Celal Bayar University Journal of Science

Co-pyrolysis of Different Coal Types with Biomass: Performance and Efficiency Evaluation by Thermogravimetric Analysis

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Received: 17 March 2025
Accepted: 27 May 2025
DOI: 10.18466/cbayarfbe.1659482

Abstract

In this study, the effect of co-pyrolysis of lignite and asphaltite, which are fossil energy sources with significant reserve potential in Turkey, with biomass sources such as walnut shell and hazelnut shell used as renewable energy sources on product efficiency and quality was investigated. The pyrolysis behavior of lignite, asphaltite, two types of biomass, lignite-biomass and asphaltite-biomass mixtures were investigated by non-isothermal thermogravimetric analysis (TGA) to evaluate the influence of biomass type, biomass mixturing ratio and pyrolysis temperature on co-pyrolysis behavior. Pyrolysis experiments were carried out at three different temperatures (400, 460, and 520°C), first with the raw samples and then with mixtures at weight ratios of 25%, 50% and 75%. Possible synergistic effects were investigated by determining the mixture ratios and temperatures with the highest solid, liquid and gaseous product yields by analyzing the pyrolysis conversions. It was observed that the calorific values obtained before the pyrolysis process showed a significant increase after the process was applied. Increasing the amount of biomass added to lignite resulted in a 13.87% increase in calorific value and a positive synergy effect was indicated. Additionally, the addition of biomass to lignite and asphaltite reduced ash content and sulfur content.

Keywords: Asphaltite, Biomass, Co-pyrolysis, Lignite

1. Introduction

In recent years, there has been great interest in the utilization of agricultural wastes such as walnut shells, hazelnut shells, tea pulp, corn cobs, rice husks as biomass sources due to their renewability, low cost and abundant availability. Biomass can be cultivated in various locations, easily stored, contributes to socio-economic development, and has more favorable environmental impacts. Today, it is used in different industries for electricity generation, as a chemical feedstock, and as a liquid fuel. Due to these advantages, biomass energy has gained considerable importance for Turkey. Turkey ranks fourth in the world in walnut production, with an annual production of 287,000 tons. Additionally, based on the last decade's average, Turkey produces approximately 765,000 tons of hazelnut annually, accounting for about 70% of global production, with nearly half of this output consisting of shells [1]. Lignite is the most abundant type of coal in Turkey. According to 2024 data, 20.53 billion tons of our country's coal reserve is lignite and approximately 19.32 billion tons of asphaltite is lignite [2].

In general, coal combustion is a major source of SOx and NOx emissions, which are the main causes of global climate change and acid rain. Biomass contains small amounts of nitrogen and phosphorus but almost no sulfur, so it produces lower emissions during its combustion. Therefore, it is considered that the co-utilization of biomass and coal can limit emission problems [3]. In our country, which has a high potential in terms of coal and biomass, this issue has been added to the chemistry and energy fields in the 11th and 12th Development Plans covering 2019-2023 in order to make these resources available for more efficient use [4]. Although a large number of studies have been carried out worldwide, especially in developed countries, studies in this field have gained momentum in Turkey in recent years. In this context, studies to be carried out for more efficient use of biomass and coal are of great importance.

Pyrolysis is the thermal decomposition of organic materials and is the first step in thermochemical conversion processes such as carbonization, gasification and combustion. It consists of a very complex set of reactions involving the formation of radicals and can be classified as a heterogeneous chemical reaction.

Some of the studies investigating the pyrolysis process of mixtures with different biomass/coal ratios by thermogravimetric analysis (TG) did not show any synergistic effect [5,6], whereas some of them showed opposite results [7-9]. In addition to these, different studies have confirmed the occurrence of synergy effect on the gas component of pyrolytic products, tar components and yields of these products [10,11].

The application of co-pyrolysis has been found to be both environmentally and economically beneficial [12]. The occurrence of synergy during co-pyrolysis is usually not certain and this effect is observed depending on the pyrolysis technique and fuels used. It has been reported that further research is needed to confirm the synergistic effect of the co-pyrolysis process and to better understand the mechanisms responsible for its synergistic effect [13,14].

Abnisa and Wan Daud [15], Mushtaq et al. [16] stated that there is limited research regarding the co-pyrolysis of coal/biomass blends. The non-isothermal thermogravimetric analysis of coal and corn stalk mixture at different heating rates indicated that the thermochemical reactivity of corn stalk is higher than that of coal [17]. The increase in tar yield and decrease in coke yield observed as the ratio of biomass to coal increased was attributed to the synergistic effect during the co-pyrolysis process [18-20].

In pyrolysis experiments, coal and biomass are two essential carbonaceous raw materials, and their co-pyrolysis has been proven to alter the fuel properties of the resulting oil and coke [21]. The co-processing of coal and biomass can increase product yield and reduce pollutant content [22]. The high H/C ratio of biomass can increase the decomposition of coal, whereas the minerals and inorganic components in coal can increase the decomposition of biomass. The effects hyper-coal yield obtained from a mixture of 80 wt% low rank coal and 20 wt% biomass on coke strength and structure were investigated. It was observed that oxygen and sulfur content decreased, ash content decreased significantly from 10.37 wt% to 0.86 wt%, and solvent thermal extraction, which was selected as the method, was found to be an effective technique to improve low-rank coal [23]. In the co-pyrolysis of low-metamorphic coal and pine sawdust, increasing the sawdust ratio from 10% to 50% resulted in an increase in tar yield from 11.58% to 16.62%. The addition of biomass shifted the pyrolysis process of coal to a low temperature region, decreased the pyrolysis temperature of the coal sample, and increased the pyrolysis rate of the sample [24].

The aim of this study is to investigate the product yields to be obtained from the pyrolysis of two types of coal and biomass resources available in Turkey, which has approximately 20 billion tons of coal reserves and to determine the synergistic effects between them. For this purpose, both the more efficient utilization of the country’s indigenous lignite and asphaltite, along with the valorization of currently underutilized biomass, reducing the environmental pollution of fossil-based coal, and activating it with biomass and increasing the efficiency of these two resources will provide a significant advantage.

2. Materials and Methods

2.1. Materials

In this study, the samples to be used as coal sources were lignite obtained from Edirne province and asphaltite sourced from Şırnak province. The biomass feedstocks consisted of walnut shells collected from the Çorum region and hazelnut shells obtained from the Black Sea region. All sample preparation and analysis procedures were conducted in accordance with ASTM standards.

The samples were first dried in an oven at 40°C for 24 hours according to ASTM D2013 standard and then ground to a particle size of less than 250 µm and stored in airtight plastic containers in the laboratory for use. Proximate analysis, including moisture, volatile matter, fixed carbon, and ash content analysis and elemental analysis (carbon, hydrogen, nitrogen, oxygen, and sulfur contents) of the samples were performed and the high heating value (HHV) was determined using a calorimeter bomb, and the results are given in Table 1. Elemental analysis was performed according to ASTM D5373 standard and calorific value determination was performed according to ASTM D5865 standard. The elemental analysis was carried out using a LECO CHN 628 analyzer and the oxygen content was calculated by difference. The sulfur content was determined in accordance with ASTM D4239 standard. The calorific values of the samples were determined by burning in a calorie bomb in a LECO AC 500 calorimeter.

2.2. Characterization

The thermogravimetric analysis (TGA) of raw samples and mixtures prepared at different ratios was performed using a LECO TGA 701 analyzer in the temperature range of 30°C -1000°C under a nitrogen atmosphere with at a flow rate of 100 mL/min. The ash content of combusted lignite and asphaltite samples was dissolved in acid, and the trace elements in the mineral matter content were determined using an ICP-OES analyzer. Due to the insufficient ash content in walnut and hazelnut shell samples, the mineral matter content in their ash could not be determined. The X-ray fluorescence (XRF) analysis of the samples was performed using a Thermo Perform X model XRF analyzer.

2.3. Prolysis Experiments

The pyrolysis processes were carried out on the fixed bed pyrolysis system shown in Figure 1 according to TS 729 ISO 647 standard. A 30 g sample is placed into the retort. The collectors are weighed when empty and then properly connected to the retorts. After programming the control unit according to the desired temperature, the furnace is started to heat up. A thermocouple is inserted into the retort to measure the ambient temperature. Initially, the retorts remain elevated in the furnace, and once the preheating process is complete, the furnace is raised using a pneumatic mechanism and the retorts are placed in the oven. After the completion of the experiment, the collector and the liquid product are weighed together. The residual solid (coke) remaining in the retort is weighed. The amount of gas product is determined by subtracting the total weight of the liquid and residual coke.

In this stage of the experimental study, initially the samples (lignite-EL and asphaltite-SA as coal source; hazelnut shell-HS and walnut shell-WS as biomass source) in their raw forms without mixing, and then lignite-biomass and asphaltite-biomass mixtures were mixed at 25% (wt), 50% (wt) and 75% (wt) by weight were pyrolyzed at 400°C, 460°C, and 520°C. Following the pyrolysis process, solid, liquid, and gaseous product yields were determined, and the pyrolysis conversion was calculated.

Figure 1. The fixed bed pyrolysis system.

3. Results and Discussion

3.1. Pre-analysis of Samples

The pre-analysis results of the raw samples and the lignite-biomass and asphaltite-biomass mixtures prepared at three different ratios are presented in Table 1. When the results are analyzed, it is observed that the calorific heating value increased by 13.87% with the increase in the amount of biomass added to lignite, whereas the calorific heating value decreased by 7.3% with the increase in the amount of biomass added to asphaltite.

Lignite and asphaltite samples have high ash contents of 33.88% and 41.12%, respectively, while walnut and hazelnut shells selected as biomass samples have very low ash contents of 0.45% and 0.80%, respectively. The addition of biomass to lignite and asphaltite samples reduces their ash content. Furthermore, the volatile matter content of the biomass samples is considerably higher compared to lignite and asphaltite. The high volatile matter content of these samples contributes to their high calorific value [25].

Table 1. Proximate analysis of samples.

Sample	Moisture (wt %)	Ash (wt %)	Volatile matter (wt %)	Fixed carbon (wt %)	Calorific value (kcal/kg)
SA	0.71	41.12	43.97	14.21	4650
EL	8.02	33.88	34.12	23.98	3507
WS	6.45	0.45	75.93	17.17	4201
HS	8.29	0.80	72.28	18.64	4193
EL75-WS25	7.71	25.06	45.28	21.96	3680
EL50-WS50	7.25	16.72	55.16	20.87	3854
EL25-WS75	6.81	8.46	65.48	19.25	4027
EL75-HS25	8.26	25.72	43.05	22.97	3678
EL50-HS50	8.27	11.68	58.65	21.41	3850
EL25-HS75	8.30	8.78	61.49	21.44	4022
SA75-WS25	2.08	34.29	49.03	14.60	4537
SA50-WS50	3.46	23.33	58.37	14.84	4425
SA25-WS75	4.86	11.30	68.91	14.93	4313
SA75-HS25	2.53	34.22	48.26	14.99	4535
SA50-HS50	4.36	23.37	56.74	15.52	4421
SA25-HS75	6.25	12.10	64.49	17.16	4307

Table 2. Elemental analysis of samples.

Sample	C	H	N	O*	S	H/C	O/C
SA	45.88	3.56	1.22	42.28	7.06	0.93	0.69
EL	40.38	2.94	1.21	52.41	3.06	0.87	0.97
WS	48.62	5.39	0.38	45.58	0.03	1.33	0.70
HS	48.79	5.16	0.53	45.50	0.02	1.27	0.70
EL75-WS25	42.44	2.69	1.00	51.36	2.51	0.76	0.91
EL50-WS50	44.50	3.35	0.80	49.67	1.68	0.90	0.84
EL25-WS75	46.56	4.02	0.59	47.97	0.86	1.04	0.77
EL75-HS25	42.48	2.57	1.04	51.40	2.51	0.73	0.91
EL50-HS50	44.59	3.13	0.87	49.73	1.68	0.84	0.84
EL25-HS75	46.69	3.68	0.70	48.07	0.86	0.95	0.77
SA75-WS25	46.57	3.78	1.01	43.28	5.36	0.97	0.70
SA50-WS50	47.25	4.09	0.80	44.27	3.59	1.04	0.70
SA25-WS75	47.94	4.39	0.59	45.27	1.81	1.10	0.71
SA75-HS25	46.61	3.68	1.05	43.30	5.36	0.95	0.70
SA50-HS50	47.34	3.87	0.88	44.32	3.59	0.98	0.70
SA25-HS75	48.06	4.06	0.70	45.37	1.81	1.01	0.71

* calculated from the difference

The elemental analysis results of the samples are presented in Table 2. It was found that the carbon and hydrogen contents of walnut and hazelnut shells selected as biomass sources are very close to each other. Compared to the raw lignite and asphaltite samples, the mixtures formed using these biomass sources exhibited increased carbon and hydrogen content. The sulfur content of the lignite and asphaltite samples was determined to be 3.06% and 7.06%, respectively, which is consistent with existing studies in the literature [26,27]. It was observed that increasing the amount of biomass added to the lignite and asphaltite samples gradually decreased the sulfur content of the asphaltite mixture to 1.81% and the lignite mixture to 0.86%.

The pyrolysis of coal produces limited liquid yields due to its low H/C ratios. To enhance the quality of liquid products, providing an additional hydrogen source is essential. Therefore, the co-pyrolysis of coal and biomass has been suggested as an effective process to improve product yields [28]. When walnut and hazelnut shell were added to lignite, the highest H/C molar ratio was obtained at a 75% mixing ratio of biomass. The H/C ratios of the lignite samples with biomass addition ranged between 0.73 and 1.04. Similarly, increasing the amount of biomass in the asphaltite samples resulted in higher H/C molar ratios, ranging from 0.95 to 1.10. The increase in the H/C molar ratio, indicating higher hydrogen content, enhances volatile matter content and calorific value, ultimately leading to the production of high-quality products. This trend is consistent with previous results suggesting that biomass addition increases hydrogen content and reduces fixed carbon dominance in coal blends, thereby improving combustion reactivity [28, 33].

Table 3. Mineral matter content in ash of lignite and asphaltite samples

Samples (ppm)	**Al**	**B**	**Ba**	**Be**	**Bi**	**As**	**Ca**	**Cd**	**Co**	**Cr**
EL	36533	253	292	5	<0.1	71	41054	1	16	103
SA	6502	45	164	2	<0.1	89	19719	62	7	235
(LOD)	0.065	0.072	0.083	0.024	0.035	0.029	0.087	0.011	0.013	0.028
	Cu	**Fe**	**K**	**Li**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**P**
EL	17	47125	6805	24	19959	381	3	4425	120	255
SA	119	17800	3263	11	23814	86	1500	856	1717	3879
(LOD)	0.009	0.033	0.093	0.048	0.082	0.071	0.063	0.071	0.043	0.084
	Pb	**Si**	**Sn**	**Sr**	**Ti**	**V**	**Zn**	**Se**	**Zr**	
EL	43	962	18	840	380	109	126	3.8	36.9	
SA	17	624	18	588	39	3156	3559	69.4	7.1	
(LOD)	0.058	0.092	0.035	0.036	0.088	0.063	0.039	0.063	0.067	

Table 3 presents the mineral matter contents of the coal and asphaltite ash samples, along with the corresponding LOD (limit of detection) values for each element. The inclusion of LOD values ensures analytical transparency and facilitates the accurate interpretation of trace element concentrations by clarifying the detection limits associated with each analyte. The high mineral matter content in lignite and asphaltite resulted in a high ash content. During the conversion of coal by thermal processes, certain elements in coal ash, such as Na, Al, Mg, and Ca, may exhibit catalytic effects. The mineral matter or ash content affects the adsorption capacity of coal seams [29]. Interactions between chlorine (Cl), sulfur (S), and alkali and alkaline earth metals (AAEM) are critical factors affecting ash formation, transformation, and accumulation during biomass and coal gasification and combustion. These problems lead to slag formation, agglomeration, corrosion, and other issues related to the safety performance of gasifiers and boilers [30].

3.2. Thermogravimetric Analysis Results of the Samples

The TGA and DTA curves obtained as a result of the analysis of the raw samples to investigate their thermal degradation are given in Figure 1.

The results of TGA analysis show that hazelnut shell, walnut shell, lignite, and asphaltite samples begin to decompose at low temperatures, and their decomposition continues up to approximately 950°C. At 950°C, mass losses are nearly 100% for walnut shell, 97% for hazelnut shell, 63% for lignite, and approximately 51% for asphaltite. The mass loss observed between 65-160°C in hazelnut shell, walnut shell, and lignite samples is attributed to moisture loss in their structures, whereas no significant mass loss is observed in the asphaltite sample at these temperatures, indicating that the sample is dry. The decomposition rate defines the rate at which a substance breaks down as a result of change over time. For hazelnut and walnut shell samples, mass loss occurs at lower temperatures, leading to a significant increase in the decomposition rate.

The TGA and DTA analysis results exhibit highly similar decomposition curves for both biomass samples. Due to the high volatile matter content of walnut and hazelnut shell samples, the total mass losses observed in their TGA curves are higher than those of lignite and asphaltite samples. The two sharp peaks observed in the DTA curves of the biomass samples can be attributed to the decomposition of hemicellulose and cellulose, respectively [31]. There are two clearly visible peaks around 255°C and 305°C in the hazelnut shell sample and 280°C and 330°C in the walnut shell sample. It can be said that significant degradation of plant-based organic matter occurs within the 250-350°C temperature range, with the degradation rate beginning to decrease from 380°C onward, stabilizing around 400°C, and lignin degradation continuing at higher temperatures. The higher decomposition temperature of walnut shell compared to hazelnut shell may be attributed to its more hemicellulose and lignin content. It has been reported that the thermal degradation of hemicellulose occurs in the 200-260°C temperature range, thermal degradation of cellulose in between 240-350°C, and thermal degradation of lignin in the temperature range of 280-500°C [32]. Based on this data, observed the low-temperature peaks (255°C and 280°C) in biomass samples are likely due to hemicellulose degradation, while at the high-temperature peaks (305°C and 330°C) can be attributed to cellulose degradation. Hemicellulose has an amorphous and moderately rigid structure, whereas cellulose consists of straight-chain molecules with a stronger structure. Therefore, the degradation of cellulose occurs at higher temperatures.

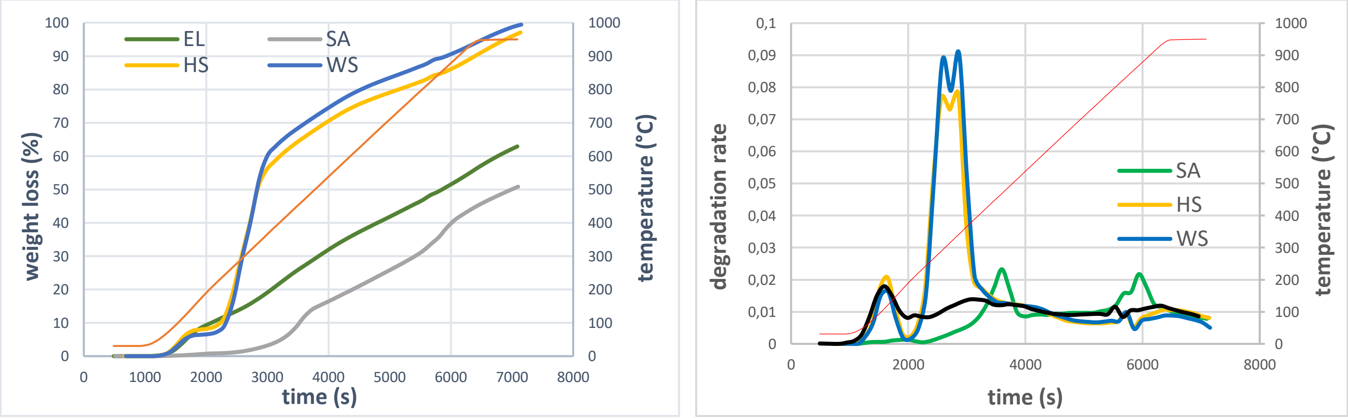

Figure 1. TGA and DTA curves for lignite (EL), asphaltite (SA) and biomass (HS and WS)

As the coal rank increases, the main pyrolytic decomposition regions shift to higher temperatures due to the strength of the bonds in the structure of the sample. The macromolecular components of biomass are linked by weak ether bonds, which exhibit low thermal resistance even at low temperatures. On the other hand, coal molecules have stronger pyrolytic aromatic hydrocarbons and C=C bonds, which show higher resistance to thermal degradation. Therefore, it can be said that lignite and asphaltite samples decompose at higher temperatures compared to biomass due to the presence of their C=C bonds. The degradation of coal samples occurred at approximately 255°C and 865°C. The degradation rate of biomass samples is considerably higher than that of coal, and these degradation rates are observed as sharp peaks in the DTA curves. In contrast, the degradation peak of coal is more widespread, indicating that the degradation process occurs over a wider temperature range.

In the lignite sample, a steady increase in mass loss is observed in the temperature range of 255-450°C, remains constant after 450°C, a peak occurs again around 800°C and remains constant again after 850°C. When the DTA curve of the asphaltite sample is analyzed, a degradation progressing at a constant rate up to 230°C is observed, but after 250°C, a rapid degradation peak is observed up to around 465°C. The degradation continues steadily in the temperature range of 510-800°C. It is observed that the first shoulder peak appears at 820°C, followed by a more distinct peak at 865°C, with decomposition proceeding in a horizontal manner from 900°C onwards. Unlike the biomass and lignite samples, the degradation rate of the asphaltite sample increases between 850-900°C, leading to further mass loss.

3.3. Thermogravimetric Analysis Results of the Mixture Samples

The TGA and DTA curves obtained as a result of the analysis of the mixture samples to investigate their thermal degradation are given in Figure 2 and 3, respectively.

In all TGA and DTA curves, it is observed that as the biomass ratio added to the lignite and asphaltite samples increases, both mass loss and degradation rates increase for the mixtures. This observation is attributed to the fact that the degradation in the structure of lignocellulosic biomass occurs at lower temperatures and at a faster rate. Additionally, as seen in the curves obtained from the analysis results, the degradation temperature decreases as the biomass mass ratio increases. The observed decrease in decomposition temperatures with increasing biomass ratio indicates the catalytic influence of biomass on thermal degradation behavior, consistent with previous studies showing that biomass facilitates the early release of volatiles and accelerates thermal breakdown of the blend [24, 31].

3.4. Experimental and Hypothetical (Theoretical) Thermogravimetric Analysis Results

Hypothetical values are calculated from the formula given in Equation 3.1 using the TGA and DTA data obtained as a result of the experiments.

$$W_{hypothetical} = X_{coal} \times W_{coal} + X_{biomass} \times W_{biomass} \tag{3.1}$$

$$\Delta W = W_{experimental} - W_{hypothetical}$$

Here, Wcoal and Wbiomass represent the mass loss amounts obtained in the raw form for coal and biomass, Xcoal Xbiomass represents the mixing ratios of coal and biomass, respectively. The Whypothetical value is calculated for each sample using the data from TGA curves. The ΔW synergistic value is used to describe the deviation between the experimental value and the calculated (hypothetical) value in the co-pyrolysis process. When the experimental values of coal and biomass samples mixed in different ratios are compared with the calculated values of the raw samples, a noticeable increase in the samples indicates a positive synergistic effect, whereas a noticeable decrease indicates a negative synergistic effect. In other words, if ΔW is significantly greater than zero, this is a positive synergistic effect; if the value is significantly less than zero, it is a negative synergistic effect.

The TGA and DTA curves obtained for the experimental and theoretical (hypothetical) calculations of the asphaltite–hazelnut shell mixtures prepared at three different ratios are given in Figure 4. As the amount of biomass added to asphaltite increases, both the experimental and theoretical results show an increase in mass loss, along with an increase in the rate and amount of degradation. In the TGA result of the asphaltite–hazelnut shell mixtures, the experimental and theoretical curves exhibit similar trends, and the pyrolytic transformations are close to each other. Increasing mass losses in experimental values around 240°C are higher than the theoretical values. At around 370°C, while the theoretical and experimental values for the SA75-HS25 and SA50-HS50 mixtures are quite close to each other, the experimental mass loss values for the SA25-HS75 mixture are lower than the theoretical values, indicating a negative synergistic effect. In the DTA result, the first peak, occurring around 110°C, indicates that the experimental values undergo degradation at lower temperatures, while the degradation rates are quite similar. In the second peak, which begins around 310°C, a decrease is observed in both the degradation amount and temperature in the experimental values.

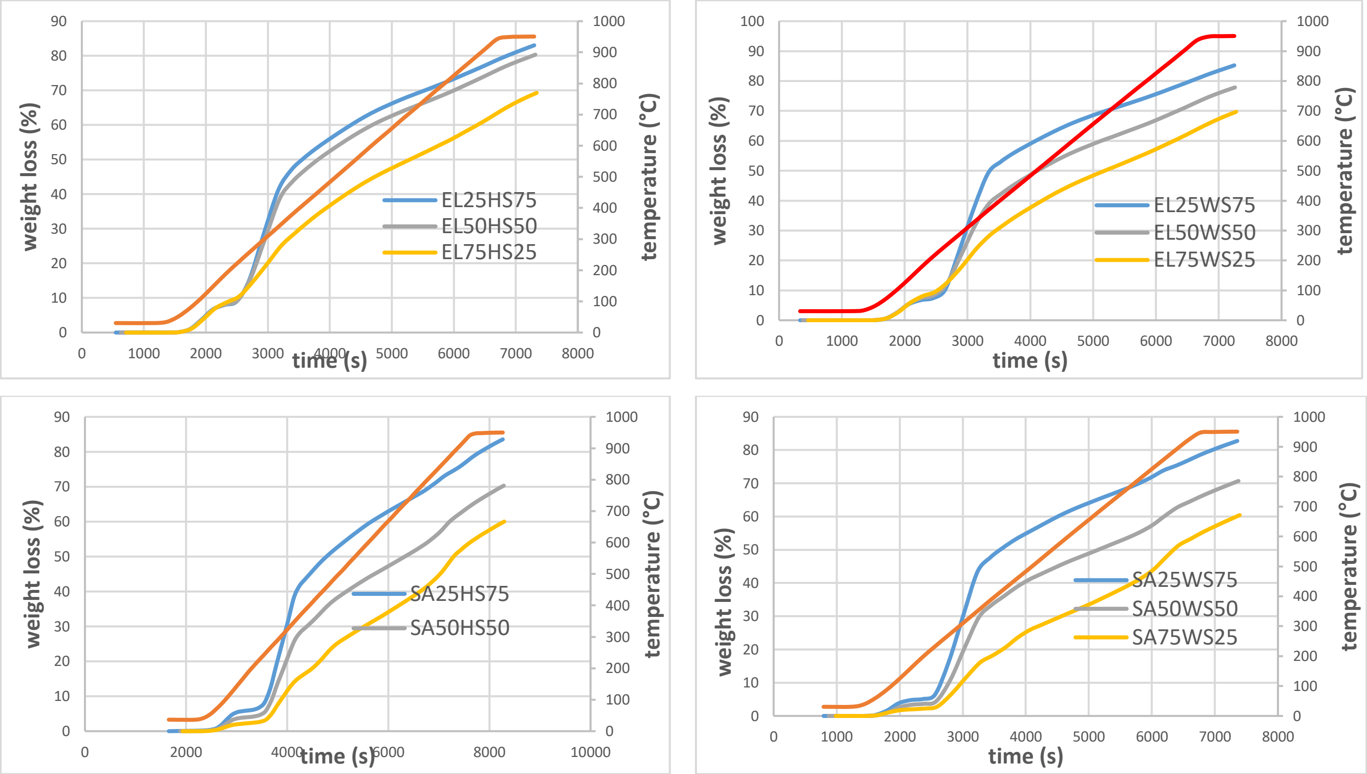

Figure 2. TGA curves for lignite-biomass and asphaltite-biomass mixtures at different ratio.

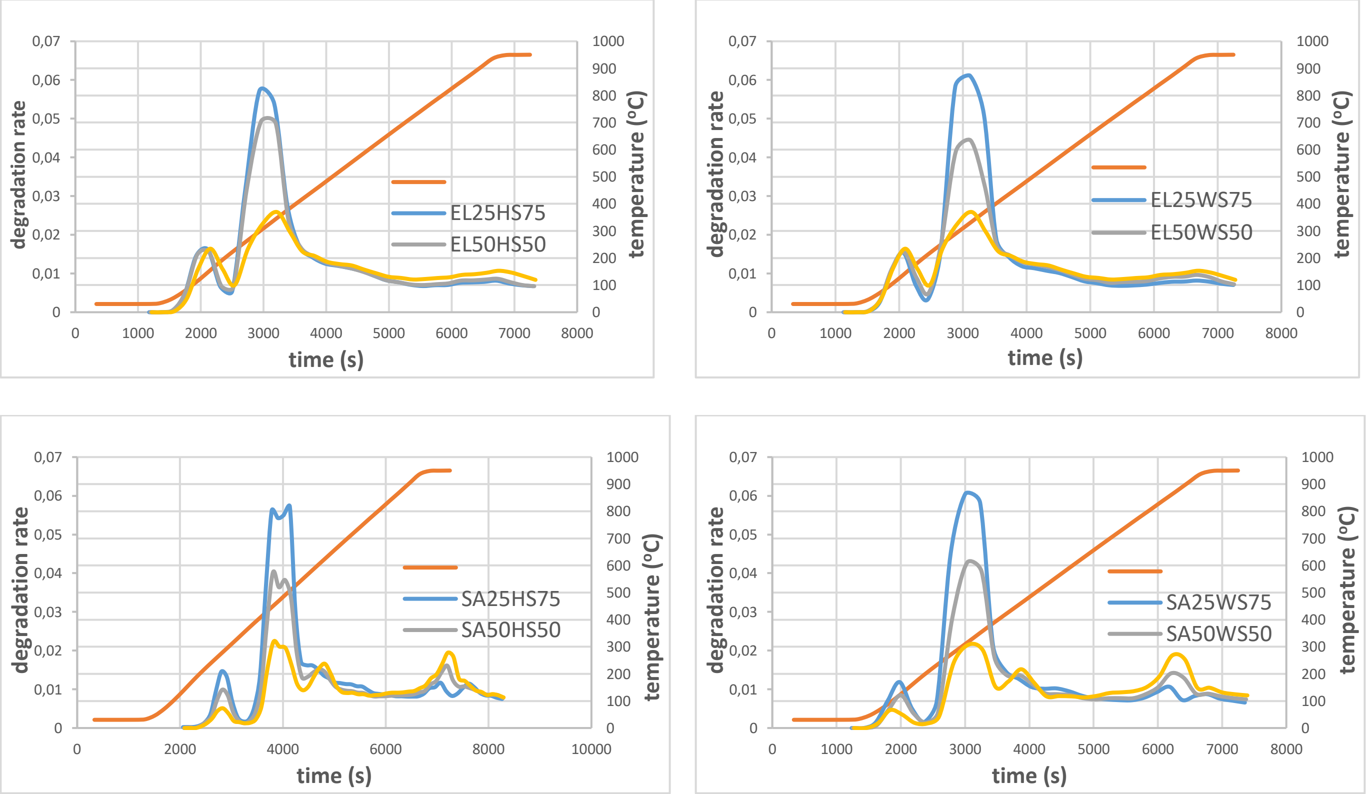

Figure 3. DTA curves for lignite-biomass and asphaltite-biomass mixtures at different ratio.

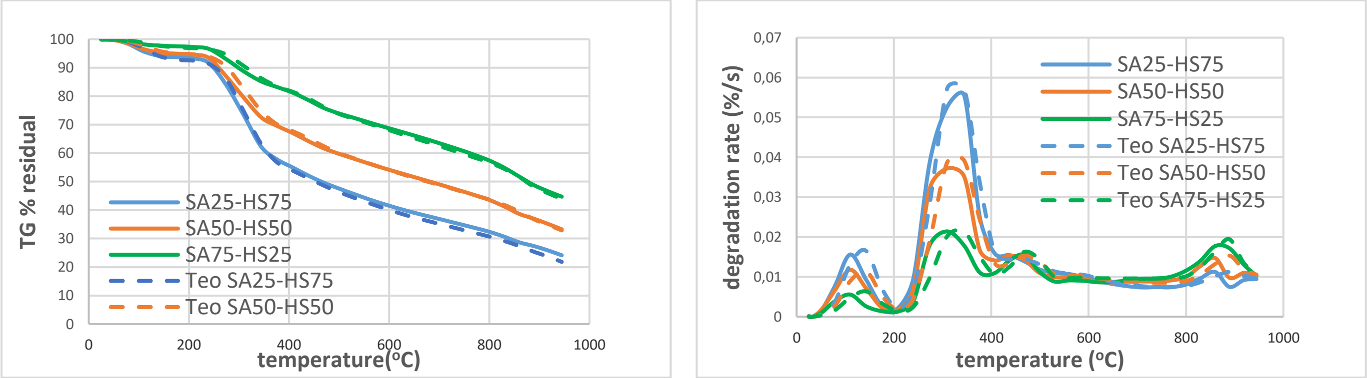

Figure 4. TGA and DTA curves for experimental and theoretical calculations of asphaltite (SA)-biomass (HS) mixture samples.

The TGA and DTA curves obtained for the experimental and theoretical (hypothetical) calculations of the asphaltite–walnut shell mixtures prepared at three different ratios are given Figure 5. In the TGA result, the mass loss observed at the first peak at around 245°C, in the experimental values is greater than the theoretical values. Up to around 380°C, the mass loss values of the experimental curves for all mixtures are higher than the theoretical values. After these temperature values, while the SA50-WS50 and SA75-WS25 mixture curves are quite close to each other, the experimental mass loss values for the SA25-WS75 mixture are higher than the theoretical values. For the DTA result, in the first peak, occurring at around 110°C, it is observed that the experimental values undergo degradation at lower temperatures, while the degradation rates are quite similar. In the second peak, which begins around 310°C, a decrease is observed in both the degradation amount and temperature in the experimental values.

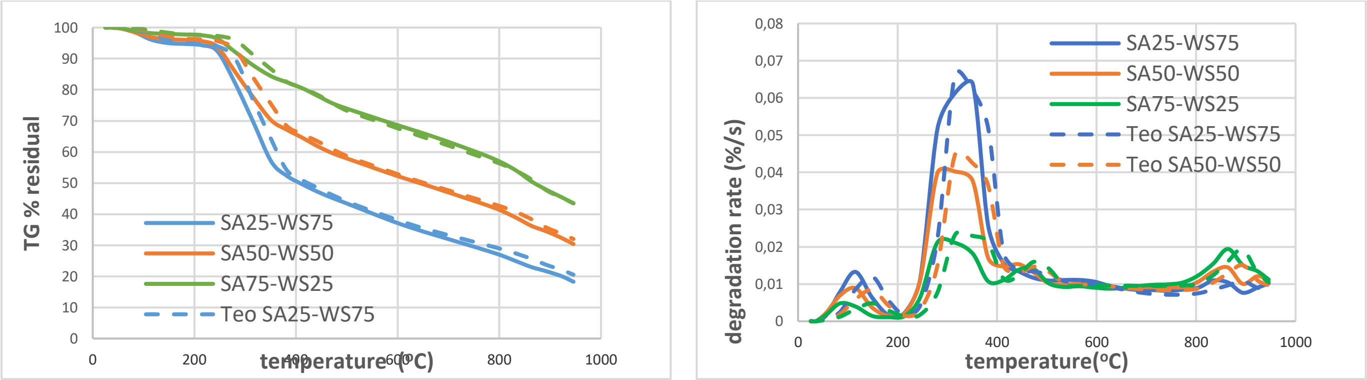

Figure 5. TGA and DTA curves for experimental and theoretical calculations of asphaltite (SA)-biomass (WS) mixture samples.

The TGA and DTA curves obtained for the experimental and theoretical (hypothetical) calculations of the lignite–hazelnut shell mixtures prepared at three different ratios are given in Figure 6. In the TGA result, the mass loss increases rapidly after 250–260°C. For all mixture samples, the theoretical values are greater than the experimental values, indicating a negative synergistic effect. For the DTA result, a decrease in both the degradation amount and rate is observed in the experimental values compared to the theoretical values. In the first peak, high degradation is observed around 130°C and this situation is similar in all mixtures. In the second peaks, around 330°C, the experimental values exhibit lower degradation amounts and rates compared to the theoretical values. Although no change is observed in the degradation temperatures, the theoretical degradation rate and amount are greater than the experimental values, resulting in a significant difference.

The TGA and DTA curves obtained for the experimental and theoretical (hypothetical) calculations of the lignite–walnut shell mixtures prepared at three different ratios are given in Figure 7. In the TGA result, mass loss increases rapidly around 240°C. The theoretical and experimental mass loss values for the EL75-WS25 and EL50-WS50 mixtures are quite close to each other. However, for the EL25-WS75 mixture, the experimental values for mass loss are considerably higher than the theoretical values, indicating a synergistic effect. For the DTA result, the experimental and theoretical degradation rates are close to each other at the first peak occurring around 130–140°C. In the second peak, which begins around 300°C, the degradation rate of the theoretical value is considerably higher than the experimental value. The experimental values have shifted to higher temperatures compared to the theoretical values and have occurred at lower degradation rates.

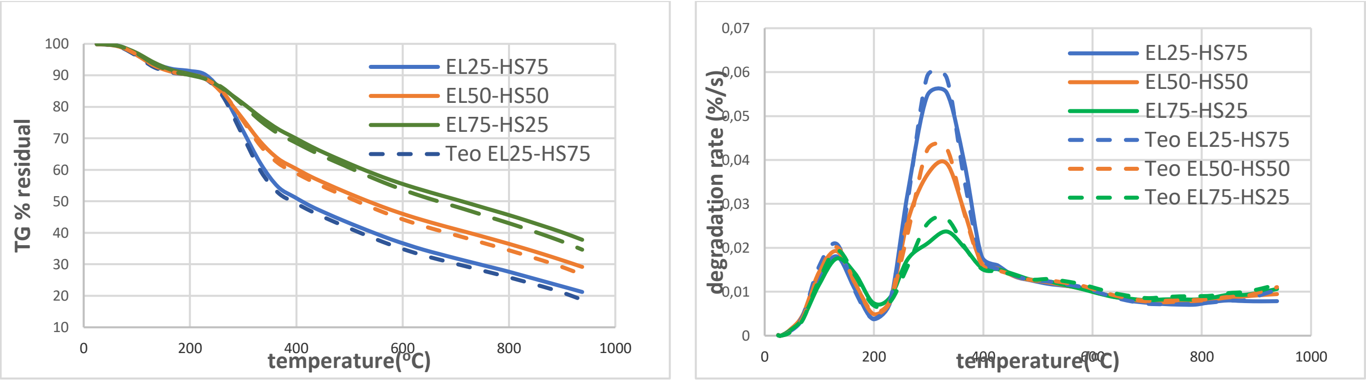

Figure 6. TGA and DTA curves for experimental and theoretical calculations of lignite (EL)-biomass (HS) mixture samples.

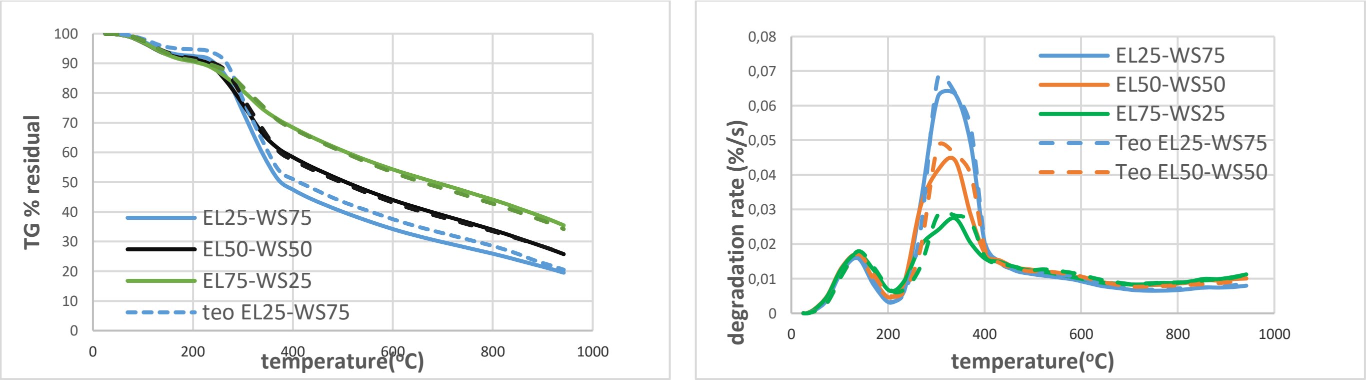

Figure 7. TGA and DTA curves for experimental and theoretical calculations of lignite (EL)-biomass (WS) mixture samples.

3.5. Pyrolyzed product yields

Coal and biomass samples were firstly pyrolyzed in their raw form and then after being mixed at varying ratios (25%, 50%, 75%) at three different temperatures of 400°C, 460°C, and 520°C. These temperatures were selected based on all TGA and DTA data, as it was determined that reasonable overall conversions were achieved within this temperature range. This selection is justified by the fact that mass loss of the samples begin around 300°C and reach their highest values within the 450–550°C temperature range. The calculated yields of solid, liquid, and gaseous products obtained after pyrolysis at 400°C, 460°C, and 520°C are presented in Table 4.

The results obtained from the table show that solid product yield decreases with increasing temperature. This is an expected outcome, as coal and biomass undergo more thermal decomposition at higher pyrolysis temperatures. The liquid product yield generally increases with temperature; however, no significant change is observed in the hazelnut shell sample. After 460°C, while the liquid yield continues to increase in the walnut shell sample, the increase slows down in the asphaltite sample. In the lignite sample, the liquid yield increases in parallel with the temperature rise. The gas product yields of the raw samples increase at 400°C and 460°C but begin to decline at 520°C. The only exception is the hazelnut shell sample, where gas product yield continues to increase with rising temperature.

Table 4. Product yields obtained from the pyrolysis experiments of raw and mixed samples at 400°C, 460°C, and 520°C.

Sample	**Solid (%)**			**Liquid (%)**			**Gas (%)**		
Temperature(°C)	**400**	**460**	**520**	**400**	**460**	**520**	**400**	**460**	**520**
SA	93.06	74.18	74.25	3.53	13.47	14.99	3.41	12.35	10.76
WS	36.06	32.62	30.22	56.08	57.19	62.79	7.86	10.19	6.99
HS	39.79	37.25	34.89	52.06	52.99	53.25	8.15	9.76	11.86
EL	86.00	80.44	75.85	13.60	18.17	23.68	0.40	1.39	0.47
EL25-HS75	59.03	48.40	45.73	36.96	44.30	45.01	4.01	7.30	9.26
EL50-HS50	64.13	59.19	55.92	32.09	35.70	37.03	3.78	5.11	7.05
EL75-HS25	70.54	70.39	66.32	27.93	25.93	27.15	1.53	3.68	6.53
EL25-WS75	48.31	44.57	41.56	45.67	46.96	48.72	6.02	8.47	9.72
EL50-WS50	61.39	56.69	53.51	35.90	35.99	38.72	2.71	7.32	7.77
EL75-WS25	75.21	69.29	64.64	23.99	26.66	29.25	0.80	4.05	6.11
SA25-HS75	55.53	51.00	46.78	44.35	42.71	44.86	0.12	6.29	8.36
SA50-HS50	64.37	62.23	58.17	35.12	29.92	34.51	0.51	7.85	7.32
SA75-HS25	83.48	69.62	65.15	15.36	22.56	24.93	1.16	7.82	9.92
SA25-WS75	52.71	46.83	43.38	41.65	45.68	46.32	5.64	7.49	10.30
SA50-WS50	67.02	59.56	55.46	26.21	34.08	36.56	6.77	6.36	7.98
SA75-WS25	82.75	68.80	65.64	15.46	24.05	22.93	1.79	7.15	11.43

Examining the mixture samples, it is observed that as the ratio of biomass (hazelnut shell and walnut shell) added to lignite increases, the solid product yield decreases, and this decrease becomes more pronounced with increasing temperature. Consequently, the decrease in solid product yield leads to an increase in liquid and gas product yields. The same trend is also observed in the asphaltite sample. It has been reported in the literature that co-pyrolysis of lignite and biomass mixtures is beneficial for gas and liquid production and that these changes are due to synergistic effect [13, 18, 24]. During co-pyrolysis, a synergistic effect occurs due to hydrogen transfer from biomass with high H/C content to coal [33]. Moreover, the variation in gas and liquid product yields with increasing temperature and biomass ratio is attributed to enhanced devolatilization and secondary cracking reactions, which is in agreement with previous studies emphasizing the temperature sensitivity of product distribution during co-pyrolysis [13, 18, 33]. The highest solid product yield is observed at 400°C for the EL75-HS25, EL75-WS25, SA75-HS25, and SA75-WS25 mixtures, while the highest liquid product yield is observed at 520°C for the EL25-HS75, EL25-WS75, SA25-HS75, and SA25-WS75 mixtures. Therefore, the optimum temperature values are determined as 400°C, where solid product yield is at its maximum, and 520°C, where liquid product yield is at its highest.

After the pyrolysis processes at 400°C, 460°C, and 520°C, the solid products obtained from the raw samples were elementally analyzed, H/C and O/C molar ratios were determined and the results obtained are shown in Table 5. As can be seen from the table, the H/C and O/C molar ratio values for the solid products obtained from pyrolysis process of the raw samples (asphaltite, lignite, walnut shell and hazelnut shell) decrease with increasing temperature.

The elemental analysis results of the raw and mixture samples that yielded the highest solid product yield at the optimum temperature of 400°C are presented in Table 6, while the comparative calorific values are shown in Figure 8.

The comparison of the H/C and O/C molar ratio values of the solid products obtained from the pyrolysis experiments in 400°C for the mixture samples showed an increase with the addition of biomass to lignite and a slight decrease with the addition of biomass to asphaltite.

Table 5. Elemental analysis results of the solid products obtained from the pyrolysis experiments of raw samples at 400°C, 460°C, and 520°C.

Sample (dry basis%)	**Asphaltite**			**Lignite**			**Walnut shell**			**Hazelnut shell**		
Temperature (°C)	**400**	**460**	**520**	**400**	**460**	**520**	**400**	**460**	**520**	**400**	**460**	**520**
Carbon (C)	45.55	39.08	38.74	43.83	44.99	45.42	77.74	81.80	87.12	77.76	81.39	86.97
Hydrogen (H)	3.38	1.94	137	2.44	2.07	1.79	3.51	3.10	2.79	3.35	2.97	2.62
Nitrogen (N)	1.17	1.28	1.30	1.45	1.49	1.39	0.73	0.74	0.76	0.77	0.78	1.23
Oxygen (O)*	49.90	57.70	58.59	52.58	51.45	51.40	18.02	14.36	9.33	18.12	14.36	9.18
H/C molar ratio	0.89	0.60	0.42	0.67	0.55	0.47	0.54	0.45	0.38	0.52	0.44	0.36
O/C molar ratio	0.82	1.11	1.13	0.89	0.86	0.85	0.17	0.13	0.08	0.17	0.14	0.08

Table 6. Elemental analysis results of the solid products obtained from the pyrolysis experiments at 400°C.

Sample (dry basis%)	**C**	**H**	**O**	**N**	**S**	**H/C**	**O/C**
WS	77.74	3.51	18.01	0.73	0.01	0.54	0.17
HS	77.76	3.35	18.11	0.77	0.01	0.52	0.17
EL	43.83	2.44	49.23	1.45	3.05	0.67	0.84
SA	45.55	3.38	43.28	1.17	6.62	0.89	0.71
EL75-W25	48.73	2.89	44.45	1.64	2.29	0.71	0.68
EL75-HS25	51.01	2.95	42.14	1.61	2.29	0.69	0.62
SA75-WS25	50.58	3.62	39.38	1.40	5.02	0.86	0.58
SA75-HS25	50.29	3.59	39.46	1.63	5.03	0.86	0.59

* Calculated from the difference

Comparing the calorific values of the solid products obtained pyrolysis at 400°C, it is observed that the calorific value of the walnut shell sample increased from 4531 kcal/kg to 6494 kcal/kg, while the calorific value of the hazelnut shell sample increased from 4625 kcal/kg to 6440 kcal/kg after pyrolysis. The pyrolysis of walnut shell and hazelnut shell, selected as biomass sources, resulted in the production of high-calorific biochar. A similar comparison for the selected coal sources shows that the calorific value of the lignite sample increased by 41 kcal/kg, whereas a decrease was observed in the asphaltite sample. As seen, the co-pyrolysis of lignite and asphaltite with biomass led to the production of more environmentally friendly, cleaner, and higher-calorific biochar, indicating an improvement in fuel quality.

4. Conclusion

In this study, the performance and efficiency evaluation of the pyrolysis process of coal samples, which have significant reserves in our country, together with two different types of biomass was investigated using the thermogravimetric analysis (TGA) method.

The addition of biomass to lignite and asphaltite samples decreases both the ash and sulfur content. It is observed that the volatile matter content of the biomass samples is significantly higher compared to the lignite and asphaltite samples. The high volatile matter content of these samples contributes to an increase in their calorific value. Furthermore, increasing the amount of biomass added to lignite and asphaltite samples results in a higher H/C molar ratio. The increase in the H/C molar ratio, meaning a higher hydrogen content, leads to an increase in volatile matter and enhances the calorific value, ultimately yielding a higher-quality product.

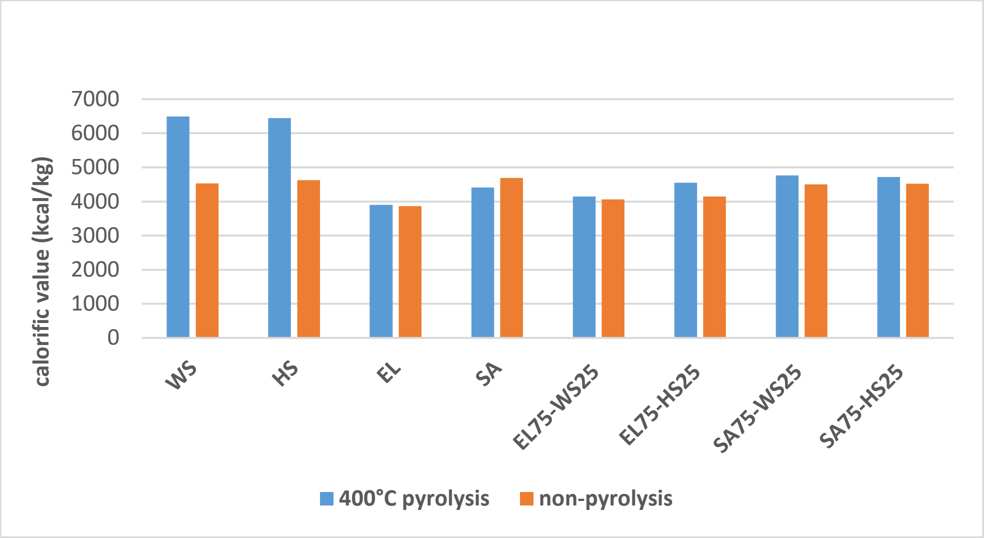

Figure 8. Calorific values of the solid products obtained from the pyrolysis experiments at 400°C.

Due to their high volatile matter content in walnut and hazelnut shell samples, the total mass loss in the TGA curves is higher compared to lignite and asphaltite samples. For the mixture samples, analysis of the TGA and DTA curves indicates that as the ratio of biomass added to lignite and asphaltite increases, both the mass loss and degradation rates increase across all mixtures, while the decomposition temperature decreases. When the experimental values of the coal and biomass samples mixed at different ratios are compared with the calculated values of the raw samples, a synergistic effect is observed, which is consistent with the results reported in previous studies, where co-pyrolysis of coal and biomass led to enhanced volatile production and improved thermal conversion efficiency through chemical interactions between the fuel components [18, 19].

In the pyrolysis process, the increase in temperature results in a decrease in solid product yield while leading to an increase in liquid and gas product yields. For the calorific values of solid products at 400°C temperature; while high calorific value biochar was obtained by pyrolysis of walnut and hazelnut shell samples, a slight increase in the calorific value of the lignite sample was observed as a result of the pyrolysis process, while a decrease occurred in the asphaltite sample. After pyrolysis with the addition of biomass to lignite and asphaltite, more environmentally friendly, cleaner and higher quality biochar with high calorific value was obtained. From this study, it can be concluded that the co-pyrolysis of coal and biomass can yield hybrid coal with a higher calorific value and greater environmental compatibility. The calorific value of the hybrid coal obtained from this study is comparable to that of bituminous coal, making it a suitable and more eco-friendly option for power plants. Similar results were also reported in studies indicating that co-pyrolysis of biomass with coal enhances the heating value and combustion behavior due to synergistic hydrogen transfer and reductions in ash and sulfur content [33].

This study is thought to provide a significant advantage by enabling the more efficient utilization of lignite and asphaltite, the valorization of waste biomass, and the reduction of environmental pollution through the enhancement of coal with biomass, thereby improving the efficiency of both resources.

Author's Contributions

Veysi Kamar: Supervised the experiment's progress, result interpretation and helped in manuscript preparation.

Pınar Acar Bozkurt: Drafted and wrote the manuscript, performed the analytical analysis and result.

Ethics

There are no ethical issues after the publication of this manuscript.

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