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Bioenergy production from olive oil mill solid wastes and their blends with lignite: thermal characterization, kinetics, thermodynamic analysis, and several scenarios for sustainable practices

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Abstract

Olive oil production is accompanied by the generation of large amount of solid wastes. In order to achieve a sustainable practice for olive mill solid wastes, the combustion of extracted olive pomace, olive stone, and their blends with lignite at different proportions was studied via several methods. Energy content, proximate, ultimate, and thermogravimetric/derivative thermogravimetric analysis (TG/DTG) were performed. Empirical chemical formulas and emission factors were calculated. Reaction kinetic parameters, such as activation energy (E), and pre-exponential factor (A) and thermodynamics parameters, such as Gibbs free energy change (ΔG_α), entropy change (ΔS_α), enthalpy change (ΔH_α), were calculated. Olive oil wastes reveal low ash (< 7%), high gross calorific value (GCV) (~ 21 MJ/kg), and lower activation energy (48.57 and 64.18 kJ/mol respectively) than lignite (70.79 kJ/mol). Maximum potential emissions were also lower. Furthermore, nine case studies with three different scenarios (%wastes into the blends) in three regions (Greece, Europe, and Worldwide) for the estimation of potential energy cover from olive oil solid wastes were developed. Quality characteristics of olive mill solid wastes seem to be appropriate to bioenergy for a sustainable practice. Even in the worst-case scenarios, olive mill solid wastes seem to be promising for waste-to-energy practices via combustion and co-combustion with lignite for small-scale applications.

Keywords Biofuel · Biomass · Characterization · Energy · Kinetics · Thermodynamics

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1 Introduction

With the current lifestyle, and the population growth, there is an increased demand for electric power [1, 2]. Coal from the industrial revolution until today has played a significant role in energy production [3, 4]. In 2018, power generation from coal was more than 38% of the globally produced electricity [5]. Growing concerns about greenhouse emissions (GHGs) force to find alternative, sustainable, and eco-friendly ways for energy production. Biomass is considered as CO_2-neutral fuel and eco-friendly [6] and it is a large renewable resource [7, 8].

From the other hand, biomass by-products/waste-to-energy (B/WtE) practice can contribute in several sectors: use a sustainable waste management, energy recovery from wastes, reduce biomass /wastes disposal, reduce landfills, reduce carbon emissions, reduce the environmental impact, etc. [9, 10]. Besides biomass (waste/residues) utilization as fuels, biomass co-combustion with lignite could be a promising alternative solution, towards a more environmentally friendly utilization of lignite [11]. Co-combustion is a simple and economical solution to produce biofuels in a pulverized boiler [12].

Biomass co-firing is an alternative solution for operating the existing coal thermal power plants reducing their emissions and the environmental impact [13].

In the last decade (2010–2019), olive production in Greece was about 23,264,758 metric tons (an average about 2,326,476 metric tons) [14]. Olive oil production has an important role in the industry of Mediterranean countries. Greece, in 2019, was number five in olive harvested areas (925,232 hectares) with an increase + 2.5% at the last 5 years [15], number four in olive production (1,525,543 metric tons) [14], and number three in olive oil production after Spain and Italy [14].

However, olive oil production is associated to huge amounts of oil mill solid wastes [16]. The produced number of wastes and their characteristics are associated with the applied technology (3-phace process or 2-phase process), olive fruit varieties, and cultivation conditions [17]. In Greece, in 2002, more than 2900 olive oil mills (80% from 3-phase process) were generated [18]. 3-Phase process of 1000 kg olives with 500 kg water produces 600 kg pomace, 750 kg wastewater, and 180 kg olive oil while 2-phase process of 1000 kg olive produces 820 kg pomace and 180 kg olive oil [17]. In the Mediterranean region (Greece, Italy, and Spain are the main producers), about 2 million tons of olive oil are produced per year resulting approx. 30 million m^3 of olive mill wastewater and 20 million tons of olive pomace [19]. The wastes generated from olive oil production can cause significant environmental issues, due to high toxic organic load, high BOD and COD, odor, etc., such as toxicity in aquatic life, toxicity in plants, ground water pollution, and soil pollution. Moreover, olive mill solid wastes can color water due to highly colored compounds such as phenols [19]. Other related environmental problem is the growth of microorganisms that in turn results in lowering the oxygen concentration in waters and thus decreasing the oxygen availability for other living organisms. Furthermore, the high phosphorus concentration of these wastes can lead to eutrophication [20].

Olive oil industry solid wastes are utilized in several applications such as combustion [21, 22], gasification [23, 24], pyrolysis [25], soil amendment [20], livestock feeding [26], and cement additives [1]. Combustion is the most important application of olive stones with low emission level and high efficiency [27]. The biomass/waste-to-energy (B/WtE) approaches based on the 5R principle (Reduce, Reuse, Recycle, Recovery, Restore) has important role in sustainable development [28]. Olive mill solid waste can be characterized as an economic B/WtE resource [29]. Basu et al. [30] studied biomass and lignite co-firing, and it was reported to be a low-cost technology for the greenhouse gas reduction. Topal et al. [13] studied olive stones via exergy analysis of a circulating fluidized bed power plant co-firing with olive pits (simulation). Sfakiotakis and Vamvuka [31] studied co-pyrolysis of olive kernel via TGA/DTG/MS. Brachi et al. [32] studied olive pomace decomposition under torrefaction with isoconversional kinetic analysis. Energy utilization techniques of solid olive mill waste are reported in a review by [17], but only few reference (13 from 135) refers to Greek studies regarding biomass/or olive oil residues, most of them studying pyrolysis, gasification, or ash behavior.

The combustion behavior of Greek olive oil wastes and their co-firing with lignite via kinetic modelling and thermodynamic analysis has not been studied in detail. Also, there have not been reported any estimations for the potential energy production and energy demand cover that could be achieved by the utilization of these wastes, either alone or in blends with lignite. The novelty of this work is that it provides answers to these questions and lies on a more comprehensive evaluation compared to other past works (energy content, proximate, ultimate analysis, thermogravimetric and derivative thermogravimetric analysis, empirical chemical formulas) of olive oil mill solid wastes and their blends with lignite for bioenergy production and the examination of several scenarios of potential cover of energy demand, in Greece, in Europe, and worldwide; such scenarios are reported for the first time in the current study. However, this is of high importance, since Greece is a considerable olive and olive oil producer and in addition has to be aligned with the Europeans goals of reduction of lignite and fossil fuel use. However, this is of high importance, since Greece is a considerable olive and olive oil producer and in addition has to be aligned with the European goals of reduction of lignite and fossil fuel use.

The aim of this study is to evaluate the energy recovery of olive oil solid wastes from oil industry in Greece. The objectives of this study are to examine (a) the potential utilization of solid wastes (olive stone and extract olive pomace) for bioenergy production, (b) the potential utilization of the same solid wastes as a secondary fuel in blends with lignite, and (c) the potential cover of energy demand, in Greece, Europe, and worldwide, from combustion of olive mill solid wastes and their co-combustion with lignite.

2 Materials and methods

2.1 Materials and sample preparation

Extracted olive pomace (EOP) and olive stone (OLS) were collected from an olive industry located in Greece (Katerini) with a 2-phase process system. A lignite sample (LIGA) was obtained from Western Macedonia mines, in Greece. All samples were firstly air-dried for 8 weeks and then ground to size less than 1 mm using a cutting mill (SM 100). Olive mill solid wastes were blended with lignite sample in proportions: 30 wt%, 50 wt%, and 70 wt%.

2.2 Analytical methods

Gross calorific value (GCV) was measured by AC500 isoperibol oxygen bomb calorimeter (by Leco Corporation), according to ASTM D5865-13 standard method [33]. The theoretical values of olive oil blends with lignite were calculated taking into account the results of raw samples (EOP, OLS, LIGA) and the percentage of the waste (30 wt%, 50 wt%, and 70 wt%) in the blend with lignite. Moreover, several %ΔGCV group categories were created in order to categorized the analyzed samples regarding the gross calorific value of the analyzed samples in comparison with lignite sample.

Proximate analysis (moisture content, volatile matter, ash content, and fixed carbon content) was performed with a LECO TGA 701 instrument, based on ASTM D7582 standard [34].

A TGA 701 instrument (LECO Inc.) was used to conduct the thermogravimetric analysis and derivative thermogravimetric analysis (TG/DTG) in order to analyze the mass loss of the samples in controlled atmosphere. About 1 g of each sample was heated from 25 up to 1000 °C. The analysis was conducted under air atmosphere with a flow rate of 3.5 l/min and a heating rate of 10 °C/min. Combustion characteristics such as ignition temperature (T_i), burnout temperature (T_b), and maximum temperature (T_{max}) at which there is the maximum rate of weight loss (R_{max}) and the total weight loss (TWL) were determined.

A FlashEA 1112 Elemental Analyzer CHNS was used to determine the elemental composition of the samples (C, N, H, and S contents). The elemental oxygen (O) content of the samples was calculated by difference. About 4 mg of every sample was combusted at 900 °C in oxygen atmosphere (99.9999%) to produce CO_2, H_2O, N_2, and SO_2, and then separated on a gas chromatographic column (CHNS/NCS Packed), and analyzed using a thermal conductivity detector (TCD). The GC oven temperature was kept steadily at 60 °C. BBOT ($C_{26}H_{26}N_2O_2S$), sulfanilamide ($C_6H_8N_2SO_2$), and L-cystine ($C_6H_{12}N_2O_4S_2$) were used as standard compounds for validation.

Empirical chemical formulas were calculated from the results of ultimate analysis [35]. The emission factors (maximum potential emissions of the fuel) were derived from the results of ultimate and calorific value analysis of the samples as applied by Fott [36]. The results of CO_2, NO_2, and SO_3 emission factors are expressed as grams of emitted gas per 1 MJ of produced energy.

All samples were analyzed at least in two replicates in order to examine the reproducibility of the results, the level of experimental error of the results. Moreover, the deviation among theoretical and experimental results (for the blends) was performed.

2.3 Kinetic modelling and thermodynamic analysis

2.3.1 Kinetic modelling

The combustion kinetics was studied through the determination of activation energy (E) and the pre-exponential factor (A), from the TG/DTG data of each sample, including blends. The TG/DTG profile of each sample was divided into various temperature regions that each one represents a different stage of the combustion. Stages I and II are associated to low molecular weight of volatiles and to moisture evaporation. For all samples, except lignite, stage III is the stage where the initiation of the combustion occurs. Therefore, the beginning of stage III coincides with the T_i and the end of the stage III coincides with the peak temperature (T_{max}) at which there is the maximum rate of weight loss (R_{max}), based on DTG profiles [37–39]. The combustion kinetics can be described by first-order kinetics in cases where the particle of the sample is small and thinly or there is an excess of air [40]. Such conditions are valid in our experiments in TG. Parameters of the reaction kinetics of the analyzed samples were determined from the Arrhenius equation (1) by the approach proposed by Cumming [40]:

$$K = A exp(-E/RT) \text{ or } logK = logA - E/2.303RT \qquad (1)$$

where E is the activation energy, kJ mol^{-1} K is the specific reaction rate, A is the pre-exponential factor (frequency factor), s^{-1}, R is the universal gas constant (8.314 JK^{-1}mol^{-1}), T is the instantaneous absolute temperature, K.

$$K = -(dW/dt)/W \qquad (2)$$

where dW/dt is the instantaneous rate of weight loss, %/min, and W is the weight of unburned combustible.

2.3.2 Thermodynamic analysis

The thermodynamic parameters, enthalpy change (ΔH_α, kJ mol^{-1}), Gibbs free energy change (ΔG_α, kJ mol^{-1}), and entropy change (ΔS_α, kJ mol^{-1}K^{-1}), were calculated from Eqs. (3) to (5) [41]:

$$\Delta H_\alpha = E - RT_\alpha \qquad (3)$$

$$\Delta G_\alpha = E + RT_m * ln(K_B * T_m / hA) \qquad (4)$$

$$\Delta S_\alpha = (\Delta H_a - \Delta G_a)/T_m \qquad (5)$$

where T_α is the final temperature of stage III (in K) (see DTG graph, Fig. 3 and Fig. S1, Supplementary material), R is the universal gas constant (8.314 JK^{-1} mol^{-1}), K_B is the Boltzmann constant (1.3819E-23 JK^{-1}), h is the Plank's constant (6.6269E-34 Js), T_m is the peak temperature (DTG profile), and β is the heating rate (10 Kmin^{-1}).

2.4 Several scenarios for sustainable management of olive oil solid waste industry

The potential energy production from olive oil solid wastes in Greece, in Europe, and worldwide was estimated/predicted based on various scenarios for several cases.

Based on data for olive oil production for the 2018/2019 year, nine different cases were developed for the future years. These cases were calculated by taking into account multiple data/ assumptions: Olive oil production from Greece, Europe, and worldwide in years 2018/2019 has been reported to be 185, 2264, and 3219 thousand tons, respectively [42]. The prediction of olive oil production for Greece, Europe, and worldwide for years 2019/2020 is 275.65 (+ 49%), 1924.4 (− 15%), and 3058 tons (− 5%) respectively [42]. For 1 l of olive oil, about 4 kg of olives are needed and 1.6 kg of solid wastes are produced and 8.00 l of water was used [16]. By using a density value for olive oil, of 0.911 kg/l, it turns out that for 1 kg of produced olive oil, 1.76 kg of solid waste are produced. By assuming that not all of the solid wastes can be recovered or might be used for other purposes, a factor of 1.5 kg of solid waste (only EOP and OLS—wastewater is not taken into account) per 1 kg of produced olive oil was used for the prediction of the available amounts of olive oil solid wastes for energy purposes, for nine different cases (corresponding to nine different olive oil productions amounts).

Based on the two extreme percentages (− 15% and + 49%), nine various percentages (− 15%, − 10%, − 5%, 0%, + 5%, + 10%, + 20%, + 49%, and + 100%) and thus nine calculations for the amount of the produced olive oil solid wastes were performed (nine cases). For each one of such a case, three different scenarios were developed: (I) firing of the available olive oil solid wastes, (II) co-firing of the available solid wastes with lignite at a proportion of 70% wastes, and (III) co-firing of the available solid wastes with lignite at a proportion of 50% wastes. The GCV results of the solid wastes and lignite, of the present study, were used in the calculations. All these estimations were performed for Greece, Europe, and worldwide. More details are presented, along with the calculations in Section 5.4.

3 Results and discussion

3.1 Energy content

Gross calorific values of olive oil solid waste samples and their blends with lignite are presented in Table 1. More specifically, this table presents the experimental gross calorific values, the theoretically calculated values of blends, the deviations of experimental and theoretical values, and the percent difference of GCV of each sample with respect to the GCV of lignite.

The percent difference of GCV of every sample in comparison to GCV of LIGA sample is calculated in Eq. (6):

$$\Delta GCV_{sample}(\%) = \left((GCV_{sample} - GCV_{LIGA}) / GCV_{LIGA} \right) \cdot 100 \quad (6)$$

where ΔGCV_{sample} is the difference between the GCV of every sample and the GCV of lignite,

GCV_{sample} is the GCV of each sample and GCV_{LIGA} is the GCV of lignite sample. In the last column of Table 1, the various samples are classified in group categories, depending on how much different their GCV is.

Both OLS and EOP raw samples reveal significantly higher GCV (22.30 and 19.63 MJ/kg respectively) compared to the one (12.68 MJ/kg) of lignite sample corresponding to ΔGCV of 75.87 and 54.84% respectively. Similar results have been reported in the literature [21, 43]. In the blends, as the proportion of olive solid waste is increased into the blend with lignite, the GCV is also increased. In order to examine in depth the correlation between GCV and the proportion of solid oil waste in blends, regression plots were made. The regression plots between $GCV_{experimental}$ and $GCV_{theoretical\ values}$ of EOP blends with lignite and OLS blends with lignite are illustrated in Fig. 1a and b respectively. In both cases, r values are greater than 0.8. Based on the scatterplots that are presented in Fig. 1 and Evans correlation guide [44], there is a defined relationship between $GCV_{exp.}$ and $GCV_{theoretical}$ of olive oil solid waste blends with lignite sample. More specifically, $GCV_{exp.}$ and $GCV_{theoretical}$ of EOP and OLS blends with lignite sample appear to have a "very strong" positive correlation ($r = 0.998$ and $r = 0.896$ respectively). It can be concluded that calorific values of blends can be calculated if the raw materials are analyzed.

3.2 Proximate analysis

The results of proximate analysis are presented in Table 2.

From the results of proximate analysis, it can be observed that all samples (raw and blends) reveal a moisture content lower than 6.5 wt%. Similar results were reported by Sanchez and Miguel via pyrolytic processing [45] and Yuzbasi and Selcuk using TGA combustion [46]. OLS and EOP raw samples revealed 4.62 wt% and 6.36 wt% ash content, respectively, while lignite sample revealed a significantly higher ash content (approx. 39 wt%). In blends of oil mill solid wastes with lignite, as the percentage of solid waste is increased in the blend, the ash content is decreased. Fuel characteristics influence the type of the technology to be used. For instance, biomass fuels (for large-scale biomass combustion) with ash content less than 10 wt% could be used by fluidized bed technology while biomass with higher ash content (but lower than 50 wt%, dry basis) could be used by moving grate technology [47]. Regarding the volatile matter, oil solid wastes reveal almost double values (average approx. 77 wt%) compared to

Table 1 Gross calorific values (experimental, theoretical, deviations of experimental and theoretical, % deviation from the GCV of lignite) of raw olive oil solid waste samples and their blends with lignite

Sample ID	GCV (MJ/kg)	s.d.	GCV$_{th.\ blends}$	%Deviation between GCV$_{exp.}$ and GCV$_{theor.\ of\ blends}$	ΔGCV (%)	ΔGCV group category
EOP	19.63	± 0.12	-	-	54.84	[45.1–60%]
EOP70 LIG30	17.02	± 0.80	17.55	− 3.03	34.19	[30.1–45%]
EOP50 LIG50	15.78	± 0.02	16.16	− 2.35	24.43	[15.1–30%]
EOP30 LIG70	14.28	± 0.06	14.77	− 3.31	12.60	[< 15%]
OLS	22.30	± 0.01	-	-	75.87	[75.1–90%]
OLS70 LIG30	18.96	± 0.38	19.41	− 2.32	49.55	[45.1–60%]
OLS50 LIG50	18.58	± 2.34	17.49	− 3.25	33.45	[30.1–45%]
OLS30 LIG70	13.54	± 0.85	15.57	− 13.04	6.75	[< 15%]
LIGA	12.68	± 0.11	-	-	0.00	0.00

lignite sample (approx. 43 wt%). Scatter plots and regressions of experimental versus theoretical values of blends of volatiles and ash content are illustrated in Fig. 2. Based on Evans correlation guide [44], OLS and EOP reveal "very strong" positive correlation of experimental volatile content versus theoretical volatile content of blends (r values: 0.9716 and 0.9986 respectively).

3.3 Thermogravimetric and derivative thermogravimetric analysis

The results of TG/DTG analysis are presented in Table 3 and the TG/DTG profiles of combustion behavior of analyzed samples are illustrated in Fig. 3 and Fig. S1 (Supplementary Material). Also, in Fig. 3, the stages that were used for the kinetics analysis are presented. EOP and OLS samples reveal a maximum rate of weight loss at approx. 314 °C (4.71 %/min) while lignite reveals a lower value of R$_{max.}$ at higher temperature (1.64 %/min, 888 °C). Furthermore, total weight loss of olive oil wastes, EOP and OLS, were 95.43 and 98.72% which means that these samples have an unburned content 4.57 and 1.28%, respectively, in contrast to the lignite sample (unburned: 36.29%). These values are in agreement with ash content of samples (see Section 5.1.2) and literature

[45, 46]. In blends with lignite, as the percentage of olive oil wastes is increased, the R$_{max}$ and TWL (total weight loss) are also increased.

3.4 Ultimate analysis and Van Krevelen diagram

The results of elemental analysis are illustrated in Table 4. Elemental composition of solid wastes of olive oil industry, average values of raw EOP and OLS samples, yields a proportion of approx. 51.95 wt% carbon, 6.46 wt% hydrogen, 1.22 wt% nitrogen, and less than 0.5 wt% sulfur. Similar results were reported by Sanchez and Miguel [45].

Van Krevelen diagram for the raw analyzed samples are presented in Fig. 4. Van Krevelen diagram presents the atomic ratios of H/C and O/C of analyzed raw olive oil solid waste samples and LIGA sample in comparison with coals and biomass. The results show that the olive oil solid waste samples contain more oxygen content than lignite sample. As it can be seen, the analyzed OLS and EOP samples have a morphology with an H/C and O/C ratios similar to that of biomass (higher H/C and O/C than the lignite).

Olive oil industry solid wastes belong to lignocellulosic biomass. Hemicelluloses, cellulose, and lignin are the main components [26]. Hemicellulose content of olive mill solid

Fig. 1 Scatterplots GCV$_{experimental}$ versus GCV$_{theoretical}$ of olive oil solid waste blends with lignite sample. **a** EOP blends with lignite sample and **b** OLS blends with lignite sample
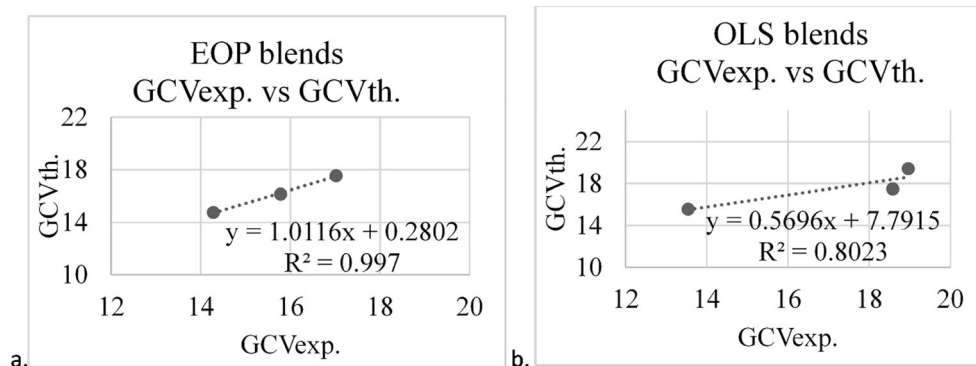
Table 2 Proximate analysis of all analyzed raw samples and their blends with lignite

Sample	Volatiles	Moisture	Ash	Fixed carbon
EOP	73.79	2.67	6.36	17.19
EOP70 LIG30	63.30	3.43	15.15	18.13
EOP50 LIG50	58.63	5.76	21.46	14.16
EOP30 LIG70	51.56	3.84	28.59	16.02
OLS	79.94	5.90	4.62	9.55
OLS70 LIG30	61.34	5.70	14.58	18.39
OLS50 LIG50	61.92	5.92	20.69	11.48
OLS30 LIG70	52.84	5.50	27.75	13.92
LIGA	42.93	6.33	38.9	11.85

wastes varies from 14.4 to 36.58% of the total weight [32, 48]. Hemicellulose degradation occurs at about 220 to 315 °C and has an atomic ratio of O/C and H/C approx. 0.80 and 1.60 respectively. Thermal degradation of cellulose typically occurs at 315 to 400 °C with 40% of total weight loss and has an atomic ratio of O/C and H/C approx. 0.83 and 1.67 respectively. Lignin degradation located between about 450 and 1000 °C with a weight loss of 25.2% of total weight loss and has an atomic ratio of O/C and H/C approx. 0.36–0.47 and 1.19 to 1.53 [32, 49, 50]. OLS is rich in lignin and this is confirmed also by the Van Krevelen diagram.

3.5 Empirical chemical formulas and CO_2, NO_2, and SO_3 emission factors

Table 5 presents the empirical chemical formulas and the maximum potential emissions of carbon, nitrogen, and sulfur oxides of the analyzed olive oil industry solid wastes and their blends with lignite. Linear regression models of %EOP and %OLS in the blend with lignite versus gCO_2/MJ are presented in Table 6 in order to predict the relationship between the gCO_2/MJ and the percentage of olive oil waste in the blend with lignite.

Empirical chemical formulas of EOP and OLS raw samples were found to be $C_{260}N_7SH_{370}O_{149}$ and $C_{295}N_5SH_{453}O_{126}$ respectively while lignite chemical formula found to be $C_{95}N_2SH_{119}O_{40}$.

EOP and OLS raw samples reveal a value of 91 gCO_2/MJ while lignite revealed a value about 103 gCO_2/MJ. This is very important, regarding the environmental impact of the samples, since the biomass samples not only qualitatively are superior to lignite since the emitted CO_2 is renewable but also quantitatively the CO_2 emissions of the biomass samples are lower than lignite.

Figure 5 presents the plot fitted model between gCO_2/MJ emissions and the proportion of olive oil solid wastes in blends with lignite. Equation (7) is the fitted model of EOP

blends with LIGA, presenting the relationship between gCO_2/MJ and the %EOP into the blend with lignite.

$$EOP : gCO_2/MJ = 100.52 - 10.6155 \cdot \%EOP \text{ into the blend} \quad (7)$$

Since the P-value is 0.0419, less than 0.05, there is a statistically significant relationship between gCO_2/MJ and %EOP into the blend at the 95.0% confidence level.

Equation (8) is the fitted model of OLS blends with LIGA:

$$OLS : gCO_2/MJ = 99.2323 - 14.4207 \cdot \%OLS \text{ into the blend} \quad (8)$$

Since the P-value is 0.1721, greater or equal to 0.05, there is no statistically significant relationship between gCO_2/MJ and %OLS into the blend at the 95.0% or higher confidence level. This may occur due to synergy effect [51] during OLS co-combustion with lignite sample.

Regarding maximum NO_2 emissions, EOP raw samples reveal similar value (2.42 g/MJ) with lignite while OLS raw samples reveal lower value (1.47 g/MJ). Maximum SO_3 potential emissions of olive oil solid waste industry reveal lower value (~ 0.60 g/MJ) compared to lignite sample (1.97 g/MJ).

3.6 Kinetic modelling and thermodynamic analysis

3.6.1 Kinetic modelling

The results of kinetic modelling are presented in Table 7. The rate data were fitted to an Arrhenius plot and showed the seven stages of combustion. Arrhenius plots of analyzed samples, for stage III, are presented in Fig. 6 and Fig. S2 (Supplementary Material). Dehydration occurs at stages I and II. Kinetic values for all samples refer to stage III except lignite that the values concern stage VI (see Table 3 and Fig. 3). OLS and EOP raw samples reveal lower activation energy (48.57 and 64.18 kJ/mol respectively) than lignite sample (70.79 kJ/mol). EOP and OLS blends with lignite reveal lower activation energy than raw samples that means that they have higher reaction rate.

OLS raw sample and blends with lignite reveal higher pre-exponential kinetic factor (A) than EOP raw sample and its blends with lignite. The pre-exponential kinetic factor (A) of all samples was found to be higher than lignite sample which means that the reaction rate is higher. The pre-exponential kinetic factor increased as the proportion of olive oil wastes increased into the blend with lignite. More specifically, high pre-exponential factor implies that more often the molecules of OLS sample and its blends collide than EOP raw sample and its blends.

In Fig. 7a, in regression between activation energy (E_3) and the %EOP into the blend with LIGA, since the P-value in the
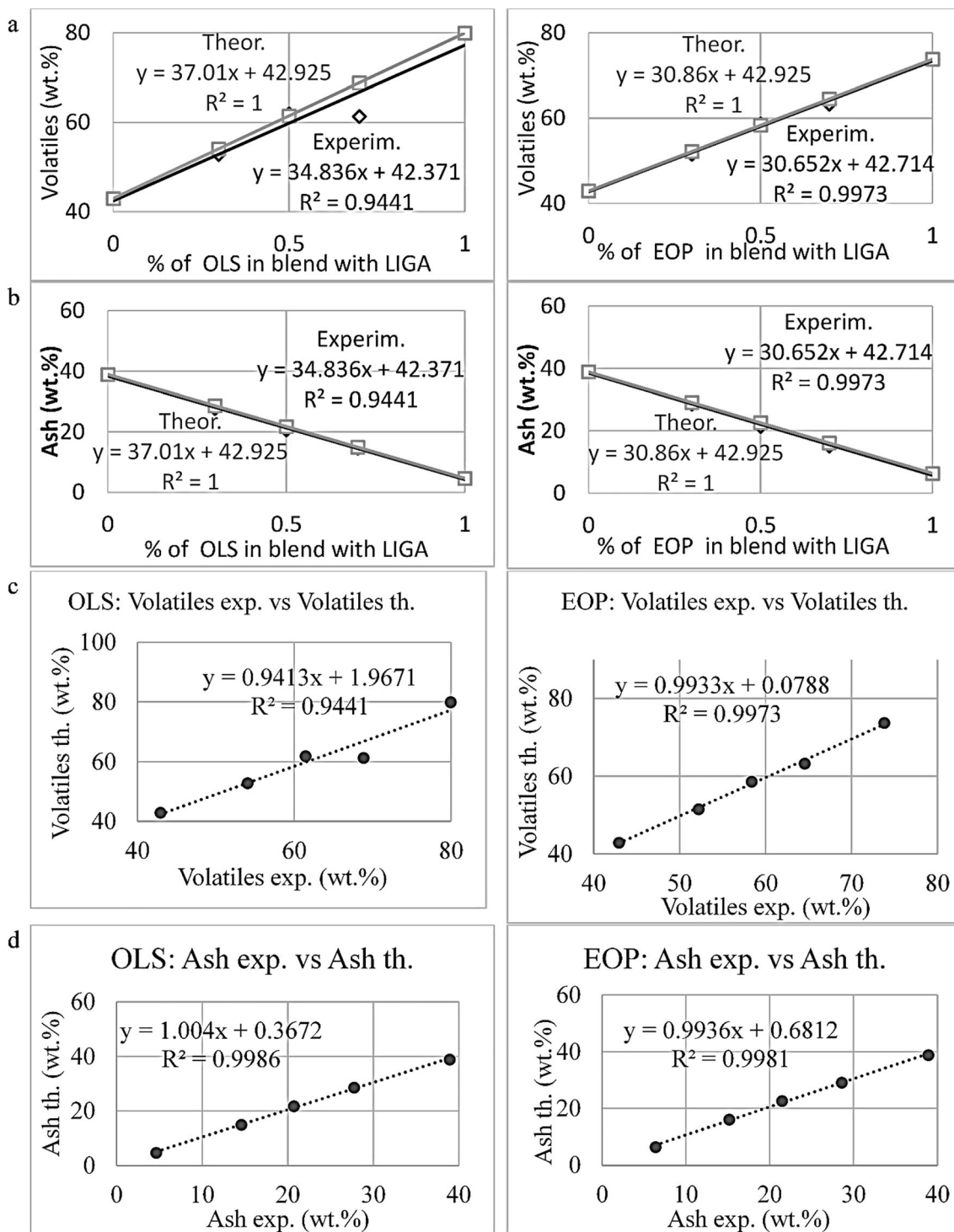
Fig. 2 Scatterplots and regressions. OLS (left) and EOP sample (right). **a** Volatile matter, experimental versus theoretical of blends. **b** Ash content, experimental versus theoretical of blends. **c** Volatile matter experimental versus theoretical (left). **d.** Ash content experimental versus theoretical (right)
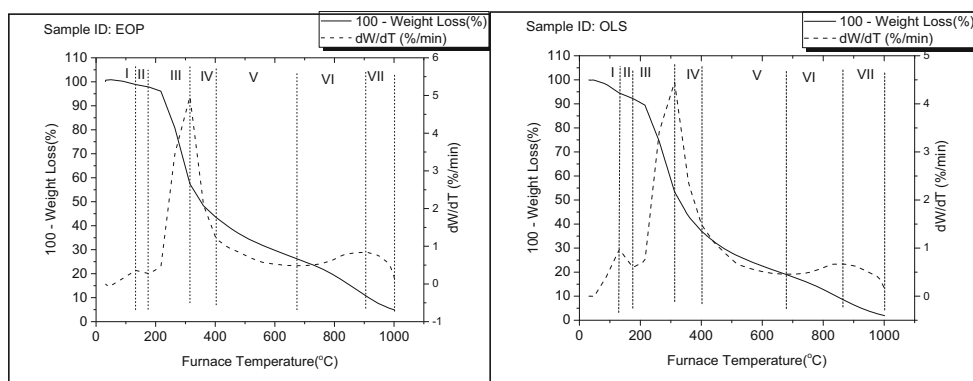
ANOVA table is greater or equal to 0.05, there is no statistically significant relationship between E_3 and EOP at the 95.0% or higher confidence level. The R-squared statistic indicates that the model as fitted explains 0.6% of the variability in E_3. The standard error of the estimate shows the standard

deviation of the residuals is 13.4. From the other hand, if the raw samples (EOP and LIGA) are not taken into account (see Fig. 7c), the P-value is greater or equal to 0.05, but the R-squared statistic indicates that the model as fitted explains 98.6% of the variability in E_3 and the standard error is only

Table 3 Combustion characteristic of raw samples and their blends with lignite

Sample ID	T_i (°C)	T_b (°C)	T_{max} (°C)	R_{max} (%/min)	t_b (min)	TWL (%)
EOP	217	1000	315	4.97	78.2	95.43
OLS	215	1000	312	4.45	78.3	98.72
LIGA	237	927	888	1.64	66.8	63.46
EOP70 LIG30	207	1000	300	4.11	78.0	86.27
EOP50 LIG50	209	1000	302	3.11	78.0	80.30
EOP30 LIG70	211	1000	305	1.90	77.9	72.73
OLS70 LIG30	189	1000	277	3.20	81.8	86.10
OLS50 LIG50	191	1000	280	2.50	81.8	79.62
OLS30 LIG70	193	1000	283	1.82	81.8	73.48

Fig. 3 Thermogravimetric analysis: TG and DTG profiles of EOP and OLS raw samples (all other TG/DTG profiles are illustrated in Fig. S1, Supplementary Material)

1.9. In Fig. 7b, in regression between activation energy (E_3) and the %OLS into the blend with LIGA, since the P-value in the ANOVA table is greater or equal to 0.05, there is no statistically significant relationship between E_3 and EOP at the 95.0% or higher confidence level. The R-squared statistic indicates that the model as fitted explains 17.2% of the variability in E_3. The standard error of the estimate shows the standard deviation of the residuals to be 13.2. From the other hand, if the raw samples (OLS and LIGA) are not taken into account (see Fig. 7d), the R-squared statistic becomes 99.1% that means that the model explains 99.1063% of the variability in E_3. The standard error, the standard deviation of the residuals, is only 1.1. Most likely, in both cases, this is happening due to synergy effect [51] of blends; that is, the energy released from the biomass at lower temperatures enables lignite ignition in the blends.

Table 4 Results of ultimate analysis of raw EOP and OLS olive oil waste samples and their blends with lignite

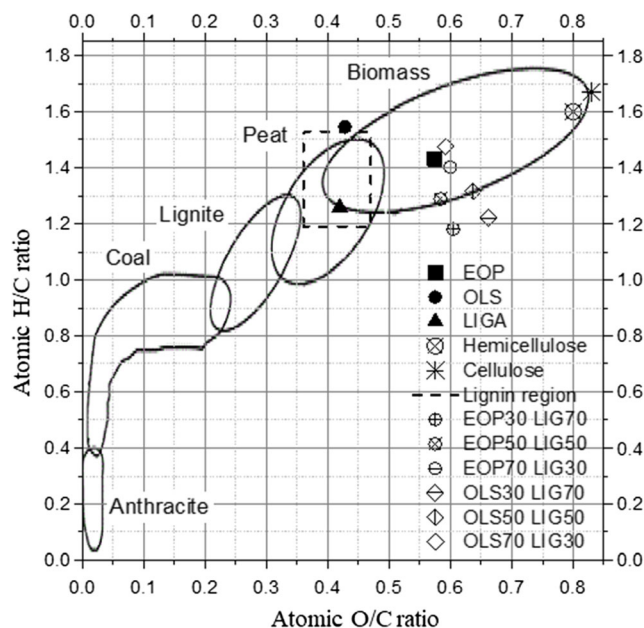| Sample ID	C (%)	H (%)	N (%)	S (%)	O* (%)
EOP	48.66	5.81	1.44	0.50	37.23
OLS	55.25	7.12	1.00	0.50	31.51
LIGA	35.58	3.73	0.90	1.00	19.89
EOP30 LIG70	36.68	3.61	1.17	0.40	29.56
EOP50 LIG50	40.75	4.37	1.30	0.41	31.71
EOP70 LIG30	43.36	5.07	1.41	0.35	34.66
OLS30 LIG70	35.53	3.61	1.12	0.64	31.35
OLS50 LIG50	39.53	4.33	1.24	0.63	33.57
OLS70 LIG30	43.71	5.38	1.21	0.60	34.53

Fig. 4 Van Krevelen diagram of the studied raw samples

Table 5 Empirical chemical formulas and maximum potential calculated emissions of carbon, nitrogen, and sulfur oxides of EOP and OLS olive oil waste samples, their blends with lignite and lignite sample

Category	Sample ID	Empirical chemical formulas	Maximum potential emissions		
			gCO_2/MJ	gNO_2/MJ	gSO_3/MJ
Raw samples	EOP	$C_{260}N_7SH_{370}O_{149}$	90.87	2.42	0.64
	OLS	$C_{295}N_5SH_{453}O_{126}$	90.84	1.47	0.56
	LIGA	$C_{95}N_2SH_{119}O_{40}$	102.88	2.34	1.97
EOP blends with lignite	EOP30 LIG70	$C_{245}N_7SH_{287}O_{148}$	94.19	2.69	0.70
	EOP50 LIG50	$C_{263}N_7SH_{336}O_{153}$	94.69	2.71	0.65
	EOP70 LIG30	$C_{330}N_9SH_{459}O_{198}$	93.43	2.72	0.51
OLS blends with lignite	OLS30 LIG70	$C_{148}N_4SH_{179}O_{98}$	96.23	2.72	1.18
	OLS50 LIG50	$C_{166}N_4SH_{217}O_{106}$	85.65	2.41	0.94
	OLS70 LIG30	$C_{195}N_5SH_{285}O_{115}$	84.51	2.09	0.79

3.6.2 Thermodynamic analysis

Thermodynamic parameters are presented in Table 7. Olive mill solid wastes and their blends with lignite reveal higher ΔG_α than lignite sample (125.95 kJ/mol). The raw solid waste samples exhibit similar ΔG_α. In the blends, by increasing the waste content, the $\Delta G\alpha$ also increases. $\Delta G\alpha$ reveals the alteration of the total energy of the system [52]. From the presented TG/DTG profiles, it becomes apparent that the combustion of solid wastes and lignite proceeds in different mechanism. More specifically, the maximum mass loss, for the solid wastes (stage III), occurs at much lower temperature than the one of lignite (stage VI). Thus, since the thermodynamic/kinetic analysis was performed for the stage of maximum mass loss rate, the parameters calculated for lignite are influenced by higher T_m temperature in comparison with the other samples. Since, for lignite, the maximum mass loss rate occurs at the last stages (near the end of combustion), it is expected that the total energy difference (ΔG_α) will not be as high as in the cases of solid wastes that their maximum mass loss occurs a lower temperature and by a completely different mechanism that involves hemicelluloses and cellulose decomposition.

All samples reveal negative $\Delta S\alpha$ while lignite sample reveal almost zero $\Delta S\alpha$. Negative $\Delta S\alpha$ with positive ΔH_α yields in positive ΔG_α. This means that the reaction is nonspontaneous. The low $\Delta S\alpha$ and ΔG_α of lignite are most likely

Table 6 Linear regressions of gCO_2/MJ vs. %EOP into the blend and gCO_2/MJ vs. %OLS into the blend

Simple regression: gCO_2/MJ vs. %EOP into the blend
 Dependent variable: gCO_2/MJ
 Independent variable: %EOP into the blend
 Linear model: Y = a + b·X
 R-squared = 79.5676 percent
 R-squared (adjusted for d.f.) = 72.7568 percent

Coefficients	Least squares	Standard	T	
Parameter	Estimate	Error	Statistic	P-value
Intercept	100.52	1.87894	53.4981	0.0000
Slope	− 10.6155	3.10579	− 3.41797	0.0419

Simple regression: gCO_2/MJ vs. %OLS into the blend
 Dependent variable: gCO_2/MJ
 Independent variable: %OLS into the blend
 Linear model: Y = a + b·X
 R-squared = 51.5374 percent
 R-squared (adjusted for d.f.) = 35.3832 percent

Coefficients	Least squares	Standard	T	
Parameter	Estimate	Error	Statistic	P-value
Intercept	99.2323	4.88436	20.3163	0.0003
Slope	− 14.4207	8.0736	− 1.78615	0.1721

Fig. 5 Plot fitted model between gCO$_2$/MJ emissions and the proportion of olive oil solid wastes. **a** EOP blends. **b** OLS blends with lignite
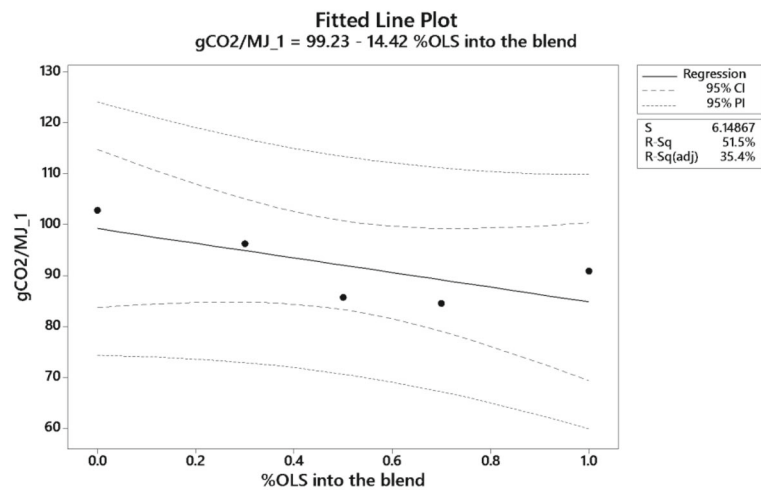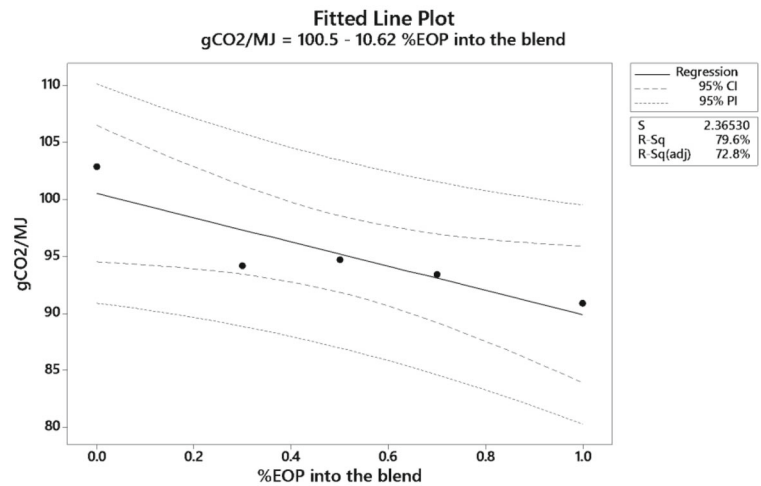

a.

b.

Table 7 Results of kinetic modelling and thermodynamic analysis

| Sample ID	Kinetic modelling (stage III except LIGA)							Thermodynamic analysis				
	$T_{i, III}$ (°C)	$T_{b\ III}$ (°C)	a_3	b_3	R^2	E_3 (kJ/mol)	A_3 (s^{-1})	T_α (K)	ΔH_α (kJ/mol)	ΔG_α (kJ/mol)	T_m (DTG peak temp. K)	ΔS_α (kJ/mol K)
EOP	178	315	− 3351.95	4.75	0.96	64.18	940.75	588	59.29	180.85	588	− 0.21
EOP70 LIG30	207	300	− 3344.29	4.68	0.97	64.03	800.37	573	59.27	175.27	573	− 0.20
EOP50 LIG50	209	302	− 2858.98	3.66	0.96	54.74	76.85	575	49.96	164.85	575	− 0.20
EOP30 LIG70	211	305	− 2125.20	2.14	0.92	40.69	2.29	578	35.89	148.72	578	− 0.20
OLS	176	312	− 2536.85	3.31	0.96	48.57	34.25	586	43.71	163.89	586	− 0.21
OLS70 LIG30	189	277	− 2753.58	3.60	0.97	52.72	67.05	551	48.15	156.92	551	− 0.20
OLS50 LIG50	191	280	− 2404.53	2.82	0.97	46.04	11.05	553	41.44	149.44	553	− 0.20
OLS30 LIG70	193	283	− 1918.30	1.76	0.95	36.73	0.96	556	32.11	138.83	556	− 0.19
LIGA (St. VI)	695	889	− 3696.99	1.74	0.97	70.79	0.93	654.79	2.90	125.95	8.31	0.00
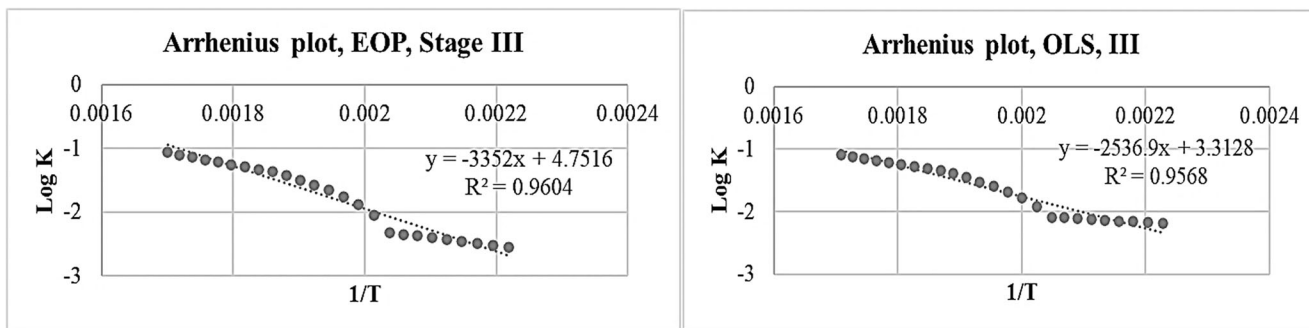
Fig. 6 Arrhenius plots of EOP and OLS sample (see Fig. S2 Arrhenius plots of all samples are presented in Fig. S2, Supplementary Material)

related to the higher temperature that its decomposition occurs. The similar values of $\Delta S\alpha$ for all samples (except lignite sample) suggest a similar tendency in reactivity [53]. In addition, the low value of $\Delta S\alpha$ for all samples suggests that at the end of the specific stage, the material is near equilibrium and thus is characterized by lower reactivity [53]. This is in agreement with the TGA results, where after the end of this stage, the mass loss (reaction rate) decreases.

The ΔH_α values are of the same order of magnitude for all samples with the exception of lignite that exhibits the lowest ΔH_α. This suggests that the energy difference between the reagent and the activated complex is low [52] for the case of lignite. This again (as in the case of ΔS_α) can be attributed to

the higher temperature of maximum mass loss rate, at the last stages of the reaction.

3.7 Several scenarios for sustainable management of olive oil solid waste industry

In Table 8, the calculations of olive oil solid waste production for nine different cases are presented. Each case corresponds to a different percentage of solid waste production with the production of the year 2018/2019 as reference. For example, in the case study 2 (− 10%), the amount of solid wastes was calculated from the actual amount of solid waste produced in 2018/2019, by assuming that there will be a reduction of 10%.
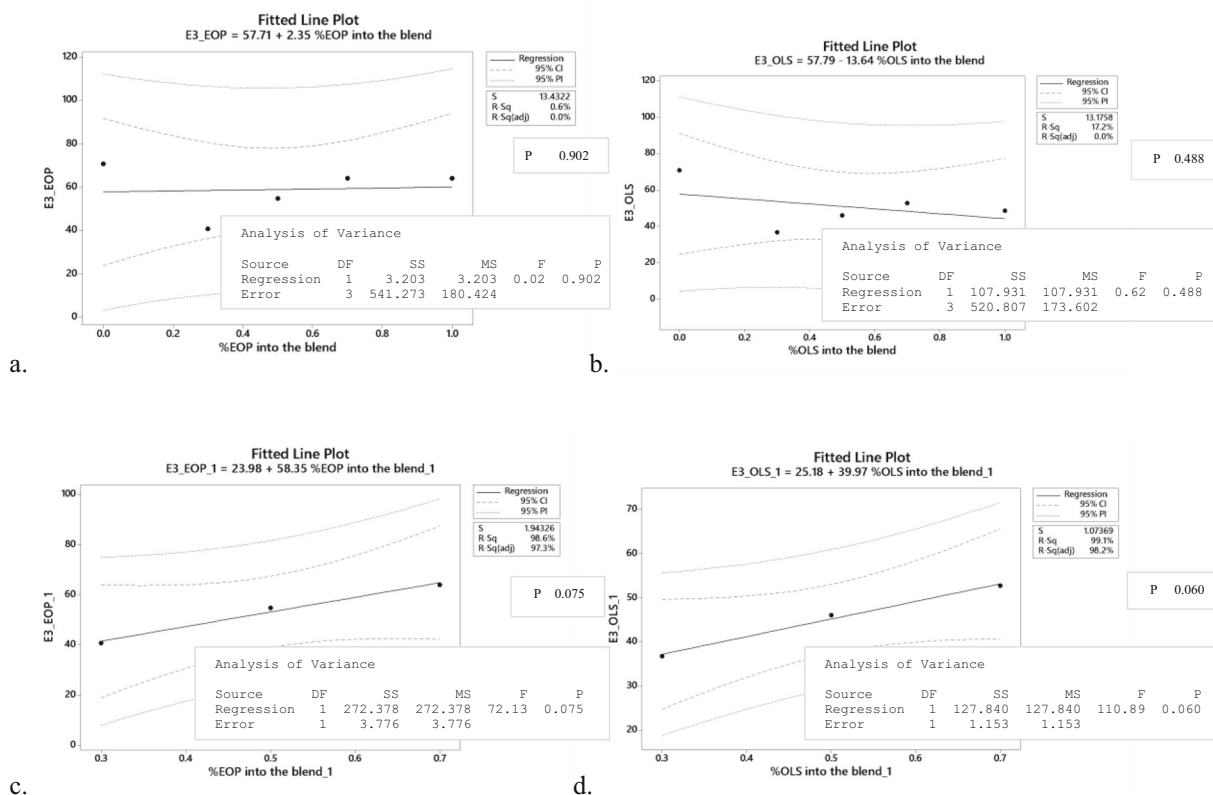

Fig. 7 ANOVA analysis, Plot of fitted model. **a** E_3 versus %EOP into the blends with lignite (raw and blends). **b** E_3 versus OLS into the blends with lignite (raw and blends). **c** E_3 versus %EOP into the blends with lignite (only blends). **d** E_3 versus %OLS into the blends with lignite (only blends), P-value = 0.060

Table 8 Various cases for the solid waste production from olive oil industry, in Greece, in Europe, and worldwide

	Region	Units	Quantity (2018/2019)	Case study 1 −15%	Case study 2 −10%	Case study 3 −5%	Case study 4 0%	Case study 5 +5%	Case study 6 +10%	Case study 7 +20%	Case study 8 +49%	Case study 9 +100%
Solid waste from oil olive production	In Greece	Thousand tons	277.50	235.88	249.75	263.63	277.50	291.38	305.25	333.00	413.48	555.00
	In EU	Thousand tons	3396.00	2886.60	3056.40	3226.20	3396.00	3565.80	3735.60	4075.20	5060.04	6792.00
	Worldwide	Thousand tons	4828.50	4104.23	4345.65	4587.08	4828.50	5069.93	5311.35	5794.20	7194.47	9657.00

In Table 9, estimations (for three scenarios and for each scenario nine different cases) of the potential energy production from olive oil solid wastes for Greece, Europe, and worldwide are presented. Scenario I refers to energy production using raw olive oil solid wastes. Scenario II refers to energy production using blends with lignite with 70% olive oil solid wastes and scenario III refers to energy production using blends with lignite with 50% olive oil solid wastes. For these scenarios, results of the current study were taken into account: The average gross calorific value of mill oil olive solid wastes (EOP and OLS sample) was 20.97 MJ/kg while 70% mill oil olive solid wastes blend with lignite (EOP70 LIG30 and OLS70 LIG30) revealed an average value of 17.99 MJ/kg and the 50% mill oil olive solid wastes blends with lignite (EOP50 LIG50 and OLS50 LIG50) revealed an average value of 17.18 MJ/kg (see Section 5.1.1).

The primary energy production in Greece is in the order of magnitude of 7.5 Mtoe corresponding to 314250 TJ [54]. The minimum and maximum values of energy production for Greece, from combustion of olive oil solid waste (scenario I) according to Table 9, are 5 and 12 TJ, respectively. These values correspond to 0.0016% and 0.0037% potential energy cover of Greece's energy production. For Europe, the percentages of the potential primary energy production cover are even smaller, since primary energy production in Europe is higher than that of Greece, and also, not all European countries are olive oil producers. These values show that olive oil solid wastes can be used only for small-scale applications or as auxiliary fuels in co-firing.

4 Conclusions

In the framework of the current study, combustion behavior of olive mill waste and their blends with lignite at different proportion was investigated by using several analytical methods: energy content determination, proximate analysis, ultimate analysis, thermogravimetric and derivative thermogravimetric (TG/DTG) analysis, kinetics and thermodynamic analysis. Several cases (nine case studies) with three scenarios (using raw olive oil waste, using 70% olive oil waste with 30% lignite, and using 30% olive oil waste and 70% lignite) for three regions (Greece, Europe, and worldwide) were studied.

Olive oil solid wastes exhibit especially attractive properties as potential solid biofuels. They exhibit almost double

Table 9 Several scenarios for sustainable energy production from olive oil industry solid wastes based on quantities of solid wastes from oil olive production. Scenario I: using only raw olive mill solid wastes; scenario II: using blends of 70% olive mill solid wastes and 30% lignite; scenario III: using blends of 50% olive mill solid wastes and 50% lignite

Energy recovery	Region	Units	Case study 1 −15%	Case study 2 −10%	Case study 3 −5%	Case study 4 0%	Case study 5 +5%	Case study 6 +10%	Case study 7 +20%	Case study 8 +49%	Case study 9 +100%
Scenario I	In Greece	TJ	4.945	5.236	5.527	11.636	6.109	6.400	6.981	8.669	11.636
	In EU	TJ	60.518	64.077	67.637	71.197	74.757	78.317	85.437	106.084	142.394
	Worldwide	TJ	86.045	91.107	96.168	101.230	106.291	111.352	121.475	150.832	202.459
Scenario II	In Greece	TJ	4.243	4.493	4.743	9.984	5.242	5.491	5.991	7.438	9.984
	In EU	TJ	51.930	54.985	58.039	61.094	64.149	67.203	73.313	91.030	122.188
	Worldwide	TJ	73.835	78.178	82.521	86.865	91.208	95.551	104.238	129.428	173.729
Scenario III	In Greece	TJ	4.052	4.291	4.529	9.535	5.006	5.244	5.721	7.104	9.535
	In EU	TJ	49.592	52.509	55.426	58.343	61.260	64.178	70.012	86.931	116.687
	Worldwide	TJ	66.985	70.925	74.866	78.806	82.746	86.687	94.567	117.421	157.612

gross calorific value than lignite, about eight times lower ash content (that is a secondary waste) and lower CO_2, NO_2, and SO_3 emission factors. Also, they exhibit lower activation energies that is translated to higher combustion rate.

The blends of olive oil solid wastes with lignite also exhibit attractive properties. Their gross calorific value and ash content can be estimated from the respective values of the raw samples. In addition, activation energy in the blends is lower than those of the raw samples, suggesting a synergy effect.

The olive oil solid waste, although generated in large amounts, can contribute to the cover of energy production at small extent (0.0016–0.0037%), even in a country like Greece, which is a major olive oil producer. Thus, utilization of these solid wastes as fuels can be performed in terms of small-scale applications (e.g., used in situ for covering energy demands of olive mill) or as auxiliary/secondary fuels.

Declarations

Competing interests The authors declare no competing interests.

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