

Article

Thermochemical and Kinetic Analysis of Combustion of Plastic Wastes and Their Blends with Lignite

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Abstract: The management of plastic waste is considered to be among the major environmental problems that must be urgently addressed. For various reasons, recycling of plastic waste is not always feasible. In this study, a comprehensive evaluation of a mixture of plastic wastes (of the municipal solid wastes, MSW) as potential fuel is performed. Precisely, the combustion of plastic waste and the co-combustion of plastic waste-lignite blends are studied. Thermochemical characteristics, chemical composition, and kinetic parameters are measured/estimated. The environmental impact of these samples is also evaluated in terms of CO₂ maximum potential emissions and ash production. In addition, the ash quality and its risk for slagging problems are explored. The random mixture of plastic waste revealed extremely high energy content (34 MJ/kg), which is higher than some well-established liquid fuels, e.g., ethanol and lower ash content (~5 wt.%), with lower activation energy and a higher maximum rate of mass loss (~9%/min) than lignite. Besides the much lower amount of produced ash, plastic waste, despite its higher carbon content, exhibits lower CO₂ maximum potential emissions (~75 g CO₂/MJ). The composition of the ash produced by plastic waste and lignite is different quantitatively but qualitatively is of the same type (similar medium risk ash). The superior characteristics of plastic waste are also evident in the blends. Provided that toxic emissions are captured, the utilization of plastic waste through combustion seems to be an attractive approach for simultaneous waste management and energy production, especially for plastic waste of limited recycling potential.

Keywords: thermal characteristics; thermogravimetric analysis; kinetics; maximum CO₂ emission factor; plastic waste; lignite; blends; synergistic effect; waste management; waste to energy (WtE)



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1. Introduction

The increasing population growth with urbanization in developing countries has led to increased production of plastic waste. Until the 1970s, rather small amounts of plastic waste were produced. Between the 1970s and 1990s, plastic waste generation tripled. In the single decade of the 2000s, plastic waste increased more than the respective amounts of the previous 40 years. Nowadays, more than 400 million tons/year of plastic waste are produced. With this trend, global production of plastic is forecasted to reach 1100 million tons by 2050 [1]. Until today, of 7 billion tons of plastic waste generated globally, only 10% has been recycled. Despite the last year's effort, about 75 to 199 million tons of plastic waste is found in the oceans. In this regard, plastic waste in ecosystems could almost triple, from 9 to 14 million tons per year in 2016 to 23–37 million per year, by 2040 [1].

Currently, it is widely accepted that the primary management approaches for plastic waste should be reuse and recycling. Indeed, reuse and recycling are related to various advantages such as low environmental impact, resource-saving, etc. However, there are factors of various origins (scientific, practical, cultural) that render practically impossible

the recycling of 100% of the produced plastic waste, at least currently or in the immediate future. In general, plastic waste recycling is rather expensive [2]. More specifically, in various countries, including Greece, the social culture for recycling is only at its beginning, e.g., plastic, paper, metal, and glass waste are collected together. This lack of recycling culture creates practical problems for recycling. For example, additional cost, energy, and labor work are needed to separate the different types of recyclable waste. Though common domestic plastic waste contains mainly six thermoplastic polymers (low and high-density poly(ethylene), poly(propylene), poly(ethylene terephthalate), poly(vinyl chloride), and poly(styrene)), other polymers may be present. For proper recycling, further separation of each polymer is required. In addition, plastic waste from food packaging typically is not cleaned by the end-user prior to disposal, and thus a portion of plastic waste is “contaminated” by food residues. This contamination is translated to various problems of additional energy and cost or even may render impossible the cleaning of the plastic and thus its recycling. In addition, it is known that recycled polymers may suffer from deteriorated properties due to low purity and/or thermal oxidation during thermal processing. Recently, it was reported that various common polymers such as cellulose esters [3,4], poly(vinyl alcohol) [4,5], and poly(vinyl chloride) [5] do not exhibit any actual melting and on the contrary, their solid–liquid (or glass-to-rubber) transition is a peculiar effect of simultaneous softening and (minor) decomposition. This minor thermal degradation is independent of any thermal oxidation and may contribute to additional deterioration of the polymer’s properties after recycling (additional thermal processing). Also, a considerable amount of plastics is already in oceans or (either legally or illegally) has been landfilled or disposed of on the ground’s surface. Such plastic waste has little potential for recycling. Similarly, multilayered plastic waste and other composite plastic materials also have limited recycling potential [6] unless delamination is carried out [7].

Consequently, it is not surprising that various research efforts focus on management approaches to plastic waste other than recycling. Such methods include pyrolysis and gasification, which aim to degrade plastic in the absence of oxygen in a controllable manner in order to obtain high-added value gas, liquid, and solid products [8–10]. However, the production of this variety of valuable products, besides the main equipment (reactor), requires additional equipment and processes for further separation and/or purification, e.g., distillation, in order to obtain a fuel that could be used in automobile applications [2]. In addition, processes such as pyrolysis are endothermic and require a countable amount of energy. Thus, an interesting alternative is the combustion of plastic waste which is an exothermic process; that is, it produces energy and also requires much less equipment for separations, etc. Of course, energy is recovered by using pyrolysis products as fuels. However, similar effects take place during the combustion of polymers. In general, thermal oxidation (combustion, presence of oxygen) and thermal degradation (pyrolysis, absence of oxygen) are distinct processes. However, for polymers, these processes are strongly related. There is a variety of complex chemical reactions during the thermal oxidation of polymers, which also include pyrolysis reactions [11]. These pyrolysis products are combusted and/or react with each other. In other words, during the combustion of polymers, to some extent, similar products as for the case of pyrolysis are produced; simply, these products are directly combusted instead of being separated, purified, and then used as fuels.

The complexity of thermal oxidation and degradation of polymers is also related to the basic disadvantage of the combustion of plastics, that is, the formation and emission of various toxic substances, such as polycyclic aromatic compounds, polychlorinated biphenyls, and others [11]. Reactions among decomposition products lead to the formation of other products and hinder complete combustion. Appropriate selection of parameters such as high gas temperature and high residence time can contribute to the minimization of such emissions [11]. In addition, excess oxygen could assist in this direction. Also, there are various available anti-pollution technologies that could be used in order to capture and recover pollutants and/or non-combusted substances.

Thus, the combustion behavior of plastic waste is a topic that attracts continuous research attention [11–14]. Also, the co-combustion of fuels may be related to certain advantages such as increased energy production, lower emissions, and better combustion behavior, e.g., due to lower activation energy arising from synergistic effects. In this direction, behavior and kinetic analysis of the co-combustion of plastic waste or plastic-derived fuel with biomass, e.g., wood, is attracting continuous attention [15–17]. Various studies have been reported on the advantages of co-combustion of biomass waste with lignite [18–21]. Plastic waste has been explored for its potential to substitute coal or to be co-fired with coal in cement kilns [14]. To the best of our knowledge, the co-combustion of plastic waste with lignite rarely has been reported. In addition, due to the complexity of polymer degradation, it is common to study the combustion of each polymer separately. Of course, very useful insights are extracted from such studies; however, as mentioned above, there are cases where the separation of the plastic waste is almost impossible, e.g., for plastic waste that has been abandoned for years on the ground's surface. For such plastic waste with random/unknown composition (from municipal solid wastes), combustion may be a viable management solution. Thus, the scope of this work is to study the combustion and co-combustion behavior (including main gas emissions and ash quality) of plastic waste of the MSW (random composition) as well as its blends with lignite.

2. Materials and Methods

In Greece, currently, there are two bins for the collection of municipal solid waste, namely the blue bin for the collection of recyclable waste (plastic, glass, paper, aluminum, or metal cans) and the green bin for the collection of the rest of the waste. The waste from the blue bin is separated in management plants. The plastic waste (PW) that was used in this study was the plastic fraction of the content of the blue bin. More precisely, plastic waste of Municipal Solid Waste (MSW) was collected from the integrated waste management plant in Kozani, Greece. These wastes contained typical plastic municipal waste such as water bottles, food packaging, packaging from cosmetic products, etc. The lignite (LIGA) sample was supplied by Agios Dimitrios Thermal Power Plant in Kozani, Greece. All samples were collected from the Western Macedonia area, located in Greece. All samples were air-dried for 2 weeks and grounded using the cutting mill SM100 Retsch. Then, the samples were dried in an oven at a temperature of 80 °C for 24 h to decrease the moisture content. Three blends with plastic wastes and lignite were prepared in different proportions: 30 wt.%, 50 wt.% and 70 wt.%. All samples/blends with lignite were analyzed with at least two replicates.

The Gross Calorific Value (GCV) of the plastic waste sample (PW) and PW blends with lignite (LIGA) were measured using a Leco AC500 Isoperibol Calorimeter according to the ASTM D5865-13 standard [22]. The % difference of GCV of every sample/blend in comparison to the GCV of the LIGA sample was calculated by Equation (1).

$$\Delta GCV_{sample}(\%) = \frac{GCV_{sample} - GCV_{LIGA}}{GCV_{LIGA}} \times 100 \quad (1)$$

where:

ΔGCV_{sample} : is the difference between the GCV of every sample/blend and the GCV of the lignite sample,

GCV_{sample} : is the GCV of each sample/blend,

GCV_{LIGA} : is the GCV of the lignite sample.

More details can be found presented in a previous study [23]. The theoretical GCV of blends was calculated (and compared with the experimental ones) as described in the previous study [24]. Briefly, the GCV of the blends were calculated from the following formula:

$$GCV_{theor.} = W_{PW} \times GCV_{PW} + W_{LIGA} \times GCV_{LIGA} \quad (2)$$

where:

GCV_{PW} : is the GCV of the PW sample.

W_{PW} : is the wt.% PW content of the blend.

W_{LIGA} : is the wt.% lignite content of the blend.

Proximate analysis (determination of moisture, volatile, ash, and fixed carbon contents) was performed using a Leco TGA 701 analyzer according to the ASTM D7582 standard [25]. Thermogravimetric Analysis and Derivative Thermogravimetric Analysis (TG/DTG) were performed using a LECO TGA 701 analyzer as described previously [26]. Kinetic analysis (determination of the activation energy, E , and pre-exponential factor, A) was performed based on the TG/DTG curves and data of the samples/blends as described in previous work [23]. Briefly, the Cumming approach, which is based on the Arrhenius equation, was used [27]:

$$\log K = \log A - E/2.303 \times R \times T \quad (3)$$

$$K = -(dW/dt)/W \quad (4)$$

where:

K : specific reaction rate.

A : pre-exponential factor.

E : Activation energy.

T : instantaneous absolute temperature.

R : universal gas constant.

W : mass of unburned combustible

dW/dt : instantaneous rate of mass loss.

From the TGA data, the K can be found. The plot of $\log K$ versus $1/T$ is linear. From the slope and intercept of this plot, the values of E and A can be found. The plot was made by using TGA data from stage III (see Figure S1 in Supplementary Material).

Also, from the TGA data, the values of the comprehensive combustion index (CCI), the ignition index (D_i), and the burnout index (D_b) were calculated [28,29]. The ignition index expresses the ignition behavior, e.g., how fast the fuel ignites, and the burnout index expresses the performance of the fuel with regard to incomplete char burnout [30]. Increased values of D_i and D_b are desirable [30]. The same holds for the CCI index (a high value is desired) [28,29]. The values of the indices were calculated from the following equations:

$$D_i = \frac{(-R_{max})}{t_i \times t_{max}} \quad (5)$$

$$D_b = \frac{(-R_{max})}{\Delta t_{1/2} \times t_{max} \times t_b} \quad (6)$$

$$CCI = \frac{(-R_{max}) \times (-R_V)}{T_i^2 \times T_b} \quad (7)$$

where:

R_{max} : the maximum mass loss rate.

R_V : the average mass loss rate.

t_{max} : the time corresponding to T_{max} .

t_b : the time corresponding to T_b .

t_i : the time corresponding to T_i .

$\Delta t_{1/2}$: the time range corresponding to the temperature range $\Delta t_{1/2}$.

T_{max} : the peak maximum temperature (Temperature corresponding to the center of the DTG peak).

T_b : burnout Temperature (Temperature at which mass loss has ended)

T_i : ignition Temperature (Temperature at which mass loss initiates).

$\Delta T_{1/2}$: the temperature range corresponding to the width of the half height of the DTG peak.

The temperatures T_i and T_b were calculated by the tangent method.

Ultimate/elemental analysis (C, H, N, and S contents) was conducted using the elemental analyzer Thermo Finnigan EA 112 CHNS as described in [31]. The potential maximum emission factor of CO_2 was calculated from the results of the ultimate analysis and the GCVs of the analyzed samples [32]. The potential maximum CO_2 emission factor was expressed as g of emitted gas per 1 MJ (MegaJoule) of produced energy. Electron microprobe analyses from ashes were carried out by using a scanning electron microscope SEM (JEOL JSM-6390LV, Tokyo, Japan) equipped with an energy-dispersive spectrometer EDS (INCA 300, Oxford, UK) as described in [33].

3. Results and Discussion

3.1. Energy Content Analysis

The results of the Gross Calorific Value (GCV and $\Delta\text{GCV}\%$) are presented in Figure 1a. As can be seen, the GCV of plastic waste is 167% higher than the one of lignite, and in absolute values, it exhibits a GCV of 33.88 MJ/kg versus 12.68 MJ/kg of lignite. The GCV of plastic waste is in agreement with literature-reported values [34]. This value is comparable to or even higher than well-established liquid fuels; e.g., ethanol has a GCV of ~ 27 MJ/kg [35]. This rather high value of the single fuel (plastic waste) is responsible for the respective increase of the GCV of the blended fuel, which is observed with the increase of the plastic waste content. Though the plastic waste is composed of millimeter-sized particles of various polymers, and thus extensive heterogeneity is expected, interestingly, the increase of the GCV value increased linearly with the content of plastic waste, as can be seen in Figure 1b. Also, as presented in Figure 1c, the experimental GCV values of the blended fuels are highly correlated with the theoretical values calculated from the values of the single fuels. This lack of deviations cannot be translated to a lack of heterogeneity and could be attributed to the similarly high GCV of each polymer that exists in the plastic waste.

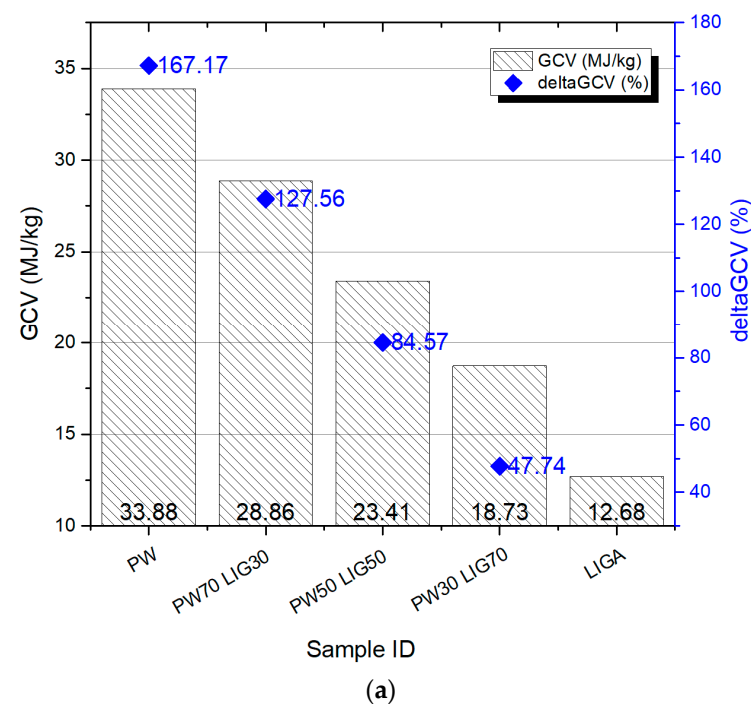


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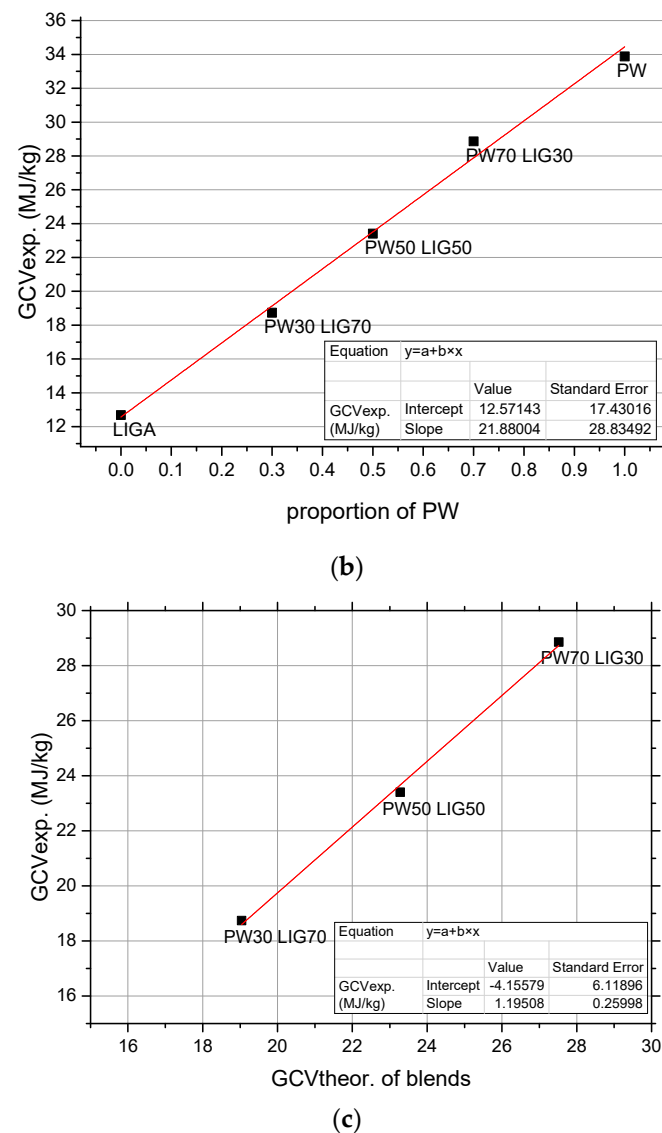


Figure 1. Results of the energy content analysis: (a) Gross calorific value of the samples and Δ GCV compared to lignite, (b) Dependent variable GCV_{experimental} (GCV_{exp.}, y) and independent variable wt.% percentage of PW into the blend with lignite (wt.% proportion of PW, x), (c) Scatterplot and linear regression model of dependent variable GCV_{experimental} (GCV_{exp.}, y) and independent variable GCV_{theoretical} (GCV_{theor.}, x).

3.2. Proximate Analysis

The results of the proximate analysis of the plastic waste sample and its blends with lignite are presented in Figure 2 as a ternary diagram. In contrast to the lignite sample, the volatile content of the plastic waste sample was found to be much higher and approximately 92 wt.%, whilst ash content was substantially lower at about 5 wt.%. Ash content is important since ash is a secondary waste and requires further management. In addition, ash (depending on its quality) can cause severe problems, e.g., depositions on the surface of the burner or other equipment. Thus, low ash content is desired. For such reasons, ash content is a crucial factor in choosing the combustion technology. There are several combustion technologies for different fuel qualities. For instance, fuels with ash content lower than 10 wt.% (dry basis, d.b.) in large-scale installation can be burned in a moving grate combustor [36]. The results of plastic waste samples are in agreement with the literature [13]. The moisture content of plastic waste was significantly lower than the one of lignite. During the combustion process, as the moisture evaporates, the energy of

the fuel cannot typically be recovered. Moisture content is a crucial characteristic of the fuel in the combustion process. High moisture content leads to a low calorific value of fuel [21]. It has been reported [37] that during the lignite co-combustion with municipal solid wastes, in a fluidized bed combustor (FBC), as the moisture increases, the combustion temperature decreases. Overall, plastic waste is superior to lignite in terms of proximate analysis. As for the case of GCV, the blending of lignite with plastic waste leads to an improvement of lignite's characteristics (lower ash, moisture, and fixed carbon) and higher volatiles' content.

Figure 3 presents the TG and DTG curves of lignite, PW samples, and their blends with lignite at the heating rate of 10 K/min. In lignite, three main stages can be recognized: dehydration of moisture, volatile release, and char combustion. In the plastic waste and the blended fuels, the second stage (release of volatiles) occurs at two sub-stages. As the content of PW increases in blends with lignite, the fuel ignites at lower temperatures and with higher reaction rates. In the TG graphs, it can be seen that in the PW sample, the combustion is completed earlier than lignite. In blends, as the PW proportion is increased, the combustion is completed at an earlier time. In other words, rapid ignition can be achieved by using mixed/composite fuel.

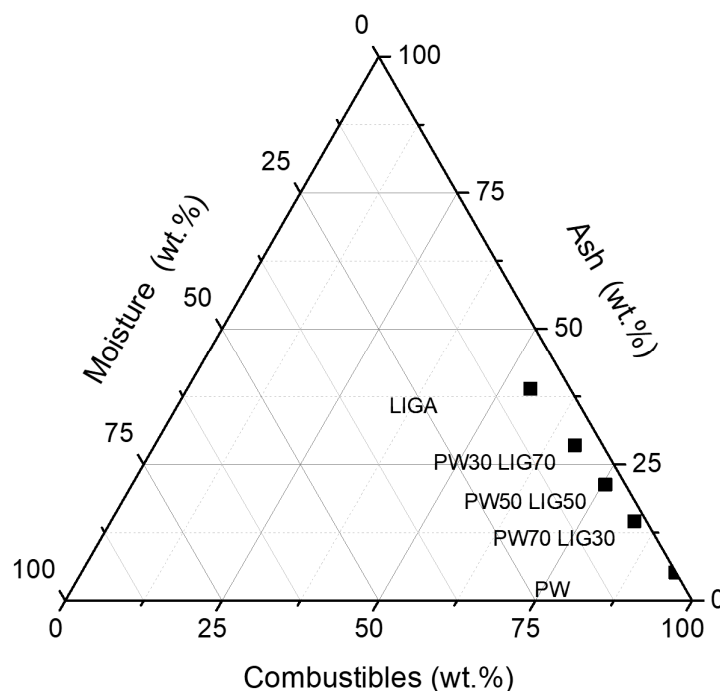


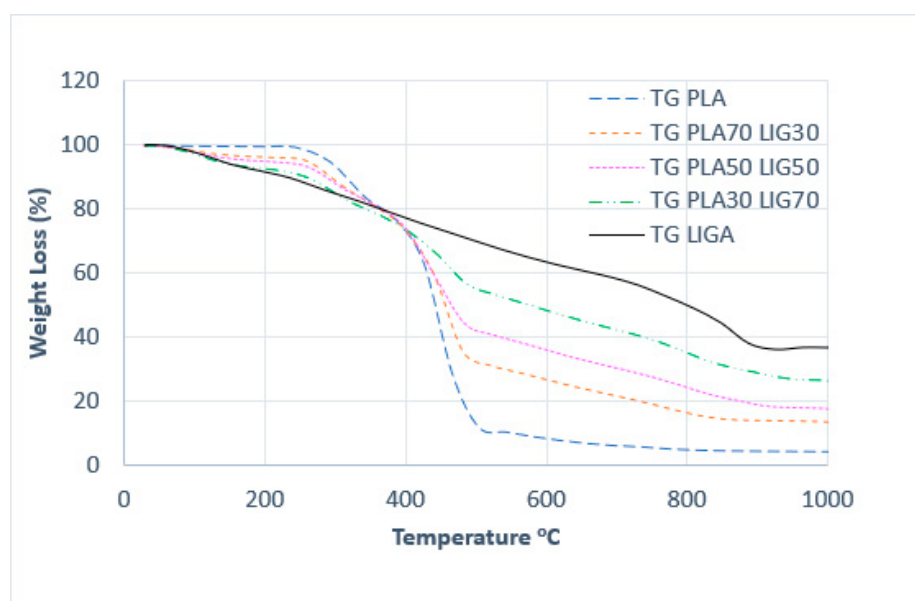
Figure 2. Proximate results of PW and its blends with LIGA presented in a Tanner diagram. More details are presented in Supplementary material.

3.3. Thermal Behaviour, Kinetic Analysis, and Synergistic Effects

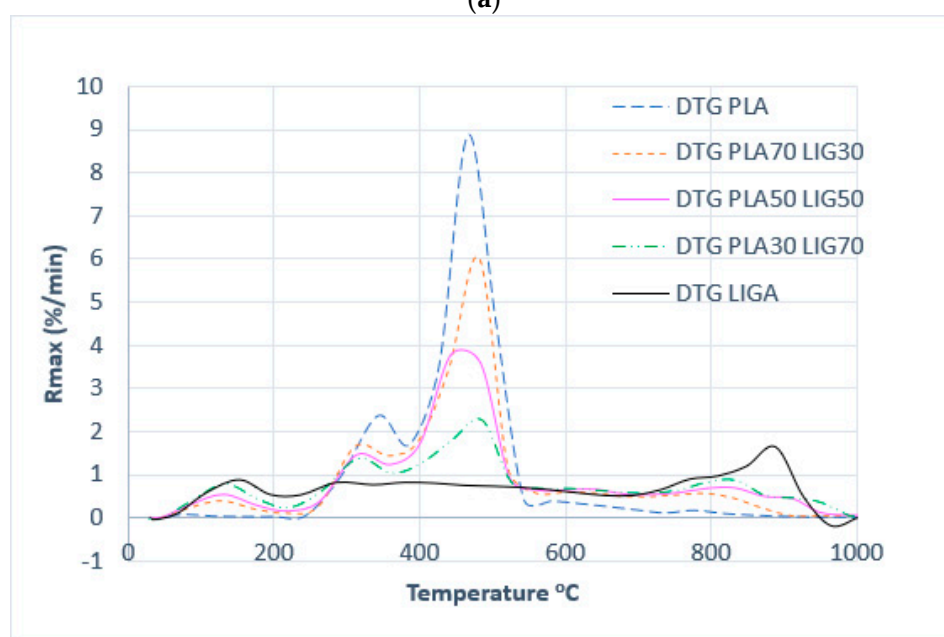
The results from thermogravimetric and derivative thermogravimetric analysis are presented in Table 1 and Figure 3. The plastic waste sample revealed the lowest maximum temperature ($T_{\max}$: 467 °C), that is, the temperature at which the mass loss rate becomes maximum. Also, plastic waste exhibited the highest maximum rate of weight loss ($R_{\max}$: ~9%/min) as well as the highest total mass loss of all samples and blends (about 96%). The high mass loss rate and the highest total mass loss are respectively in agreement with the volatile content and ash content of proximate analysis (see the results of the proximate analysis and Figure S2, Supplementary Material). Fuels with a high maximum rate of weight loss ignite easier, and fuels with low $T_{\max}$ reveal low NO_x emissions as they burn in lower combustion temperatures [36].

Table 1. Combustion characteristics of the analyzed sample (PW) and their blends with lignite in different proportions, as determined by TG/DTG analysis.

Sample ID	T _i (°C)	T _b (°C)	T _{max} (°C)	R _{max} (%/min)	t _b (min)	Total Mass Loss (%)
PW	273	815	467	8.86	52.38	95.91
PW70 LIG30	262	871	482	6.02	59.02	86.76
PW50 LIG50	264	911	443	3.77	62.83	82.95
PW30 LIG70	221	951	486	2.27	70.77	74.44
LIGA ¹	237	927	888	1.64	66.77	63.46

¹ LIGA results are from previous work [23].

(a)



(b)

Figure 3. Thermogravimetric analysis: TG/DTG graphs of all raw PW samples and their blends with lignite in different proportions under an air atmosphere with a flow rate of 3.5 L/min and heating rate of 10 °C/min. (a) TG graphs, (b) DTG graphs.

The above is also evident in the data presented in Table 1; however, for the $T_{\max}$, there is no linear trend, e.g., the PW50-LIG50 sample exhibits the lowest $T_{\max}$ value. This could be partially attributed to the heterogeneity of the plastic waste. However, it could also be considered to be an indication of synergistic effects in the blended fuels. For this reason, the DTG curves of the blend samples were calculated theoretically by the DTG curves of the single fuels (assuming that no interaction/synergy takes place) and compared to the experimental DTG curves of the blended fuels (Figure 4). As can be seen in Figure 4, the comparison of the experimental and theoretical DTG curves of the blended fuels points out that there is no full matching, and some small deviations can be observed. The main peak at around 450 °C, in the experimental curves, is slightly shifted to higher temperatures, and the experimental mass loss rate (the height of the peak) is lower than the theoretical one for all three blends. However, the main peak of lignite (around 900 °C) is shifted to lower temperatures in the experimental curves. It seems that lignite “captures” some of the volatile matter of plastic waste or reacts with the char that is formed and causes the alterations of the peak of plastic waste at around 450 °C, but this char-lignite residue combusts at lower temperatures. Though these deviations are not substantial enough, they could be considered as an indication of the possibility of the existence of synergistic effects.

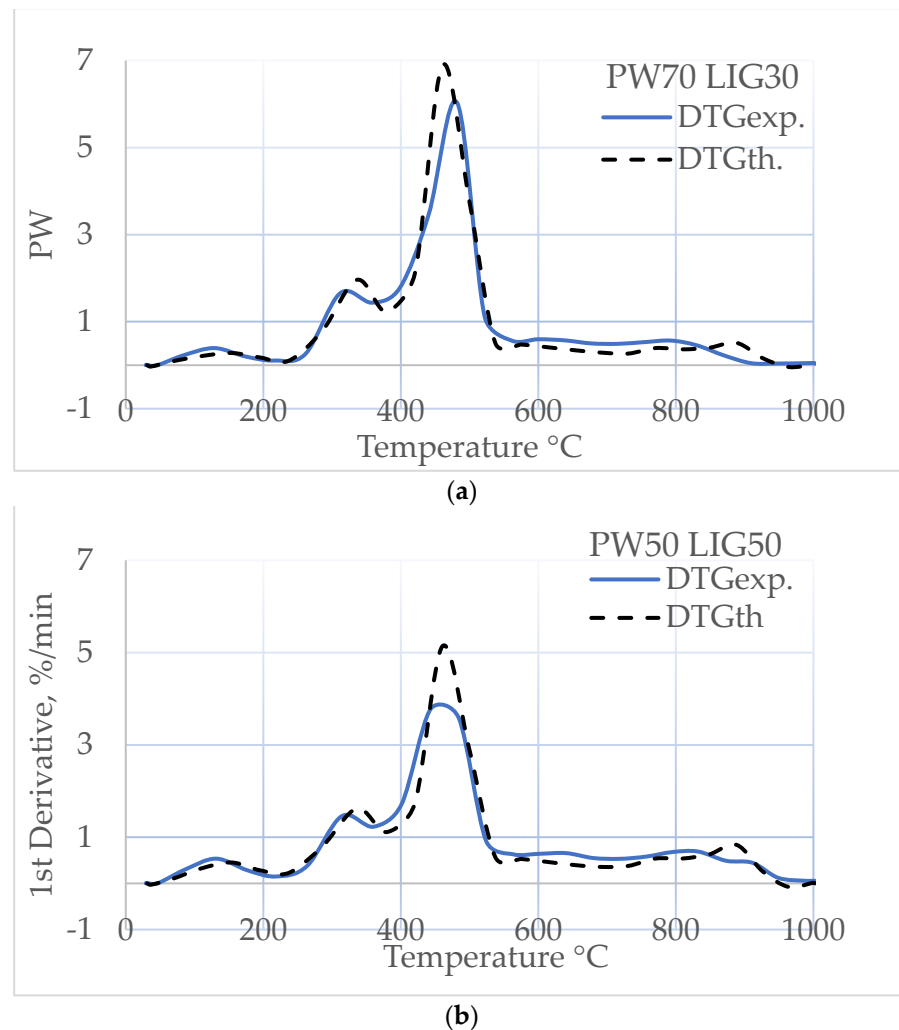


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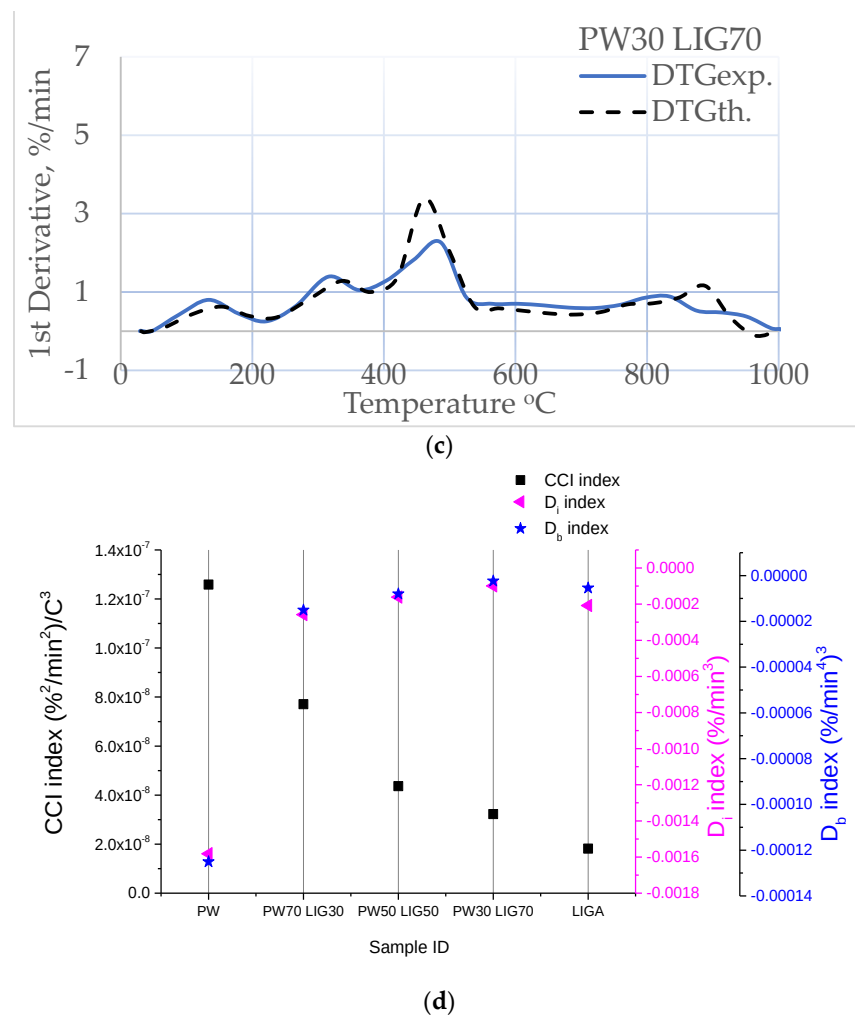


Figure 4. (a–c) Synergistic effect. DTG experimental vs. DTG theoretical blends: PW blends with lignite, (d) Synergistic effect. CCI, D_i and D_b indices.

Besides the above results from TG/DTG, indications for the existence of some synergistic effect can also be supported by the results of the Arrhenius kinetic analysis, which are presented in Table 2 (Arrhenius plots of the analyzed plastic wastes samples and blends with lignite are presented in Figure S2 of Supplementary Material). The activation energy of plastic waste is lower than the one of lignite. Of course, the reaction rate also depends on the pre-exponential factor A, which is orders of magnitude lower in the case of plastic waste than lignite. This lower value is counterbalanced by the lower activation energy resulting in a higher reaction rate for plastic waste. The blends exhibit even lower activation energy, suggesting the existence of synergistic effects. As mentioned in the Introduction, polymer oxidation involves a variety of chemical reactions. In the presence of lignite, such reactions are altered. In addition, the heat released by the combustion of some volatile products can be used for lignite decomposition leading to the shift of the peak in the DTG curve.

Based on the above, the results of the co-combustion performance indices can be understood (Figure 4d). The results showed that the highest values of the CCI index were exhibited by PW. The blends, compared to lignite, exhibited higher CCI values, with the PW70 LIG30 samples exhibiting a higher value, followed by blends with 50% plastic and 30% plastic, respectively. The values of the D_i and D_b indices of PW were maximum (as absolute values). In the blends, the values were similar to the ones of lignite, but the differences among the single fuels and the blends are less pronounced for the case of D_i and D_b . The results of the above-mentioned indices suggest that co-combustion enhances

combustion. In general, a higher heating rate leads to increased values of the CCI index, which means that a better ignition and burnout performance is achieved [38].

Table 2. Results of Arrhenius kinetic analysis.

Sample ID	From T (°C)	To T (°C)	a	b	R ²	E (kJ/mol)	A (1/s)
PW	250	467	−2884.29	3.01	0.8859	55.23	1.69×10^1
PW70 LIG30	217	482	−2609.61	2.47	0.9365	49.97	4.88×10^2
PW50 LIG50	219	443	−2153.17	1.69	0.9351	41.23	8.16×10^{-1}
PW30 LIG70	221	486	−1312.95	0.28	0.9132	25.14	3.14×10^{-2}
LIGA ¹	695	889	−3697.0	1.74	0.9686	70.8	9.26×10^6

¹ LIGA results were taken from previous studies of the authors [24,31].

3.4. Maximum Potential CO₂ Emissions and Environmental Impacts of Solid Waste Production

Table 3 presents the results of the elemental analysis of the samples/blends. The main elements in both plastic waste and lignite are Carbon (C), Hydrogen (H), and oxygen (O). Mikulčić et al. [13] found similar carbon and hydrogen content in polyurethane samples, and N and S content were about 6 wt.% and 0.6 wt.%, respectively (on an air-dried basis).

Table 3. Ultimate analysis (determination of C, H, N, S, O) of the PW sample and its blends with lignite. All values are expressed in wt.%.

Sample ID	C (%)	H (%)	N (%)	S (%)	O ¹ (%)
PW	68.81 ± 14.01	9.22 ± 3.09	Not detected	Not detected	16.81
PW70 LIG30 ²	58.84	7.57	0.27	0.30	18.44
PW50 LIG50 ²	52.20	6.47	0.45	0.50	19.07
PW30 LIG70 ²	45.55	5.37	0.63	0.70	19.23
LIGA ³	35.58 ± 0.05	3.73 ± 0.06	0.9 ± 0.09	Not detected	19.89 ⁴

¹ Oxygen was calculated by difference. $O = 100 - C - H - N - S - \text{Ash}$. ² Values of C, H, N, S for the blended fuels were not measured experimentally but were calculated from the respective values of the individual fuels.

³ LIGA results were taken from a previous study by the authors [23,26]. ⁴ Oxygen of lignite was calculated with a maximum value of S.

The C content of plastic waste is substantially higher (almost double) than the one of lignite. Thus, it would be expected that the (maximum) potential CO₂ emission of plastic waste will be double that of lignite. Indeed, this is true if the CO₂ emissions are expressed per kg of fuel. However, one kg of fuel (lignite or plastic waste) does not produce the same amount of energy. Consequently, it is proper to express the emissions per MJ of produced energy. Thus, by taking into account the results from the ultimate analysis and the GCV values, the emission of plastic waste (g of CO₂ per 1MJ of produced energy) is somewhat lower than the one of lignite, as presented in Table 4. It should be stressed that although lignite has lower overall carbon content, it exhibits higher fixed carbon content (see Table S1 in Supplementary Material). This inconsistency is apparent since fixed carbon expresses the non-volatile carbon. In other words, lignite exhibits lower content of overall and volatile carbon and higher content of non-volatile (fixed) carbon.

From the proximate analysis as well as the TG curves, it is obvious that plastic waste combustion results in a significantly lower amount of produced ash. Suggestively, in Table 4, the amount of ash produced by the combustion of 100,000 tons of fuel is presented. As can be seen, plastic waste results in an 84% reduction of produced ash. If the amount of produced ash is expressed, as for the case of CO₂ emission, per produced energy (environmental footprint indicator, EFI_w), then the difference between plastic waste and lignite in terms of ash production becomes even higher (95%) as can also be seen in Table 4. The lower CO₂ emissions and lower ash production of plastic waste are also evident in the blended samples, which are superior to lignite. Of course, the amount of produced ash is

important, but its quality is also important. In what follows, we present and discuss the results of the qualitative and quantitative composition of the ash produced by lignite and plastic waste.

Table 4. Maximum potential CO₂ emissions and environmental footprint indicator (EFI_w) of single and blended fuels.

Sample ID	gCO ₂ /MJ	Ash Production from Production 100,000 t Fuel (t)	%Deviation of Sample Produced Ash from Lignite Combustion Ash (%)	EFI _w Ash per Megaloule (kg/MJ)	%Deviation of Sample Produced Ash per MJ from Lignite Combustion Ash (%)
PW	74.5	5160	−86.74	0.0015	−95.04
PW70 LIG30	74.8	14,580	−62.52	0.0051	−83.53
PW50 LIG50	81.8	21,310	−45.22	0.0091	−70.33
PW30 LIG70	89.2	28,510	−26.71	0.0152	−50.38
LIGA ¹	102.9	38,900	0.00	0.0307	0.00

¹ LIGA results were taken from a previous study by the authors [24]

3.5. Ash Quality

In Table 5, the composition of the ash produced, which was produced by the combustion of plastic waste and lignite, is presented (the values of the blended fuels were estimated theoretically). These values were derived from the EDS spectrums obtained during the observation of the ash samples with SEM. In Figure 5a,b, some SEM micrographs are presented suggestively, along with the areas used to obtain the EDS spectra.

Table 5. Results of chemical ash composition of the analyzed plastic waste sample and its blends with lignite.

Sample ID	SiO ₂ (%)	CaO (%)	K ₂ O (%)	P ₂ O ₅ (%)	Al ₂ O ₃ (%)	MgO (%)	Fe ₂ O ₃ (%)	SO ₃ (%)	Na ₂ O (%)	TiO ₂ (%)
PW	4.60	22.35	10.89	23.42	0.90	5.84	4.71	1.25	15.01	0.28
PW70 LIG30 ¹	9.37	26.81	11.70	17.42	1.54	9.33	3.30	1.62	10.51	0.19
PW50 LIG50 ¹	12.54	29.78	12.24	13.43	1.97	11.66	2.35	1.87	7.51	0.14
PW30 LIG70 ¹	15.72	32.75	12.78	9.43	2.39	13.99	1.41	2.12	4.50	0.08
LIGA ²	20.49	37.20	13.60	3.44	3.03	17.48	0.00	2.50	0.00	0.00

¹ Chemical ash composition results of PW blends with lignite were calculated. ² LIGA results were taken from a previous study [33].

The evaluation of the ash quality can be facilitated by the ternary diagrams, in which the various oxides being present in ash are presented in three groups, namely, SiO₂ + Al₂O₃ + Fe₂O₃ + Na₂O + TiO₂, CaO + MgO + MnO, and K₂O + P₂O₅ + SO₃. Depending on the relative contents of each group, the ash is characterized as type C (calcium type), S (silicon type), K (potassium type), and the intermediate type CK. Increased amounts of silicon and potassium are related to the potential formation of silicates and potassium salts, which are considered likely to cause deposits; thus, ash types S and K are considered ashes with high deposit risk. Type C is considered to be of low deposit risk since calcium salts typically exhibit higher melting points than potassium salts. Consequently, the intermediate type CK is considered medium-risk ash for deposition and slagging problems [39]. As can be seen in Figure 5c, lignite's ash, due to its high Ca content, is close to the C type but actually is marginally within the region of the CK type. The ash from plastic waste has lower Ca content but is also within the region of the CK type. Consequently, the ash quality of lignite and plastic waste is different, but it is of the same type, and thus similar medium slagging problems are expected.

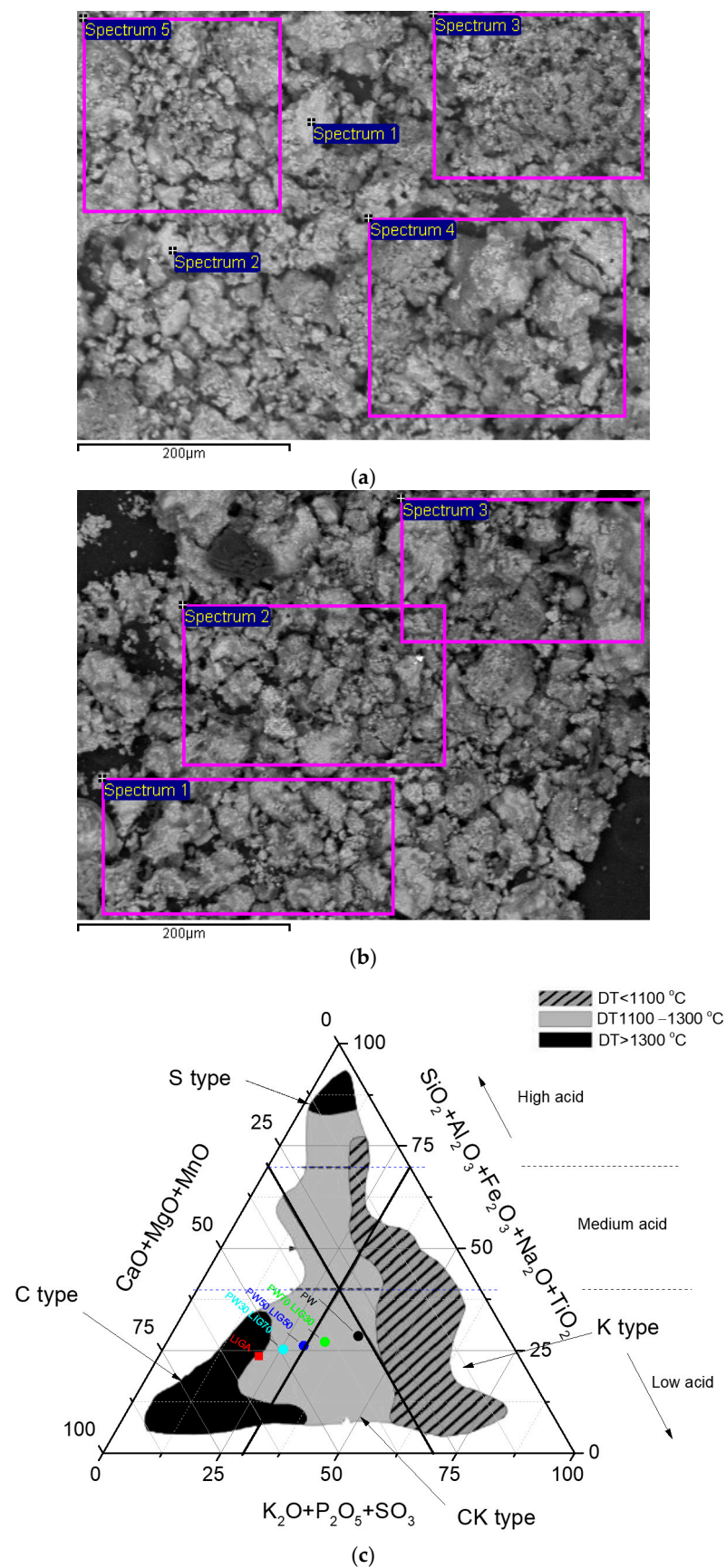


Figure 5. (a,b) SEM spectrum results of PW sample, and (c) Ash composition presented in ternary diagram.

4. Conclusions

The plastic waste from municipal solid waste was characterized by various methods in terms of energy content, thermal behavior, kinetic analysis, emissions, quality, and amount of produced ash. The plastic waste was compared to a well-established solid fuel, namely lignite. Three different plastic waste-lignite blends were also studied. Plastic waste was found to be superior to lignite in terms of calorific value and thermal and kinetic behavior (lower temperature of maximum mass loss rate, lower activation energy, and higher reaction rate). In terms of production of the main waste/pollutants (CO₂ and ash), plastic waste was also found to be superior. More precisely, despite the fact that plastic waste contains almost double the carbon content than lignite, due to its higher calorific value, it exhibits a decreased maximum potential CO₂ emission (expressed per produced energy and not per mass of fuel). Plastic waste combustion is related to the considerably lower amount of produced ash, either in the case of ash per kg of fuel or in the case of ash per produced energy. The high Ca content of lignite is responsible for better ash quality (lower slagging and deposition problems). However, the ash from plastic waste is of the same type as the one of lignite. The advantages of plastic waste can also be utilized in blends with lignite. Overall, if anti-pollution technology is applied to capture toxic compounds produced by plastic waste, then the combustion of plastic waste seems to be a viable solution for plastics with low potential for recycling, such as already surface-disposed plastics, laminated plastics, etc. Thus, future work could focus on the study of emissions from plastic waste combustion, how they are affected by the co-combustion with lignite, and explore various technologies for their capture.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/app13148141/s1>; Figure S1: Stages of TG/DTG graphs of all samples and blends with lignite, Figure S2: Arrhenius plots of the analyzed plastic waste sample and its blends with lignite, and Table S1: Results of the proximate analysis of plastic wastes sample (PW), and its blends with lignite, in wt.%.

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