجر الزيتون. بلغ معامل الانحدار التربيعي للجذر التربيعي (٠,٩٨٥٩، ٠,٩٥٣٤، ٠,٩٦٣١). وتعتبر قيم طاقة التنشيط منخفضة ، مما يحدد سهولة الاحلال الحراري والتغويز لمخلفات تقليم شجرة الزيتون المصرية.