Sustainable Valorization of Olive Pomace Waste to Renewable Biofuels, Biomaterials and Biochemicals Via Pyrolysis Process: Experimental and Numerical Investigation

Mohamed Hechmi Aissaoui (✉ amohamedheshmi@gmail.com)

Universite de Tunis El Manar Faculte des Sciences de Tunis <https://orcid.org/0000-0003-0069-5634>

Aïda Ben Hassen Trabelsi

Centre de Recherches et Technologies de l'Energie

Gmar Bensidhom

Centre de Recherches et Technologies de l'Energie

Selim Ceylan

Ondokuz Mayıs Üniversitesi: Ondokuz Mayıs Üniversitesi

James.J Leahy

University of Limerick

Witold Kwapinski

University of Limerick

Research Article

Keywords: Pyrolysis, olive pomace wastes, DAEM model, kinetics, biofuels, biofertilizers

Posted Date: September 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-831293/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Sustainable valorization of olive pomace waste to renewable biofuels, biomaterials and biochemicals via pyrolysis process: experimental and numerical investigation

Mohamed Hechmi Aissaoui^{1,2}, Aïda Ben Hassen Trabelsi¹, Gmar Bensidhom¹, Selim Ceylan³, James J Leahy⁴; Witold Kwapinski⁴

¹Research and Technology Centre of Energy, Technopôle Borj-Cédria, B.P N°95, 2050, Hammam-Lif, Tunisia.

² Faculty of Sciences of Tunis, Tunis El Manar University, Campus Universitaire El-Manar, 2092, El Manar, Tunisia.

³ Ondokuz Mayıs University, Faculty of Engineering, Chemical Engineering Department, 55139, Kurupelit, Samsun, Turkey.

⁴Department of Chemical Sciences, University of Limerick, Bernal Institute, V94 T9PX Limerick, Ireland.

Corresponding author: amohamedheshmi@gmail.com

Highlights:

- Slow pyrolysis of OPW was conducted using a fixed-bed reactor and a TGA apparatus
- The released permanent gases show an interesting LHV up to 11 MJ/Kg
- The biochar characteristics and composition emphasize its use as fertilizer
- The activation energy (Ea) ranged from 121.6 to 151.6 kJ/mol

Abstract

This work demonstrates, experimentally and numerically, the potential of Olive Pomace Waste (OPW) to produce renewable biofuels (pyrolytic oil and gas), bio-chemicals (tars as source of bioactive molecules) and bio-fertilizers (chars) through slow pyrolysis. Experimental pyrolysis runs were conducted at 500, 600 and 700 °C as final pyrolysis temperature, 15, 20 and 25 °C/min as heating rate and 1h as residence time, in a fixed bed pyrolyzer. In the optimum pyrolysis conditions (600°C and 15°C/min), 33 wt.% of oil, 30.00 wt.% of char and 37 wt.% of gas were produced. Recovered pyrolytic oil presents good energy value (HHV between 15.96 and 20.94 MJ/kg) with a great bioactive potential. The released permanent gases show an interesting energy content (LHV up to 11 MJ/Kg) which emphasizes their application in a gas engine to provide renewable electricity in rural olive groves area. The recovered OPW biochar presents a high carbon (C 72.54 wt.%) and nutrients contents (up to 8.42 mg/g of Ca, up to 8.69 mg/g of K and up to 2.02 % of total N) which make it suitable for soil amendment and for long-term carbon sequestration. Kinetic study of OPW pyrolysis, performed using the Distributed Activation Energy Model (DAEM), gives an activation energy values ranging from 121.6 to 151.6 kJ/mol. The investigation of the OPW thermal behavior and reactivity under pyrolysis conditions is useful approach to design and operate slow pyrolysis process at commercial scale, which could be useful by farmers for OPW in olive fields.

Keywords: Pyrolysis, olive pomace wastes, DAEM model, kinetics, biofuels, biofertilizers

1. Introduction

As a signing party to the 2015 Paris Climate Agreement (COP21), Tunisia has committed to reduce its greenhouse gas emissions, especially in energy sector, with the integration of renewable sources of energy, with a target of at least 30% of Tunisia's total electricity produced by renewable energy sources in 2030. Among promotive and available renewable resources, biomass and bioenergy from agricultural residues present great potential in Tunisia with an estimated contribution around 1.6 Mtep per year, around 10% of the national needs for primary energy especially for traditional applications in rural regions (cooking, heating, baking needs...)(Haddad 2016).

Among Tunisian agricultural by-products, Olive Pomace Waste (OPW) – which are the one of the largest available biomasses in Tunisia – are produced in large quantities (around 400 000 tons per year (Mekki et al. 2008)) since Tunisia is the second largest producer of olive oil after the EU, contributing to around 6% of total production and 18% of global exports by volume (IOC 2017). The management of olive oil industry residues such as OPW is a typical problem in Tunisia and in other Mediterranean countries and the use of these agricultural residues to produce biofuels and biochemicals facilitates the OPW management in these countries and improves the transition to an efficient circular bio economy based on waste.

These OPW are heterogeneous mixture of olive skin, pulp (70-90%), stone (9-27%) and olive seeds (2-3%). The OPW are usually valorised as organic fertilizer via composting (Ameziane et al. 2020; Tsivas et al. 2021) or through direct spreading in agricultural land (Innangi et al. 2017), as source of nutrients and active molecules (Mallamaci et al. 2021; Ribeiro et al. 2021), or also as chemicals feedstock (Paz et al. 2020). The OPW were also reused for crude oil production (Pasqualone et al. 2016). The energy recovery of OPW can be performed by alcoholic fermentation for bioethanol production (López-Linares et al. 2020) or by anaerobic digestion for biogas production (Timpanaro

et al. 2021), or by thermochemical processes which involve combustion, gasification and pyrolysis (De la Torre Maroto et al., 2020; Dorado et al., 2021; Nunes et al., 2020). Knowing the OPW low biodegradability and the high content of organic matter, the thermochemical conversion of these residues has several advantages over conventional biochemical processes as it helps to reduce the process costs by producing economic-value products applicable in several fields: energetic as biofuels, agronomic as biofertilizers and chemical as source of bioactive molecules. Pyrolysis, which is the primary step of all thermochemical processes, is a successfully commercialized technology, which can be suitable for the complete conversion of OPW into liquid (pyrolytic-oil), gaseous (gas) biofuels and solid biochar.

Thermogravimetric analysis TGA is applied as a numerical instrument widely used to evaluate kinetic and thermodynamic parameters as well as the impact of different main variables such as temperature, heating rates, and raw material. Many mathematical models have been established to explain the pyrolytic decomposition of biomass using isothermal and non-isothermal TGA measurements. The Distributed Activation Energy Model (DAEM), proposed by (Vand 1943) and summarized by (Miura 1995), suggests that the several heterogeneous chemical reactions that occur during pyrolysis exist simultaneously as irreversible first-order parallel reactions of various rates. This study examines the thermal degradation action, kinetics, and thermodynamics of OPW using the DAEM with the help of thermogravimetric analysis TGA at different heating rates (5, 10 and 20°C/ min).

During last decades, several studies have been accomplished concerning OPW pyrolysis. Table 1S (given as supplementary material) summarizes the most important studies performed on OPW pyrolysis. As it can be observed from literature given in Table 1S, all previous studies focused on the production of biochar and the detailed characterization and application of these chars. Pellerá et al (Pellerá and Gidarakos 2015) studied the effects of biochar produced by dried olive pomace

pyrolysis at 400°C and 700°C on the as soil amendments for cadmium and nickel immobilization and reported that the addition of biochar to soil caused an increase in soil pH and organic matter content. In another study, (İlay 2020) investigated the conversion of OPW in terms of biochar yield, properties, leaching experiment and soil use. Other studies (Aydemir 2014; Khalideh Al bkoor Alrawashdeh et al. 2017; Surahmanto et al. 2020) were interested to the evaluation of the potential for energy production through thermogravimetric analyses and/or through mathematical modelling.

To the best of the authors' knowledge, so far, there is no complete experimental and numerical study on OPW pyrolysis for the simultaneous production of biofuels (bio-oil and gas) and biomaterials (biochar). Besides, in Tunisia, OPW recovery via pyrolysis for bioenergy applications is still unknown or not investigated. Thus, this work could be considered as an innovative way to convert OPW into biofuels, biochemicals and biofertilizers. It aims to evaluate, experimentally and numerically, the potentiality of energy valorization of Tunisian OPW through slow pyrolysis process, to recover biofuels (pyrolytic oil and combustible gas) and to recover biomaterials and biochemicals in forms of bioactive molecules from pyrolytic oil and renewable nutrients from biochar.

2. Material and methods

2.1. Batch pyrolysis plant and Rock-Eval pyrolysis

The pyrolysis facility used in this study is a batch laboratory scale pyrolysis plant developed in the Research and the Technology Centre of Energy (CRTEn – Tunisia). The layout of the pyrolysis plant, the detailed procedure of the pyrolysis test and the obtained products yields calculation were advanced by (Trabelsi et al. 2017). Operating parameters were chosen based on TGA/DSC tests as follows: final pyrolysis temperature of 500, 600 and 700°C; heating rate (HR) of 15°C/min, 20

°C/min and 25 °C/min. During pyrolysis experiment, the reactor is continuously flushed with nitrogen (0.3 l/min). Pyrolytic oil and biochar yields are determined as indicated in Eq. 1.

$$\text{pyrolytic oil or Biochar yield (wt. \%)} = \frac{\text{Mass of liquid or char}}{\text{Mass of raw material}} \times 100 \quad (1)$$

The syngas yield was determined by difference as indicated in Eq. 2:

$$\text{Syngas (wt. \%)} = 100 - (\text{pyrolytic oil (wt. \%)} + (\text{biochar (wt. \%)})) \quad (2)$$

The Rock-Eval® pyrolysis – which is a basic method for the evaluation of petroleum source rock potentiality in organic geochemistry field – was applied in this study in order to evaluate the potential of OPW to produce thermovaporizable hydrocarbons through pyrolysis process, to estimate the maximum temperature of thermal cracking in inert medium. For this purpose, 17.9 mg of the powdered OPW sample was introduced into a steel nacelle. The IFP 160000 sample was used as an external standard. The analytical conditions for the used Bulk Rock method are as follow: the first step which is a pyrolysis step under inert conditions (N₂) started at T1 = 300 °C. T1 was maintained as a plateau for 3 minutes. Then, from initial T1, the temperature was programmed to increase at a HR 25 °C/min, up to T2 = 650 °C. T2 was maintained as a plateau for 3 minutes. During this step, the thermovaporizable hydrocarbons are released, detected and measured by a flame ionization detector (FID). Thereafter, the nacelle containing the pyrolysis residue is transferred by means of an autosampler into the combustion furnace (air as oxidant agent), under a gradual increase in temperature from 300 °C to 850 °C with a HR 20 °C/min. CO and CO₂ gases released during pyrolysis and combustion are continuously detected by infrared cells.

2.2.Feedstock and products characterization

OPW samples were provided by a modern unit of olive oil extraction, "Ben Yedder" triphasic centrifugal olive mill, located in Mannouba (near Tunis, Tunisia). The collected samples were first

air-dried and then characterized with their biochars, using proximate analyses according to standard methods (AFNOR, 2010) : (i) AFNORXP CEN/TS 14774-3 for moisture content, (ii) AFNOR XP CEN/TS 14775; ASTM method D-1762-84, ASTM, 1990 for ash content and (iii) ASTM method D-1762-84, 1990 for volatile matter (VM) content. The fixed carbon (FC) content was obtained as indicated in Eq. 3:

$$FC = DM - (VM + Ash) \quad (3)$$

FC: Fixed Carbon content (%); DM: Dry Matter content (%); VM: Volatile Matter content (%), Ash: ash content (%).

The ultimate composition of OPW and their biochars was determined according to ASTM D5373-13 (ASTM, 2008), by means of a Perkin Elmer 2400 model CHN analyzer. The oxygen (O) content was calculated by difference as indicated in Eq. 4:

$$O \text{ (wt. \%)} = 100 - (C + H + N + Ash) \quad (4)$$

The OPW high heating value (HHV) and Low Heating Value (LHV) were calculated according to (Sheng and Azevedo 2005) and (Oyebanji et al. 2018), respectively as indicated in Eq. 5 and 6:

$$HHV \text{ (MJ/kg)} = -0.3675 + 0.3137 C + 0.7009 H + 0.0318 O \quad (5)$$

$$LHV \text{ (MJ/kg)} = HHV - (2.442 \times 8.936 (H/100)) \quad (6)$$

The inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is performed using Agilent® 5100 ICP-OES Spectrometer in order to evaluate the potential of OPW and its biochar as soil amendment. The analyzed elements were Al, Ca, Fe, Mg, K, P, Na, Si. For each sample 0.2 g was calcined at 450 °C for 3h, then the cooled ash was stirred for 16 h with 20 ml of 3.5 M HCl. The mixture was then centrifuged at 4000 tours/min for 15 min and filtered using 0.45 µm filters as described by (Ghanim et al. 2018) and their concentration was calculated as the average of three determination.

The raw material, biochar, and pyrolytic oil were FTIR spectroscopically analyzed using a Perkin Elmer Spectrum BX spectrophotometer in absorbance mode between 4000 and 400 cm^{-1} , on pellets made of a mixture of pre-dried OPW and 0.2 g KBr with a ratio of (1: 5 OPW: KBr). The FTIR characterization was performed to identify the main functional groups (phenols, alcohols, aliphatics, aromatics, among others) contained in the studied biomass and after thermal treatment to investigate the main components variation.

Pyrolytic-oil molecular composition was carried in two steps: (1) a silylation step using BSTFA (N,O-Bis(trimethylsilyl) trifluoroacetamide and 100 μl of TMCS (Trimethylchlorosilane) as derivatization reagent in these conditions: 10 mg of pyrolytic-oil was mixed with 100 μl of BSTFA. The solution was then mixed on vortex and putted in a bain-marie at 70 $^{\circ}\text{C}$ during 1 hour. (2) GC/MS molecular analysis of using an Agilent 7890A GC equipped with Agilent 5975C massive-selective detector (MSD). The capillary column is a HP-5MS (5% diphenyl 95% dimethylpolysiloxane) capillary column (30 m $\times$ 0.25 μm film thickness). The oven temperature program is as follows: initial temperature of 70 $^{\circ}\text{C}$ during 2 min, then a temperature increase from initial temperature to 300 $^{\circ}\text{C}$ with a HR 7 $^{\circ}\text{C}/\text{min}$ and finally an isotherm of 10 min at 300 $^{\circ}\text{C}$. The injector temperature is about 250 $^{\circ}\text{C}$. Helium is the vector gas with a flow rate around 1 ml/min. The identification of compounds is determined according to the NIST database.

The following AFNOR criteria were used to characterize the bio-oil fuel properties: acidity index (ISO 6618, acid-base titration method); ash content (NF T 60-111, calcination method); HHV (NF M07-030 using an oxygen bomb calorimeter); color (ISO 2049) and flash point (ISO 2719. 2002).

The non-condensable gases were first cleaned using a water bubbler to remove the tars, then an activated carbon column to adsorb the remaining dust and particles and finally a set of gas filters before the analysis. A syngas analyzer (GEIT 3160 model) equipped with an IR detector for CO, CO₂, CH₄, C_nH_m tests, a thermal conductivity detector (TCD) to calculate H₂, and an

electrochemical cell for O₂ measurements are used to measure and monitor online the chemical composition of syngas.

2.3. Thermal analysis

Thermodynamic analysis was done using the thermogravimetric analysis TGA/DSC (TA instruments Q600) to investigate the mass loss mechanism of OPW. After placing the sample in the TGA, the temperature was increased from room temperature to 1000°C at the several HRs 5, 10 and 20°C/min. Throughout the procedure, continuous flow nitrogen at 100 ml/min was used.

2.4. Kinetic analysis via distributed activation energy analysis model

The DAEM is widely used as a convenient method to identify the thermal kinetic parameters and the complex reactions that occur during pyrolysis of biomass (Yaras et al. 2021). For lignocellulosic materials, the DAEM investigated the totality of volatiles released or the amount of an individual volatile constituent. The DAEM presents a great harmony with the experimental data to understand the pyrolysis kinetics of biomass especially at low HRs (Qi et al. 2021). DAEM involves parallel, dependent and first-to-n-order reactions with activation energies, and various activation energies reveal the binding properties of biomass components. The DAEM method assumes that all reaction activation energies have the same pre-exponential factor k_0 at the same conversion rate, and the activation energies have a continuous distribution.

The devolatilization process can be explicit in this way Eq. 7:

$$1 - V/V^* = \int_0^\infty \exp\left(-\frac{k_0}{\beta} \int_0^t e^{-E/RT} dT\right) f(E) dE \quad (7)$$

The DAEM represents the change of the total volatile matter of the solid where V is the volatile matter content at the absolute temperature T when the HR is β , V/V^* is the effective volatile matter content of the solid (V^* is the effective volatile content at any time t), and k_0 is the frequency factor

corresponding to the given E value. f(E) is the activation energy distribution curve, which encapsulates the range and change of the activation energy of the first-order irreversible reaction at the same time.

Miura and Maki.(Miura 1995) have simplified distribution function as indicated in Eq. 8:

$$v / v^* = 1 - \int_{E_a}^{\infty} f(E_a) dE_a = \int_0^{E_a} f(E_a) dE_a \quad (8)$$

The DAEM Eq. obey to Arrhenius Eq. law and is simplify in this way Eq. 9:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{Rk_0}{E_a}\right) + 0.6075 - \frac{E_a}{R} \frac{1}{T} \quad (9)$$

The activation energy E_a and related frequency factor in eq.(9) are calculated using three unique TGA curves, each with its unique HR, by graphing the natural log of (a/T^2) vs inverse temperature at different conversion (V/V^*) values. As a result, the activation energy obtained from the Arrhenius plots base on Eq. 9 represents amount of solid pyrolysis degradation.

3. Results and discussion

3.1.OPW characteristics

The OPW proximate parameters are summarized in Table 1. OPW presents a high VM content about 73 wt.% on dry basis which shows the promoting potential of devolatilization of the biomass (Alcazar-Ruiz et al. 2021) and relatively low ash content (about 2%) compared to other olive residues reported in literature (Dorado et al. 2021) (Table 1). The OPW moisture content as received is about 10.44 wt.% and it reaches 3.44 % after air-drying, which is tolerable for thermochemical conversion via pyrolysis process since moisture content is one of the main parameters in biomass pyrolysis, because it inhibits the process if it surpasses 10% by weight (Alcazar-Ruiz et al. 2021).

The CHN-O elemental composition of studied OPW reveals high carbon and hydrogen contents (C 47.3 wt.% and H 6.6 wt.%, respectively) which are comparable to those reported in previous studies ((Khalideh Al bkoor Alrawashdeh et al. 2017; Dorado et al. 2021), Table 1). The OPW nitrogen content is relatively high compared to other lignocellulosic biomass indicating the potential use of the residual pyrolytic char as nutrient-rich fertilizer. Based on the CHN-O elemental composition, the calculated HHV of OPW is around 20.48 MJ/kg (Table 1), which is comparable to those reported for other olive pomace substrates (20.30 MJ/kg, (Aydemir 2014); and 19.88 MJ/kg; (Khalideh Al bkoor Alrawashdeh et al. 2017). To be used as solid fuel directly, a thermal treatment step (such as a slow pyrolysis) is required to enhance the POW calorific value.

OPW mineral composition, given in Table 1, reveals the richness of OPW with K (6.46 mg/g of sample) and Ca (4.64 mg/g of sample). The concentrations of other elements are ranging from 0.21 mg/g of sample for Na to 0.43 mg/g of sample for P. The high amounts of K and Ca emphasize the use of the obtained biochars as nutrient rich amendment. Besides, the occurrence of inorganic minerals in raw biomass could be an important factor to consider because some minerals especially the alkali (K, Na, etc.) and alkaline- earth metals (Mg, Ca, etc.) could have acted as catalysts during thermal process (Dinc and Yel 2018; Alcazar-Ruiz et al. 2021). While studying the effect of inorganic metals (K, Mg and Ca) on thermal degradation of lignocellulosic biomass, reported that the K contained in the lignocellulosic biomass has a catalytic effect by favoring solid char formation and by decreasing bio-oil yield, whereas Mg and Ca have some effects on the biomass degradation rate. In the case of OPW, the high content of K leads these substrates suitable for char production whereas the presence of Ca seems to not giving changes in the formation of pyrolytic compounds (Eom et al. 2012).

The pre-dried OPW FTIR spectrum given in Figure SI 1 shows a large band centred on 3369 cm^{-1} attributed to the stretching vibration of O-H contained in phenols and alcohols. Then, two intense

peaks at 2921 cm^{-1} and 2852 cm^{-1} could be related to the stretching vibration of C–H in the lignin structure (Fan et al. 2017) and also to methylene and methyl groups of fatty acids since OPW contains remaining olive oil. The weak peaks centered on 1436 and 1379 cm^{-1} correspond to the asymmetric bending of C–C in the lignin structure (Lestander et al. 2018). Besides, another peak around 1245 cm^{-1} could be attributed to the presence of C–O–C in the cellulose biopolymer chain (Dorado et al. 2021). Moreover, the intense band centered on 1058 cm^{-1} showed a high intensity peak which could be associated to C–O–H stretching vibrations linkages in cellulose and hemicellulose or to the presence of C–O–R in alcohols or esters (Ceylan and Goldfarb 2015). The large band centred around 600 cm^{-1} is usually associated with aromatic compounds (Fan et al. 2017). OPW are complex and heterogeneous materials with a remaining fatty acids and with a considerable lignocellulosic phase (around 21.5% of cellulose, 24.3% of hemicelluloses and 38.0 % of lignins (García-Ibañez et al. 2006)). FTIR spectroscopy has proved to be powerful tool to comply with the purpose of comprehensive characterization of these local agricultural by-products. The OPW mass loss (TG) and the derivative mass loss (DTG) curves with respect to temperature in the N_2 atmosphere at $10^\circ\text{C}/\text{min}$ are given in Figure 1. As it can be seen from the obtained results, the DTG curve revealed three classic degradation steps. The first mass loss step occurred at low temperatures ($< 180^\circ\text{C}$) and it attributed to moisture release. The second mass loss step, which is the key pyrolysis stage of OPW, happened between 180 and 600°C and is usually associated to the primary devolatilization of the main components. A great part of volatiles are released between 180 and 400°C whereas lignins continue their degradation after 400°C . (Bensidhom et al. 2018) reported that the most critical devolatilization of biomass enclosed by 180 and 400°C , it is known as the active pyrolysis zone. Within the devolatilization zone, it can be seen that two zones could be observed: the first between 180 and 340°C that involves the hemicelluloses and cellulose degradation. The lignins decomposition starts after 350°C with a slow rate (Bensidhom et al.

2021), more it gradually degrades up to the ultimate pyrolysis temperature of 600 °C. After this temperature, the passive zone started where the devolatilization practically finished and there is no loss of additional mass. Similar results were reported by (Dorado et al. 2021) when the temperature reaches 600°C, the weight loss rate was about 0 %wt./min.

3.2. Rock-Eval® pyrolysis results

The POW Rock-Eval® analysis - applied in order to investigate the OPW thermal behaviour and to evaluate their potential to produce hydrocarbons – reveals some valuable indicators shown on Figure SI 2, which are mostly: the Total Organic Carbon (TOC) is around 43.5% whereas the mineral carbon (C_{min}) is around 1.8%. The S1 parameter, which is around 103.2 mg/g indicating that POW contains high amounts of hydrocarbons already present whereas the S2 parameter is around 125.1 mg/g which indicates that the hydrocarbons produced during pyrolysis reveals that POW are promising raw materials to produce volatiles during thermal cracking. The relative amounts of S1 and S2 are dependent on the type of organic matter and on the thermal energy (time and temperature). The T_{max} parameter is around 315 °C. T_{max} corresponds to the temperature at the maximum production of hydrocarbons during pyrolysis gives an indication of the temperature of the maximum of the production of volatiles. The Hydrogen Index (HI) is around 288 mg of HC/g of TOC of the sample. The high HI indicates the good potential of OPW to produce di-hydrogen. The oxygen index (OI) is around 165 of CO₂/g of TOC of the sample. The oxygen index is associated to the lignin-cellulose and hemicellulose contents.

3.3. Pyrolytic products distribution

3.3.1. Effect of final pyrolysis temperature

The investigation of the effect of the final pyrolysis temperature (500, 600 and 700 °C) at constant HR (15°C/min) on the pyrolysis products distribution (Figure 2) indicates that the liquid oil yield

increases from 26 wt.% at 500 °C to 33 wt.% at 600 °C and then decreases up to 27 wt.% at 700 °C. The enhancement of the bio-oil yield with the temperature increase is due to the emphasis of the primary pyrolysis reactions (devolatilization) with thermal stress (Brindhadevi et al. 2021). However, the decrease of the oil fraction at much higher temperature could be attributed to the occurrence of secondary pyrolysis reactions and namely to vapors cracking and gasification at high temperature (Irfan et al. 2016). Thus, 600 °C was retained as the optimal condition for the maximum production of oil fraction. The secondary reactions of volatiles cracking into small gaseous molecules, occurring at high temperature are confirmed by the increase of syngas yield at 700 °C (47 wt.%) compared to 600 °C (37 wt.%). For the solid char, we distinguish a monotonous amount decrease from 32 wt.% at 500 °C to 30 wt.% at 600°C and to 26 wt.% at 700 °C. This tendency may be explained by the further degradation of organic materials with temperature increase (Li et al. 2021).

3.3.2. Effect of the heating rate

The results of the investigation of the effect of the pyrolysis HR (15°C/min, 20 °C/min, 25 °C/min) at constant temperature (600°C) on the recovered products distribution are given in Figure 2. According to these results, a decrease in the bio-oil yield (from 33% at 15°C/min to 29% at 20 and 25°C/min) and an improvement in the gas yield, with the HR increase from 15°C/min to 25°C/min are observed. Xiong et al. (Xiong et al. 2018) reported that a large proportion of bio-oil might be evaporated as gas phase volatile at fast HR and for temperature more than 500°C. For the solid fraction, the mass yield is almost constant (around 30%) for all HR; this indicates that the higher HR promoted the cracking of the organic components remaining in the char and the condensable volatiles to form the gaseous products [37].

3.4. Pyrolysis products characteristics

3.4.1. Pyrolytic oil properties

The CHN-O elemental composition of recovered oils at different temperature and HR are given in Table 2. The CHN-O results show that the C content ranges from 50.58 to 67.55 wt.%, the H content ranges from 6.99 to 9.85 wt.% and the O is between 22.25 and 39.05 wt.%. These findings are comparable to those published for bio-oils derived from olive oil residues from several origins reported by Guida et al. (Guida 2017). The pyrolytic oil HHV increased from 22.9 to 23.49 MJ/kg while temperature increases from 500°C to 700°C, and then slightly decreased until 27.81 MJ/kg with the increase of HR at 25°C/min.

The fuel properties of the recovered organic fraction at final temperature 600°C and HR 15°C/min are reported in Table 2. The acidity index is relatively high (72 mg de KOH/g sample) and have to be improved to reach the values required by petroleum derivates standards (acidity index do not exceed 5 mg KOH/g of sample for Tunisian Diesel(Amdouni et al. 2021). The measured HHV is about 17.79 MJ/kg and the flash point was 44°C, the ash content 0.012% and the color was DIL8. These fuel properties are in the same range that those reported for other pyrolytic oils by (Channiwala and Parikh 2002).

The OPW pyrolytic oil FTIR spectra in all experimental conditions are given in Figure SI 1. From the obtained patterns, it is noted that all recovered bio-oils are composed of high amount of hydroxyl (-OH) groups contained in alcohols, phenols and in water obtained in the band 3400 cm⁻¹. The absorbance of the band between 2800 and 3000 cm⁻¹ (assigned to C-H) disappear in bio-oil spectra compared to the raw material which indicates the degradation of aliphatic compounds under heating (Fan et al. 2017). The aromatic groups are present in all pyrolytic-oils at 1690 cm⁻¹ (C=C) and 1450 cm⁻¹ (C-O). For the bands between 1475 cm⁻¹ and 1000 cm⁻¹ when the temperature increased to 700 °C and HR raised to 25°C/min, the peaks are well distinguished which indicates that the alcohols, phenols and ethers groups are still present in the pyrolytic oils (Ceylan and

Goldfarb 2015). The OPW bio-oil FTIR characterization revealed that it is a complex mixture consisting of different classes of functional groups, i.e., aliphatic, aromatic and oxygenated compounds.

The GC/MS investigation leads to the identification of potential bioactive chemical constituents contained in pyrolytic bio-oils produced from OPW at different pyrolysis conditions. The obtained results (Table SI 2 and Figure SI 3) indicates that around thirty-seven compounds have been identified. These compounds are mainly fatty acid esters, phenols and nitrogenous compounds...etc. The major components identified in OPW pyrolysis bio-oils identified as trimethylsilyl (TMS) derivatives were: (i) organic acids with 82.6%; (ii) Nitrogenous compounds with 7.4%; (iii) Phenolic compounds with 4.2% for BO-OMW; (iv) Monoglycerides with 1. 8%. The antibacterial, antifungal, antioxidant, anti-cancer, anti-inflammatory, and hypocholesterolaemia activities of the majority of the discovered compounds have been noted in the literature.

Importantly, GC/MS results showed that OPW pyrolytic oils are potential antioxidant agents with many bioactive phytochemical compounds. This is not surprising to find such active molecules in studied pyrolytic bio-oils because in traditional medicine in Tunisia, the pyrolysis tars coming from mainly olive tree by-products carbonization are used as a popular remedy and as an additive to drinking water as flavouring agent in drinking water.

3.4.2. Char characteristics

The ultimate and proximate analysis and HHVs for the chars produced by quick pyrolysis of olive pomace at various temperatures and HR are shown in Table 2. Carbon is the most prevalent ingredient in chars, far exceeding amounts present in raw materials. The C content increased as the pyrolysis temperature increased, while the H and O contents decreased. Higher temperatures promote the scission of weaker bonds within the char structure, which results in hydrogen and

oxygen losses. The chars' HHVs were about 24 and 25 MJ/kg, which are comparable to solid fossil fuels like lignite and anthracite (Raveendran and Ganesh 1996), implying that the chars could be used as solid fuels.

The ultimate, CHN, and elemental analyses of the created char are shown in Table 2. The existence of a residual percentage of volatiles in the char, ranging between 34.8 and 43.9%, indicates that the pyrolysis processes did not complete at the target temperature of 600 °C.

The recovered chars FTIR spectra obtained at various temperatures and HRs (Figure SI 1) show the absence of the OH bands at 3400 cm⁻¹ attributed to alcohols and phenols while the presence of aliphatic groups (alkanes). This absorbance of the band between 2700 and 3000 cm⁻¹ (ascribed to C-H) in biochar is weak and disappear with the temperature increase up to 700°C which indicates the presence of alcohol and carboxylic acid (Fan et al. 2017). The aromatic groups are present in all the chars at band around 1690 and 1450 cm⁻¹. For the bands between 1475 cm⁻¹ and 1000 cm⁻¹ when the temperature and HR increase to 700 °C and 25°C/min, respectively, the spectra of the chars became nearly flat, which indicates that the alcohol, phenol and ether groups (C-O) were lost (Ceylan and Goldfarb 2015) compared to the raw material which confirm the results obtained by the CHN-O analysis.

SEM results were used to determine the morphology of the OPW char produced at 600°C with 15°C/min as HR. As Figure 3 shows, the recovered biochar shows a porous structure on the surface with pore sizes until 50 µm. This integrated structure without considerable pores could be associated with the release of VM under heating and the loss of the original structure of the raw material which is composed by lignin, cellulose and hemicelluloses (Dorado et al. 2021). This leads to the formation of large pores suitable for the adsorption process and the removal of organic and inorganic contaminants in aqueous solutions (Sizirici et al. 2021). In addition, the SEM patterns reveal the presence of some needle like crystals, formed and distributed on the char surface, which

confirmed the elemental results by ICP (P and K richness) and which emphasizes its use as fertilizer (An et al. 2020).

3.4.3. OPW Gas composition

The recovered non condensable gas composition obtained at 600°C and 15°C/min indicate that it is a complex mixture of CO (up to 41.1 wt. %), CO₂ (up to 0.59 wt. %), H₂ (up to 4.63 wt. %), CH₄ (up to 6.87 wt. %) and C_nH_m (up to 1.72 wt. %). Due to the high yield of methane (CH₄), carbon monoxide (CO), and di-hydrogen (H₂), the gas has a high energy content (LHV approximately 8.14 MJ/Nm³), which allows it to be utilized as an alternative fuel source for internal combustion engines and industrial combustion operations, as well as to supply heat for the pyrolysis process.

3.5. Kinetics of thermal decomposition

Many researches are focusing on numerical modelling in order to have a better understanding of the pyrolysis process. In fact, modelling is a mathematical methodology that allows for the following: assessing the performance of pyrolysis; investigating the possibilities of optimizing their performance in order to achieve desired product yields and distribution; saving time and money, particularly for full-scale processes; and forecasting and studying biomass thermal breakdown and studying the influence of different operating conditions. The different elements of equilibrium and kinetics models of the thermochemical process have been explored numerically (Baruah and Baruah 2014; Sharma et al. 2015; Solarte-Toro et al. 2021). The non-isothermal TG/DTG experimental results of the pyrolysis of the studied sample olive pomace at 5, 10 and 20°C/min in an inert environment were used for kinetic modelling Figure 4. The results show that the devolatilization occurs when the temperature elevated with the increase of the HR.

Thermal DTG confirmed that the degradation of biomass started from 230°C to 360°C. The plots presented by DAEM are non-linear and show different behaviours. This phenomenon may be

caused by multiple chemical reactions occurring at the same time. As shown in Table 4, through the conversion value (x) from 0.2 to 0.8, the correlation coefficient (R^2) varies between 0.94 and 0.99, indicating the best model fitting value. The activation energy calculated using the DEAM model is between 121.6 and 151.1 kJ mol⁻¹. In addition, the frequency factor (k_0) varies from $1.69 \cdot 10^{10}$ to $9.86 \cdot 10^{13}$. The kinetic results confirmed that the activation energy depends on the conversion value, which indicates that the olive pomace experienced complex degradation processes related to various reactions. The relevant Equations and coefficients obtained using the equations are listed in Table 4. Figure 4 shows the iso-conversion diagram, as well as the activation energy and frequency factor obtained at each conversion level. Since the correlation coefficient (R^2) of each conversion point is greater than 0.94, we believe that the hypothesis of DAEM and its multiple simultaneous primary decomposition reactions is a reasonable model for predicting the activation energy of olive pomace pyrolysis. The activation energy of pyrolysis is between 121.6 and 151.6 kJ/mol, with an average value of 138.1 ± 11.9 KJ mol⁻¹. As the thermal decomposition progresses, the apparent activation energy value changes with the conversion rate, thus emphasizing the complex mechanism of pyrolysis, which changes with the change of the material composition. However, as shown in Figure 4, we found a good agreement between the TG curves calculated using the kinetic parameters obtained from DAEM and the measured data at each HR. Therefore, we are confident in the applicability of DAEM in describing the complex pyrolysis reaction of UP degradation.

The activation energy calculated here has advantages over the pyrolysis activation energy of lignocellulose using the DAEM method and different models in the literature, as shown in Table 5. Diverse models have been applied to Olive oil residues such as KAS, FO, FWO and other modified model (Buratti et al. 2016; Guida and Hannioui 2016; Martín-Lara et al. 2017, 2018; Sfakiotakis and Vamvuka 2018). The originality for applying DAEM model to these types of Olive

waste is that it is done for the first time (no published data of DAEM with olive pomace). Moreover, according to the recommendations of the ICATC: International Confederation for Thermal Analysis and Calorimetry (ICTAC), the DAEM is recommended. Using the FWO method the activation energy of olive pomace is calculated and ranging from 116 to 203.0 kJ mol⁻¹ at HRs 2 to 20 K min⁻¹ (Khalideh Al bkoor Alrawashdeh et al. 2017) and using the KAS method is ranged from 35.77 to 247.8 kJ mol⁻¹ at HRs 5 to 25°C min⁻¹ (Ghouma et al. 2017). Other researchers determined , the activation energy of olives at HRs of 5, 10, and 15 K min⁻¹ using two models, DAEM and FWO, respectively, which were 110, 18 and 113.8 kJ mol⁻¹ (Fernandez et al. 2018). (Çepelioğullar et al. 2018) have also determined the activation energy for olive oil residue (OOR) and other Lignocellulosic forest residue (LFR) with different model Friedman, FWO, and KAS, respectively and they found that the activation energy have the same value for each biomass about 186 kJ mol⁻¹ for OOR and about 155 kJ mol⁻¹ for LFR at HRs 5, 10, 20 and 50°C min⁻¹. (Biagini et al. 2008) employed different HRs 5, 10, 15, 20, 40, 60 and 100 K min⁻¹ for olive cake and they reported that the activation energy found were 112.1, 117.8 and 103.2 kJ mol⁻¹ using Friedman FWO, and KAS models, respectively. The activation energy value of biomass obtained by analysis of the fuel produced (bio-oil and produced gas) and the characteristics of biochar is important to know to optimize the process of fuel recovery and recovery of the biochar produced.

3.6.Future Application of the OPW pyrolysis products

Pyrolysis as a thermochemical conversion technique and one of the promising process in recent years (Das et al. 2021), It presents a multiple advantages such as saving the environment from the negative impact of wastes and creating usable feedstock's without damaging the environment. It converts waste into three different products. The bio-char recovered in this study from OPW pyrolysis can be used in the future as organic fertilizers, amendment, activated carbon and

adsorbent. Beyond the possible use of produced bio-oil as alternative liquid biofuel in the traffic sector, there is an interest in its application as source of fine chemicals and bio-active molecules. Therefore, based on biochemical compounds exploration and function identification, sustainable and innovative application path of pyrolytic-oil as precursor of active molecules have to be developed for the enhancement of the pyrolysis process efficiency. Furthermore, the syngas produced could be used in the combustion in boilers and generators and as a supporting agent in the pyrolysis process by supplying heat in the pyrolyzer.

4. Conclusion

Based on the findings of this study, we can claim that energy recovery of OPW by pyrolysis is a promising methodology for addressing environmental issues associated with by-products of olive oil extraction processes and turning these organic wastes into usable products. The experimental study reveals that in the optimum conditions (600°C and 15°C min⁻¹), up to 33.3 wt.% of oil, 30 wt.% of char and 36.7 wt.% of gas were produced. The recovered pyrolytic oil have a low HHV and show a good bioactive potential (antioxidant, antimicrobial, etc.). The OPW remaining char presents high C amount and high nutrients contents that makes it suitable for amendment in agricultural soils and for long term carbon sequestration. The released non condensable gases show high energy content (LHV around 8.14 MJ/Nm³) suitable for its application as an alternative fuel source or to supply heat for driving the pyrolysis process. The DAEM may be used to calculate the kinetic parameters of pyrolysis and offers a satisfactory match to the experimental data. This integrated novel approach of bio-valorisation of OPW into renewable fuels and high-value added materials can be adopted by olive farmers and industrials to convert these olive residues into wealth.

- **Acknowledgements**

This work is carried out in collaboration between University of Liemerick (Faculty of Engineering, Chemical Engineering Department), Ondokuz Mayıs University (Faculty of Engineering, Chemical Engineering Department, Samsun, Turkey) and Research and Technology Centre of Energy, Technopôle Borj-Cedria, Tunisia. This work was supported and funded by the Ministry of Higher Education and Scientific Research (MESRST) in Tunisia and under a Contract between the MESRST and the Research and Technology Centre of Energy (CRTEn). The authors gratefully acknowledge the Tunisian Ministry of Higher Education and Research for financial support.

- Ethical Approval

- Not applicable

- Consent to Participate

- Not applicable

- Consent to Publish

- Not applicable

- Authors Contributions

- Mohamed Hechmi Aissaoui: carried out experimental work; interpreted results and has a major contribution in the redaction of the manuscript;
 - Aïda BEN HASSEN TRABELSI: verified the analytical results; supervised the findings of this work and has a major contribution in the redaction of the manuscript;
 - Gmar Bensidhom: helped in numerical verification and their results interpretation;
 - Selim Ceylan: contributed in results discussion, numerical verification and manuscript revision
 - James J Leahy: contributed in results acquisition, discussion and manuscript revision

- Witold Kwapinski: contributed in results acquisition, discussion and manuscript revision

All authors discussed the results, provided critical feedback and helped shape the research, analysis and manuscript.

- **Funding**

- This work was supported and funded by the Ministry of Higher Education and Scientific Research (MESRST) in Tunisia and under a Contract between the MESRST and the Research and Technology Centre of Energy (CRTEn).

- **Availability of data and materials**

- Not applicable

- **Competing Interests**

- The authors have no conflicts of interest to declare that are relevant to the content of this article. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript. The authors have no financial or proprietary interests in any material discussed in this article.

References

- Alcazar-Ruiz A, Garcia-Carpintero R, Dorado F, Sanchez- Silva L (2021) Valorization of olive oil industry subproducts: ash and olive pomace fast pyrolysis. Food Bioprod Process 125:37–45. <https://doi.org/10.1016/j.fbp.2020.10.011>
- Amdouni S, Ben Hassen Trabelsi A, Mabrouk Elasmı A, et al (2021) Tannery fleshing wastes conversion into high value-added biofuels and biochars using pyrolysis process. Fuel 294:.

533 <https://doi.org/10.1016/j.fuel.2021.120423>

534 Ameziane H, Nounah A, Khamar M, Zouahri A (2020) Composting olive pomace: Evolution of
535 organic matter and compost quality. *Agron Res* 18:5–17.
536 <https://doi.org/10.15159/AR.20.004>

537 An X, Wu Z, Yu J, et al (2020) Copyrolysis of Biomass, Bentonite, and Nutrients as a New
538 Strategy for the Synthesis of Improved Biochar-Based Slow-Release Fertilizers. *ACS*
539 *Sustain Chem Eng* 8:3181–3190. <https://doi.org/10.1021/acssuschemeng.9b06483>

540 Aydemir SBK and H (2014) Pyrolysis of Olive Pomace and Copyrolysis of Olive Pomace with
541 Refuse Derived Fuel. *Am Inst Chem Eng Env* 8:649–656. <https://doi.org/10.1002/ep>

542 Baruah D, Baruah DC (2014) Modeling of biomass gasification: A review. *Renew Sustain*
543 *Energy Rev* 39:806–815. <https://doi.org/10.1016/j.rser.2014.07.129>

544 Bensidhom G, Ben Hassen-Trabelsi A, Alper K, et al (2018) Pyrolysis of Date palm waste in a
545 fixed-bed reactor: Characterization of pyrolytic products. *Bioresour Technol* 247:363–369.
546 <https://doi.org/10.1016/j.biortech.2017.09.066>

547 Bensidhom G, Ben Hassen Trabelsi A, mahmood MA, Ceylan S (2021) Insights into pyrolytic
548 feedstock potential of date palm industry wastes: Kinetic study and product characterization.
549 *Fuel* 285:119096. <https://doi.org/10.1016/j.fuel.2020.119096>

550 Biagini E, Fantei A, Tognotti L (2008) Effect of the heating rate on the devolatilization of
551 biomass residues. *Thermochim Acta* 472:55–63. <https://doi.org/10.1016/j.tca.2008.03.015>

552 Brindhadevi K, Anto S, Rene ER, et al (2021) Effect of reaction temperature on the conversion of
553 algal biomass to bio-oil and biochar through pyrolysis and hydrothermal liquefaction. *Fuel*
554 285:119106. <https://doi.org/10.1016/j.fuel.2020.119106>

555 Buratti C, Mousavi S, Barbanera M, et al (2016) Thermal behaviour and kinetic study of the olive
556 oil production chain residues and their mixtures during co-combustion. *Bioresour Technol*

214:266–275. <https://doi.org/10.1016/j.biortech.2016.04.097>

Çepelioğullar Ö, Mutlu İ, Yaman S, Haykiri-Acma H (2018) Activation energy prediction of biomass wastes based on different neural network topologies. *Fuel* 220:535–545. <https://doi.org/10.1016/j.fuel.2018.02.045>

Ceylan S, Goldfarb JL (2015) Green tide to green fuels: TG-FTIR analysis and kinetic study of *Ulva prolifera* pyrolysis. *Energy Convers Manag* 101:263–270. <https://doi.org/10.1016/j.enconman.2015.05.029>

Channiwala SA, Parikh PP (2002) A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81:1051–1063. [https://doi.org/10.1016/S0016-2361\(01\)00131-4](https://doi.org/10.1016/S0016-2361(01)00131-4)

Das P, Chandramohan VP, Mathimani T, Pugazhendhi A (2021) Science of the Total Environment Recent advances in thermochemical methods for the conversion of algal biomass to energy. *Sci Total Environ* 766:144608. <https://doi.org/10.1016/j.scitotenv.2020.144608>

de la Torre Maroto M, la Cal Herrera JA, Vilar MM (2020) Dry olive pomace gasification to obtain electrical energy in a downdraft gasifier. *WIT Trans Ecol Environ* 247:137–144. <https://doi.org/10.2495/WM200131>

Dinc G, Yel E (2018) Self-catalyzing pyrolysis of olive pomace. *J Anal Appl Pyrolysis* 134:641–646. <https://doi.org/10.1016/j.jaap.2018.08.018>

Dorado F, Sanchez P, Alcazar-Ruiz A, Sanchez-Silva L (2021) Fast pyrolysis as an alternative to the valorization of olive mill wastes. *J Sci Food Agric* 101:2650–2658. <https://doi.org/10.1002/jsfa.10856>

Eom IY, Kim JY, Kim TS, et al (2012) Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass. *Bioresour Technol* 104:687–694. <https://doi.org/10.1016/j.biortech.2011.10.035>

581 Fan L, Zhang Y, Liu S, et al (2017) Bio-oil from fast pyrolysis of lignin: Effects of process and
 582 upgrading parameters. *Bioresour Technol* 241:1118–1126.
 583 <https://doi.org/10.1016/j.biortech.2017.05.129>
 584 Fernandez A, Palacios C, Echegaray M, et al (2018) Pyrolysis and Combustion of Regional
 585 Agro-Industrial Wastes: Thermal Behavior and Kinetic Parameters Comparison. *Combust*
 586 *Sci Technol* 190:114–135. <https://doi.org/10.1080/00102202.2017.1377701>
 587 García-Ibañez P, Sánchez M, Cabanillas A (2006) Thermogravimetric analysis of olive-oil
 588 residue in air atmosphere. *Fuel Process Technol* 87:103–107.
 589 <https://doi.org/10.1016/j.fuproc.2005.08.005>
 590 Ghanim BM, Kwapinski W, Leahy JJ (2018) Speciation of Nutrients in Hydrochar Produced
 591 from Hydrothermal Carbonization of Poultry Litter under Different Treatment Conditions.
 592 *ACS Sustain Chem Eng* 6:11265–11272. <https://doi.org/10.1021/acssuschemeng.7b04768>
 593 Ghouma I, Jeguirim M, Guizani C, et al (2017) Pyrolysis of Olive Pomace: Degradation Kinetics,
 594 Gaseous Analysis and Char Characterization. *Waste and Biomass Valorization* 8:1689–
 595 1697. <https://doi.org/10.1007/s12649-017-9919-8>
 596 Guida MY (2017) Bio-oil and bio-char feedstocks from pyrolysis of olive mill wastes, such as
 597 olive mill solid waste and Olive mill wastewater. *Indian J Environ Prot* 37:632–646
 598 Guida MY, Hannioui A (2016) A review on thermochemical treatment of biomass: Pyrolysis of
 599 olive mill wastes in comparison with other types of biomass. *Prog Agric Eng Sci* 12:1–23.
 600 <https://doi.org/10.1556/446.12.2016.1>
 601 Haddad MEL (2016) Development of Renewable Energies in Tunisia. 1–8
 602 İlay R (2020) Short-lived Effects of Olive Pomace Biochar Produced at Different Temperatures
 603 on Nitrate (NO₃-), Bromide (Br-), Sulfate (SO₄²⁻) and Phosphate (PO₄³⁻) Leaching from
 604 Sandy Loam Soils. *Commun Soil Sci Plant Anal* 51:2223–2243.

605 <https://doi.org/10.1080/00103624.2020.1822375>
 606 Innangi M, Niro E, D'Ascoli R, et al (2017) Effects of olive pomace amendment on soil enzyme
 607 activities. *Appl Soil Ecol* 119:242–249. <https://doi.org/10.1016/j.apsoil.2017.06.015>
 608 IOC (2017) Market Newsletter No 121 – November 2017. Int Olive Counc
 609 Irfan M, Chen Q, Yue Y, et al (2016) Co-production of biochar, bio-oil and syngas from
 610 halophyte grass (*Achnatherum splendens* L.) under three different pyrolysis temperatures.
 611 *Bioresour Technol* 211:457–463. <https://doi.org/10.1016/j.biortech.2016.03.077>
 612 Khalideh Al bkoor Alrawashdeh, Katarzyna Słopiecka, Abdullah A. Alshorman, et al (2017)
 613 Pyrolytic Degradation of Olive Waste Residue (OWR) by TGA: Thermal Decomposition
 614 Behavior and Kinetic Study. *J Energy Power Eng* 11:. [https://doi.org/10.17265/1934-](https://doi.org/10.17265/1934-8975/2017.08.001)
 615 [8975/2017.08.001](https://doi.org/10.17265/1934-8975/2017.08.001)
 616 Lestander TA, Sandström L, Wiinikka H, et al (2018) Characterization of fast pyrolysis bio-oil
 617 properties by near-infrared spectroscopic data. *J Anal Appl Pyrolysis* 133:9–15.
 618 <https://doi.org/10.1016/j.jaap.2018.05.009>
 619 Li C, Hayashi J ichiro, Sun Y, et al (2021) Impact of heating rates on the evolution of function
 620 groups of the biochar from lignin pyrolysis. *J Anal Appl Pyrolysis* 155:.
 621 <https://doi.org/10.1016/j.jaap.2021.105031>
 622 López-Linares JC, Gómez-Cruz I, Ruiz E, et al (2020) Production of ethanol from hemicellulosic
 623 sugars of exhausted olive pomace by *escherichia coli*. *Processes* 8:1–10.
 624 <https://doi.org/10.3390/PR8050533>
 625 Mallamaci R, Budriesi R, Clodoveo ML, et al (2021) Olive Tree in Circular Economy as a
 626 Source of Secondary Metabolites Active for Human and Animal Health Beyond Oxidative
 627 Stress and Inflammation. *Molecules* 26:. <https://doi.org/10.3390/molecules26041072>
 628 Martín-Lara MA, Blázquez G, Zamora MC, Calero M (2017) Kinetic modelling of torrefaction of

629 olive tree pruning. *Appl Therm Eng* 113:1410–1418.

630 <https://doi.org/10.1016/j.applthermaleng.2016.11.147>

631 Martín-Lara MA, Ronda A, Blázquez G, et al (2018) Pyrolysis kinetics of the lead-impregnated

632 olive stone by non-isothermal thermogravimetry. *Process Saf Environ Prot* 113:448–458.

633 <https://doi.org/10.1016/j.psep.2017.11.015>

634 Mekki H, Anderson M, Benzina M, Ammar E (2008) Valorization of olive mill wastewater by its

635 incorporation in building bricks. *J Hazard Mater* 158:308–315.

636 <https://doi.org/10.1016/j.jhazmat.2008.01.104>

637 Miura K (1995) A New and Simple Method to Estimate $f(E)$ and $k_o(E)$ in the Distributed

638 Activation Energy Model from Three Sets of Experimental Data. *Energy and Fuels* 9:302–

639 307. <https://doi.org/10.1021/ef00050a014>

640 Nunes LJR, Loureiro LMEF, Sá LCR, Silva HFC (2020) Evaluation of the potential for energy

641 recovery from olive oil industry waste: Thermochemical conversion technologies as fuel

642 improvement methods. *Fuel* 279:118536. <https://doi.org/10.1016/j.fuel.2020.118536>

643 Oyebanji JA, Okekunle PO, Lasode OA, Oyedepo SO (2018) Chemical composition of bio-oils

644 produced by fast pyrolysis of two energy biomass. *Biofuels* 9:479–487.

645 <https://doi.org/10.1080/17597269.2017.1284473>

646 Pasqualone A, Di Rienzo V, Sabetta W, et al (2016) Chemical and Molecular Characterization of

647 Crude Oil Obtained by Olive-Pomace Recentrifugation. *J Chem* 2016:.

648 <https://doi.org/10.1155/2016/4347207>

649 Paz A, Karnaouri A, Templis CC, et al (2020) Valorization of exhausted olive pomace for the

650 production of omega-3 fatty acids by *Cryptocodinium cohnii*. *Waste Manag* 118:435–444.

651 <https://doi.org/10.1016/j.wasman.2020.09.011>

652 Pellerá FM, Gidarakos E (2015) Effect of dried olive pomace - Derived biochar on the mobility

653 of cadmium and nickel in soil. *J Environ Chem Eng* 3:1163–1176.

654 <https://doi.org/10.1016/j.jece.2015.04.005>

655 Qi Y, Ge B, Cao Q, et al (2021) Science of the Total Environment Application of sectionalized

656 single-step reaction approach (SSRA) and distributed activation energy model (DAEM)

657 on the pyrolysis kinetics model of upstream oily sludge : Construction procedure and data

658 reproducibility. *Sci Total Environ* 774:145751.

659 <https://doi.org/10.1016/j.scitotenv.2021.145751>

660 Raveendran K, Ganesh A (1996) Heating value of biomass and biomass pyrolysis products. *Fuel*

661 75:1715–1720. [https://doi.org/10.1016/S0016-2361\(96\)00158-5](https://doi.org/10.1016/S0016-2361(96)00158-5)

662 Ribeiro TB, Oliveira A, Coelho M, et al (2021) Are olive pomace powders a safe source of

663 bioactives and nutrients? *J Sci Food Agric* 101:1963–1978.

664 <https://doi.org/10.1002/jsfa.10812>

665 Sfakiotakis S, Vamvuka D (2018) Study of co-pyrolysis of olive kernel with waste biomass using

666 TGA/DTG/MS. *Thermochim Acta* 670:44–54. <https://doi.org/10.1016/j.tca.2018.10.006>

667 Sharma A, Pareek V, Zhang D (2015) Biomass pyrolysis - A review of modelling, process

668 parameters and catalytic studies. *Renew Sustain Energy Rev* 50:1081–1096.

669 <https://doi.org/10.1016/j.rser.2015.04.193>

670 Sheng C, Azevedo JLT (2005) Estimating the higher heating value of biomass fuels from basic

671 analysis data. *Biomass and Bioenergy* 28:499–507.

672 <https://doi.org/10.1016/j.biombioe.2004.11.008>

673 Sizirici B, Fseha YH, Yildiz I, et al (2021) The effect of pyrolysis temperature and feedstock on

674 date palm waste derived biochar to remove single and multi-metals in aqueous solutions.

675 *Sustain Environ Res* 31:. <https://doi.org/10.1186/s42834-021-00083-x>

676 Solarte-Toro JC, González-Aguirre JA, Poveda Giraldo JA, Cardona Alzate CA (2021)

677 Thermochemical processing of woody biomass: A review focused on energy-driven
 678 applications and catalytic upgrading. *Renew Sustain Energy Rev* 136:.
 679 <https://doi.org/10.1016/j.rser.2020.110376>
 680 Surahmanto F, Saptoadi H, Sulistyo H, Rohmat TA (2020) Investigation of the slow pyrolysis
 681 kinetics of oil palm solid waste by the distributed activation energy model. *Biofuels* 11:663–
 682 670. <https://doi.org/10.1080/17597269.2017.1387750>
 683 Timpanaro G, Cosentino S, Danzi C, et al (2021) Prickly pear for biogas production: technical-
 684 economic validation of a biogas power installation in an area with a high prevalence of cacti
 685 in Italy. *Biofuels, Bioprod Biorefining* 1–22. <https://doi.org/10.1002/bbb.2190>
 686 Trabelsi ABH, Ghrib A, Zaafour K, et al (2017) Hydrogen-Rich Syngas Production from
 687 Gasification and Pyrolysis of Solar Dried Sewage Sludge: Experimental and Modeling
 688 Investigations. *Biomed Res Int* 2017:.. <https://doi.org/10.1155/2017/7831470>
 689 Tsivas D, Vlyssides A, Vlysidis A (2021) Monitoring of a III-Phase Olive Pomace Composting
 690 Process Using the CIELAB Colorimetric Method. *Waste and Biomass Valorization*.
 691 <https://doi.org/10.1007/s12649-021-01363-8>
 692 Vand V (1943) A theory of the irreversible electrical resistance changes of metallic films
 693 evaporated in vacuum. *Proc Phys Soc* 55:222–246. [https://doi.org/10.1088/0959-](https://doi.org/10.1088/0959-5309/55/3/308)
 694 [5309/55/3/308](https://doi.org/10.1088/0959-5309/55/3/308)
 695 Xiong Z, Wang Y, Syed-Hassan SSA, et al (2018) Effects of heating rate on the evolution of bio-
 696 oil during its pyrolysis. *Energy Convers Manag* 163:420–427.
 697 <https://doi.org/10.1016/j.enconman.2018.02.078>
 698 Yaras A, Demirel B, Akkurt F, Arslanoglu H (2021) Thermal conversion behavior of paper mill
 699 sludge: characterization, kinetic, and thermodynamic analyses. *Biomass Convers*
 700 *Biorefinery*. <https://doi.org/10.1007/s13399-020-01232-9>

701 **Table 1. Proximate, ultimate, heating value and mineral composition of studied OPW**

Analysis		OPW (this study)	(Sibel Basakçılardan Kabakci and Hilal Aydemir 2014; Khalideh Al bkoor Alrawashdeh et al. 2017)	(Dorado et al. 2021)	(Alcazar-Ruiz et al. 2021)	
Proximate analysis (wt.%)						
Moisture		3.44	4.52-2.75	2.12-3.64	2.75	
Volatile matter		73.22	86.71-67.2	63.30-80.73	67.05	
Ash		2.02	5.81	4.77-11.90	8.63	
Fixed carbon ^a		21.32	7.48	12.38-24.80	24.32	
Ultimate analysis (wt.%)						
Carbon		47.34	51.80-48.4	47.07-51.22	49.06	
Hydrogen		6.6	6.76-6.4	5.89-8.76	-	
Oxygen ^a		43.33	40.12	31.62-33.11	1.93	
Nitrogen		2.73	1.32-1.8	1.54-1.93	31.26	
HHV ^b		20.48	19.88-20.30	-	-	
Rock Eval Pyrolysis						
COT (%)	Cmin (%)	S1 (mg/g)	S2 (mg/g)	Tmax (°C)	HI (mg of HC/g of TOC)	OI (mg of CO2 per gr of TOC)
43.46	1.79	103.16	125.11	315	288	165
Mineral composition (mg/g)						
Al	0.25	-	-	0.16-0.23	-	-
Ca	4.64	-	-	2.99-8.21	6.4	-
Fe	0.22	-	-	-	-	-
Mg	0.337	-	-	0.5-1.41	3.6	-
K	6.4625	-	-	0.7-8.1	39	-
P	0.43	-	-	-	-	-
Na	0.21	-	-	0.18-0.48	2.19	-
Si	0.28	-	-	0.1	-	-

702
703 a: by difference

704 b: HHV (MJ kg⁻¹)= Higher heating value (HHV) calculated by (Shah et al 2012) formula HHV=-
705 1.3675+ 0.3137C + 0.7009H+0.0318O
706

707 **Table.2. Pyrolytic oil (PO) and biochar (BC) CHN-O elemental composition and HHV**

Analysis	PO-500-15	PO-600-15	PO-700-15	PO-600-20	PO-600-25		
Ultimate analysis (wt%)							
Carbon	50.58	57.32	51.38	66.73	67.55		
Hydrogen	8.80	6.99	9.33	9.85	8.97		
Oxygen ^a	39.05	34.30	37.98	22.17	22.25		
Nitrogen	1.57	1.39	1.3	1.25	1.23		
Heating Value							
HHV ^b	22.9	23.6	23.49	28.17	27.81		
LHV	20.98	22.07	21.46	26.02	25.86		
Fuel properties							
HHV (MJ/kg)	Flash point (°C)		Ash (wt.%)		Color		
17.79	44		0.02		DIL 8		
	BC-500-15	BC-600-15	BC-700-15	BC-600-20	BC-600-25		
Proximate analysis (wt.%)							
Moisture	8.7	6.7	6.0	9.8	7.3		
Volatile matter	34.8	35.2	43.9	37.8	39.7		
Ash	6.7	7.2	8.0	7.9	8.5		
Fixed carbon ^a	58.6	57.6	48.1	54.3	51.9		
Ultimate analysis (wt.%)							
C	67.80	72.54	73.38	67.80	82.03		
H	3.87	2.02	2.37	2.68	3.10		
N	4.15	2.12	2.77	5.32	7.27		
O	24.18	23.32	21.48	24.20	7.60		
High Heating Value (MJ/kg)							
HHV	24.38	24.75	24.99	23.55	27.78		
LHV	23.54	24.1	24.47	22.96	27.1		
H/C	0.79	0.38	0.45	0.55	0.53		
O/C	0.31	0.28	0.25	0.31	0.08		
Mineral composition (mg/g)							
Al	Ca	Fe	Mg	K	P	Na	Si
0.56	8.43	0.43	0.47	8.70	0.64	0.29	0.56

708
709 a: by difference

b: HHV= Higher heating value (HHV) calculated by (Shah et al 2012) formula
 $[HHV = -1.3675 + 0.3137 \cdot C + 0.7009 \cdot H + 0.0318 \cdot O]$

Table 3. Previous kinetics model results of olive by-products and other biomasses

Raw material	Applied Model	Heating rate	Activation energy				References
Olive pits	DAEM	5, 10 and 15 K/min	110.18				(Fernandez et al.. 2018)
	FWO		113.8				
Olive Pomace	KAS	5, 10, 15, 20 and 25°C/min	E1	E2	E3		(Ghouma et al.. 2017)
			102.49-104.38	283.43-246.79	35.77-43.84		
Olive tree pruning	FWO	2. 5. 10 and 15 K/min	26.57-185.7				(Khalideh Al bkoor Alrawashdeh et al.. 2017)
Olive pomace			116.4-202.99				
Olive kernel			26.58-214.94				
	Modified IPR model	5. 10. 20. 30. 40 and 50°C/min	E1	E2	E3	E4	(Sfakiotakis and Vamvuka. 2018)
Olive kernel			185	132.9	46.2	47.9	
Sewage Sludge			134	133.7	33.9	44.8	
Municipal solid waste			92	152.5	31.8	-	
	Fr, FWO and KAS	5. 10. 20 and 50°C/min	Fr	FWO	KAS		(Çepelioğullar et al.. 2018)
Olive oil residue			187.2	185.9	185.6		
Lignocellulosic forest residue			158.9	155.2	153.4		
	Fr, FWO and KAS	5. 10. 15. 20. 40. 60 and 100 K/min	Fr	FWO	KAS		(Biagini et al.. 2008)
Rice husks			135.5	128.1	112.5		
Olive cake			112.1	117.8	103.2		
Caco shell			127.7	129.6	65.3		

Table 4. Fitted equations and correlation coefficients with resulting activation energies and frequency factors for Olive Pomace pyrolysis obtained by DAEM

x	Equation	R²	E	k0
0.2	$y = -18004x + 22.853$	0.9984	149.7	8.3E+13
0.25	$y = -18227x + 23$	0.9982	151.5	9.7E+13
0.3	$y = -18216x + 22.717$	0.9964	151.4	7.3E+13
0.35	$y = -18010x + 22.085$	0.9939	149.7	3.8E+13
0.4	$y = -17633x + 21.133$	0.9929	146.6	1.5E+13
0.45	$y = -16833x + 19.452$	0.9814	139.9	2.6E+12
0.5	$y = -15960x + 17.642$	0.9691	132.7	4.0E+11
0.55	$y = -15147x + 15.96$	0.9606	125.9	7.0E+10
0.6	$y = -14630x + 14.807$	0.9504	121.6	2.1E+10
0.65	$y = -14634x + 14.567$	0.9489	121.7	1.7E+10
0.7	$y = -14998x + 14.946$	0.9488	124.7	2.6E+10
0.75	$y = -16086x + 16.539$	0.9537	133.7	1.3E+11
0.8	$y = -17597x + 18.814$	0.9665	146.3	1.4E+12

Figure 1 : TGA/DTG curves of OPW at different heating rate 5, 10 and 20°C/min

735
736
737

Figure 2 : Pyrolytic products yields variation (A) with final pyrolysis temperature and (B) with heating rate

743
744

Figure 3: SEM of biochar produced at 600°C

745
746
747

Figure 4: Isoconversional plot for determination of activation energy of pyrolysis of olive pomace via the distributed activation energy model.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [04SupplementaryInformation.docx](#)
- [0Graphicalabstrat.docx](#)