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Valorization of Sewage Sludge with Pine Sawdust as Biochar: Optimization of the Torrefaction Conditions and Biochar Quality

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Highlights

- Optimization of co-torrefaction was determined using the Box-Behnken design.
- Temperature and mixing ratio were significant parameters on the response variables.
- The ash fusion characteristics of the sewage sludge and biochar were investigated.

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Keywords

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Abstract

This work explores the effects of the temperature (250, 280, 310°C), time (20, 40, 60 min), sewage sludge mixing ratio (25, 50, 75%) on the solid fuel quality and yield of the biochar produced from sewage sludge blended with pine sawdust. The optimal conditions for the torrefaction of sewage sludge and pine sawdust were investigated by the response surface methodology. Mathematical models were developed on the weight yield, high heating value and ash content and experimental data were examined through analysis of variance. The results depicted that the effects of temperature and mixing ratio were more considerable than residence time for the three response variables. The optimum point for weight yield, HHV, ash were predicted to be 60.82%, 21.58 MJ kg-1 and 18.78% at 310°C, 20 min and sewage sludge mixing ratio of 25%, respectively. The experimental results show that the average values of the experiments were 56.4%, 22.9 MJ kg-1, and 21% for weight yield, HHV and ash content, respectively.

1. INTRODUCTION

Depletion of fossil resource due to population growth, urbanization, and economic development have led people to become more interested in clean and renewable energy sources [1,2]. Biomass stands out as the most plentiful and sustainable energy reservoir used to produce biofuels, power, and heat using various conversion methods. The utilization of biofuels based on biomass provides the reduction of fossil fuels usage [3]. Nevertheless, biomass comes with certain limitations including moisture content, low energy density, high transportation costs in the direct utilization for power and energy generation [4]. To overcome these drawbacks, biomass can be transformed into biofuels through biochemical, biological, and thermochemical conversion techniques. Among the thermochemical technologies, torrefaction is an attractive pre-treatment to overcome the obstacles concerning biomass [5]. Torrefaction enhances the fuel properties of biomass in the temperature range between 200-300 ° C without oxygen. Torrefaction can be used as a pre-treatment for thermochemical technologies including gasification and co-firing [6]. In the torrefaction process, the thermal decomposition of organic components, primarily hemicellulose, leads to the production of biochar, along with condensable and non-condensable compounds from the high volatile fraction [7,8]. Biochar is an appropriate fuel for heat and power generation technologies, such as pyrolysis, gasification, and co-firing, thanks to its reduced moisture content, elevated calorific value, enhanced grindability [9,10].

Sewage sludge is the residue from wastewater treatment plants, which is rich in organic matter and essential nutrients [11,12]. However, sewage sludge may contain hazardous organic compounds (polychlorobiphenyls, dioxins, pesticides), heavy metals and pathogenic microorganisms. Thus, the proper

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treatment and disposal of sludge are important to provide further barriers to potential risks to the environment and public health [13,14]. According to Turkish Statistical Institute Waste Statistics, the amount of treatment sludge formed in urban wastewater treatment plants is 314,325.4 tons (dry matter) in 2020 [15]. To achieve treatment of sewage sludge, conventional treatment methods are used, including incineration, composting, and land application [16,17]. Compared to conventional approaches, thermochemical processes are suitable methods for the treatment of sludge due to achieving disposed of pathogenic microorganisms in sewage sludge as well as biofuel production [18]. Among the existing thermochemical processes, torrefaction is used is to optimize the energy and mass yield of solid matter by facilitating removal of volatile components containing hydrogen and oxygen and conserving content in sewage sludge [19,20]. During torrefaction, a rise in the carbon content in sludge causes a decline in the O/C and H/C ratio, improving fuel properties [21]. To obtain desired properties, biochar can be modified by adjusting production conditions or selecting suitable feedstock [22,23].

Numerous studies have concentrated on how the thermal behavior of sludge. For example, [24] carried out torrefaction of sewage sludge in a reactor at a temperature of 250°C and 275°C for 13 min and 24 min. The researchers observed a reduction in catalyst utilization attributed to the lower production of vapors from the pyrolysis of sewage sludge biochar. [25] investigated how torrefaction of sewage sludge influenced the liquid product. The results revealed that torrefaction pretreatment had no impact the gases and char yield, while yield of organic compounds decreased at 320 °C for residence time exceeding 6.1 min. [26] reported the impact of particle size and temperature on biochar characteristic. Torrefaction trials were experienced within temperature range of 240-300 °C for 8 h for torrefaction. This study emphasized the significance of temperature. It was observed that the weight loss of the resulting biochar escalated from 14.2% to 27.6% from 240 to 300 °C. [27] analyzed the effects of the torrefaction on biomass and sludge at temperatures of 230 °C, 260 °C, 290 °C, with varying durations of 0.5 h, 1.0 h, and 1.5 h. They reported the mass loss of 55.4% for wood biomass biochar and 17.0% for sewage sludge biochar at 290°C, while the mass loss of 19.7% for wood biomass biochar and 17.0% for sewage sludge biochar at 240°C. The results highlighted that temperature had a more pronounced impact on biomass compared to sewage sludge. Similar results were reported by [28]**,** who carried out torrefaction experiments with wood and sewage sludge. From 325 °C to 525 °C, pine wood experienced mass loss of 97%, while sewage sludge showed a mass loss of 55%. This disparity was attributed to the distinct structural composition of the respective feedstocks.

This work investigated the optimization of torrefaction of sewage sludge and pine sawdust. Torrefaction was conducted to determine the effects of different temperatures, time (20, 40 and 60 minutes), the sewage sludge mixing ratios (25%, 50% and 75%) on the weight yield, the heating value and the ash of the biochar. RSM was employed to identify optimal conditions by minimizing ash content while maximizing weight yield and high heating value. The physicochemical properties and thermal characteristics of both biochar and feedstocks were also analyzed.

2. MATERIAL METHOD

2.1. Materials

Sewage sludge was procured from Çiğli Wastewater Treatment Plant, İzmir, Turkey. The moisture in sewage sludge was 5% by weight. The pine sawdust was supplied from Izmir and dried in an oven at 105 ° C for 24 hours. Table 1 presents the physicochemical properties of materials.

***Table 1**. Properties of raw materials*

		Raw material	
		Sewage sludge	**Pine sawdust**
Ultimate analysis (%)	**C**	28.19	50.3
	H	4.54	6.4
	N	3.54	1.1
	S	1.01	0.1
	O	11.73	41.7

Proximate analysis (%)	**Moisture**	5.05	6.3
	Ash	50.99	0.4
	Volatile matter	48.62	88.4
	Fixed carbon	2.37	4.9
	HHV (MJ/kg)	11.52	18.39
	Cellulose	1.99	44.5
	Hemicellulose	-	12.3
	Lignin	16.33	30.6

2.2. Torrefaction Process

The sludge and pine sawdust samples were combined with mixing ratios of 25: 75 (SS25%), 50: 50 (SS50%) and 75: 25 (SS75%). 120 g of mixture with a 25:75 ratio and 200 g of mixture with 50:50 and 75:25 ratios were fed into the reactor. Torrefaction of dried sewage sludge and pine sawdust was experienced in a 2.5 kW electrical heater integrated batch stainless steel reactor at different temperatures. The feedstock was hold in reactor for 20, 40, and 60 min. The co-torrefaction parameters were determined according to research present in the literature [29–31]. Lastly, the biochars were stored in plastic containers for further analysis. The biochar yield ($Y_{biochar}$) was determined with the following formula Equation (1):

$$Y_{biochar}(\%) = \frac{m_{biochar}}{m_{feedstock}} x100 \quad (1)$$

where $m_{feedstock}$ is the dry mass of the feedstock and $m_{biochar}$ is the biochar mass [4].

2.3. Raw Material and Biochar Characterization

The moisture, volatiles and ash of both the feedstock and resulting biochar were analyzed according to ASTM D7582. Samples were dried at 105 ° C for 24 h and then the moisture was detected by mass loss. 1 g of the dried sample was kept in a furnace at 750°C for 3 h and the ash was found. 1 g of the dried sample was kept in a furnace at 950±10°C for 7 min and then volatile matter was evaluated [32,33].

The C, H and N of the feedstock and biochar were defined using a Leco TruSpec® Analyzer. The oxygen is calculated by Equation (2):

$$O\ (\%) = 100 - Ash\ (\%) - C\ (\%) - H\ (\%) - N\ (\%)\ [34]. \quad (2)$$

The HHV of the feedstock and biochar was evaluated using a bomb calorimeter according to ASTM D 5865 [35]. Sample pellet of 1 g was placed into the crucible and combusted in a pressurized oxygen atmosphere. Calibration of calorimeter was performed using benzoic acid.

The pH and electrical conductivity of biochar were determined using a 1:20 biochar solution in water. After stirring the solution for 48 hours at room temperature, the results were determined using a conductivity and pH meter [36].

2.4. Experimental Design

RSM is a well-known statistical technique that uses a combination of experimental design to determine the optimal conditions [8]. Torrefaction experiments were performed with regard to the three-level box Behnken design. SPSS was employed for evaluation of impact of temperature, time, and mixing ratio on weight yield, high heating value, and ash of the biochars. Parameters for the torrefaction process are given in Table 2**.**

Table 2. *Box Behnken design for torrefaction experiments*

Run no	Temperature (°C)	Residence time (min)	The mixing ratio (%)
1	280	20	25
2	250	20	50
3	280	40	50
4	250	40	75
5	280	60	25
6	280	20	75
7	310	60	50
8	310	40	75
9	310	40	25
10	250	60	50
11	310	20	50
12	280	40	50
13	250	40	25
14	280	60	75
15	280	40	50

The fitness of the regression quadratic polynomial models was assessed using analysis of variance at a confidence level of 95% [37]. P-value, F value, R-Squared (R^2), and adjusted R-Squared (R^2adj) are various descriptive statistical analyses to compute the statistical significance of the quadratic polynomial models [7]. Additionally, the response surface models contain the first-order terms of temperature, residence time, the mixing ratio [38].

2.5. Thermogravimetric Analysis (TGA)

TGA was achieved under argon atmosphere (40 ml min^{-1}) a thermogravimetric analyzer. 10 mg of sample was taken into the Al_2O_3 crucible and subjected to heating, increasing between 30°C and 1200°C. For analysis, temperature range and heating rate were determined according to [34] and [39]. Additionally, derivative thermogravimetric (DTG) analysis was carried out to identify the thermal degradation behavior and the reactivity of raw material and biochar.

2.6. Ash Sample Preparation and Ash Fusion Analysis

The biochar and biomass ash samples were obtained according to ASTM E1755-01 by heating the sample at 575°C for at least 3 h [40]. The analysis of the ash fusion temperatures (AFTs) of the samples was carried out using an ash fusion temperature analyzer (YX-HRD3000) under air atmosphere according to ASTM D1857. At 400°C, the cone was introduced in the furnace until reaching a temperature of 1600°C [41]. During the analysis, the temperature of deformation (DT), the softening (ST), the hemispheric (HT) and the fluid (FT) of the ashes were determined according to morphological transformations.

2.7. Determination of Biochar Safety: Heavy metal and Nutrients

The concentrations of 15 elements in raw materials and biochar were examined to detect the safety of biochar in environmental fields. 0.5 g sample was decomposed in 10 ml of HNO_3/HCl (v:v, 3:1) through a microwave (MARS6, CEM, USA) at 180 ° C for 10 minutes according to the EPA Method 3051 A protocol and detected by inductively coupled plasma spectrometry [42].

3. RESEARCH FINDINGS AND DISCUSSION

3.1. Properties of Raw Biomass and Biochars

Understanding impacts of reaction temperature, residence time and sewage sludge on biochar properties may help to comprehensively evaluate the feasibility of biochar fuel applications. Table 3 depicts the analysis results of biochar produced. The carbon of biochar ranged from 33 to 50% and was higher in dried sewage sludge (28.19%). Thus, an increase in the mixing ratio negatively affected the carbon of biochar. This result was attributed to the high amount of ash in the sewage sludge (50.99%). Compared to the ash of pine sawdust (0.4%), sewage sludge has a more ash content. Furthermore, the high heating value of sewage sludge (11.47 MJ kg^{-1}) is lower than that of pine sawdust (18.33 MJ kg^{-1}). The reason for the low calorific value of sewage sludge is precisely associated with its high ash [19]. The pinewood sawdust contained a high carbon content (50.3), which was significantly higher than that of sewage sludge (28.19). The analysis results are very similar to those of other biomass in previous studies [27,43].

Table 3. *Analysis results of biochars*

Torrefaction parameters	C (%)	H (%)	N (%)	S (%)	O (%)	VM (%)	Ash (%)	FC (%)	pH	EC (µS/cm)	Weight yield (%)	HHV (MJ kg^{-1}, daf)
310-40-SS75%	33.24	3.29	3.00	0.55	4.60	31.96	55.33	9.67	7.66	355	77.10	13.34
280-60-SS75%	33.19	3.46	3.06	0.59	8.84	33.87	50.86	12.13	7.54	308	77.55	13.15
280-20-SS75%	34.38	3.59	3.09	0.57	6.05	31.87	52.32	13.50	7.68	311	78.85	13.89
250-40-SS75%	33.74	3.80	3.17	0.57	7.79	34.13	50.93	12.17	7.49	509.5	83.30	13.17
310-60-SS50%	45.19	4.41	2.58	0.38	9.60	37.28	37.84	21.97	7.27	163	71.00	17.46
310-20-SS50%	38.47	3.88	2.50	0.39	23.22	33.33	31.53	31.97	7.49	205	71.50	16.83
250-60-SS50%	41.69	4.38	2.63	0.44	15.32	46.56	35.53	12.68	7.19	412	81.80	16.50
250-20-SS50%	43.56	4.85	2.29	0.41	18.45	45.52	30.44	20.01	7.41	439	83.10	17.32
310-40-SS25%	50.16	4.44	1.62	0.27	17.13	32.21	26.37	37.99	7.22	70.55	56.50	22.92
280-60-SS25%	41.57	4.68	2.47	0.44	28.91	47.72	21.93	27.40	7.38	135	71.58	20.43
280-20-SS25%	47.04	5.66	1.37	0.22	28.71	59.79	17.00	19.59	6.85	322	83.33	19.89
250-40-SS25%	44.11	5.54	1.44	0.28	30.83	60.92	17.80	17.61	6.86	233	82.75	18.63
280-40-SS50%	45.23	4.62	1.83	0.25	11.45	37.95	36.62	20.88	7.71	343.5	88.25	17.32
280-40-SS50%	49.76	5.13	1.44	0.20	7.50	38.23	35.96	21.26	7.45	204.5	86.15	17.41
280-40-SS50%	39.29	4.22	2.47	0.37	16.79	36.69	36.86	22.44	7.36	250.6	86.85	17.27

As given in Figure 1, the H/C of biochar ranged from 1.06 to 1.51, whereas the O/C of biochar ranged between 0.1 to 0.52, respectively; both ratios were lower than those of the raw sewage sludge. It is related to the increase in temperature and the mixing ratio of sewage sludge during torrefaction [44]. For example, the molar ratios H/C and O/C of biochar (SS25%) were 1.35 and 0.52, while the molar ratios H/C and O/C of biochar (SS75%) were 1.25 and 0.20 at 280 ° C for 60 minutes, respectively.

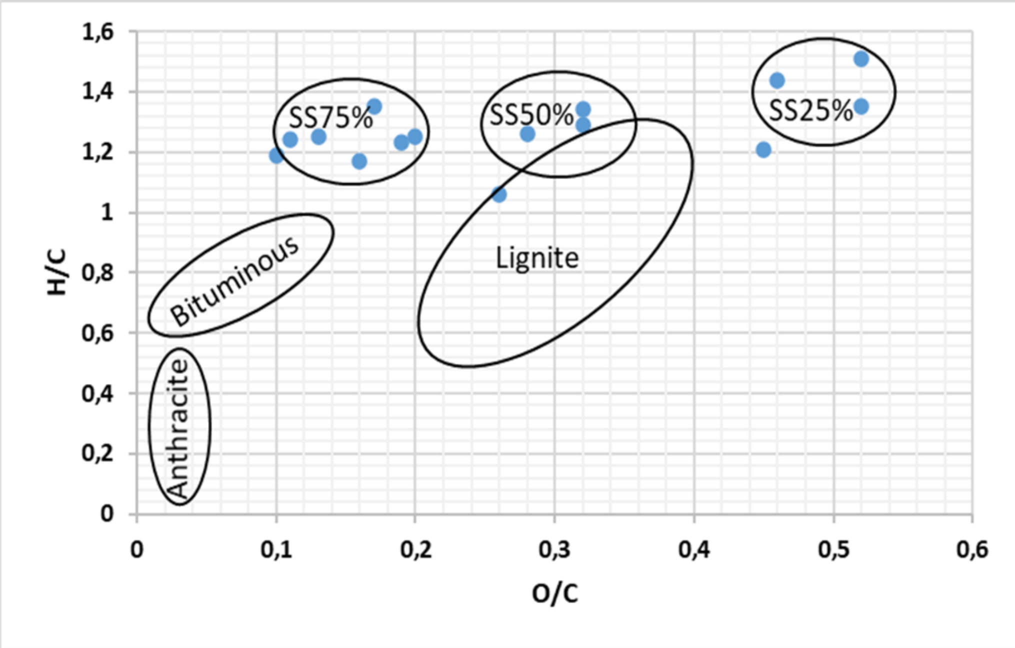

Figure 1. *Van-Krevelen diagram of biochar produced under different torrefaction conditions*

3.2. Statistical Analysis

RSM was used for optimization of the minimum ash content, the maximum weight yield, and the HHV. Furthermore, SPSS was used to test the fit of the final model and to evaluate the experimental results. Results are summarized in Table 4.

The positive or negative effect of independent variables on response is associated with coefficients. the effect of independent variables on the responses is greater when a parameter has a high coefficient [45]. In Table 4, the temperature was determined as a significant model term for weight yield, whereas HHV and ash content substantially depended on the effect of mixing ratio owing to its high coefficient.

Table 4. *ANOVA for the weight yield, HHV, and ash*

Source	Sum of Squares	df	Mean Square	F Value	p-value (Prob > F)	
Weight yield						
Model	880.57	9	97.84	6.19	0.0294	significant
Temperature	376.07	1	376.07	23.79	0.0046	R^2 : 0.9176
Residence time	27.57	1	27.57	1.74	0.2439	
Mixing ratio	64.07	1	64.07	4.05	0.1002	
HHV						
Model	108.92	9	12.10	25.37	0.0012	significant
Temperature	3.04	1	3.04	6.37	0.0529	R^2 : 0.9786
Residence time	0.019	1	0.019	0.040	0.8496	
Mixing ratio	100.25	1	100.25	210.17	< 0.0001	
Ash content						
Model	2101.48	9	233.50	57.44	0.0002	significant
Temperature	33.50	1	33.50	8.24	0.0350	R^2 : 0.9904
Residence time	27.64	1	27.64	6.80	0.0478	
Mixing ratio	1995.22	1	1995.22	490.80	< 0.0001	

The summary statistics of the parameters of the model are given in Table 4. The coefficient of variation of a model is desirably greater than 0.95 because it describes 95% of the data variability. The adjusted coefficient of determination (R^2_{adj}) is used to control the suitability of the model [7]. The coefficient of variation (R^2) for the weight yield, HHV and ash content were 0.9176, 0.9786, and 0.9904 while the R^2_{adj} for the weight yield, HHV, and ash content was 0.7694, 0.9400, and 0.9732, respectively. For standard deviations of weight yield, HHV and ash content were 3.98, 0.69, and 2.02, respectively.

Optimization of Weight Yield, HHV, and Ash Content

3D surface plots were used to evaluate the influence of independent variables on weight yield, HHV and ash content, as shown in Figure 2. The response surface plots for the weight yield, HHV, and ash content of biochars were obtained by varying significant model terms that included the temperature and mixing ratio values while the third parameter was kept constant. In Figure 2a, as the temperature of torrefaction increased from 250 to 310°C, the mass yields of biochar produced with the minimum sewage sludge mixing ratio (25%) decreased from 82.75% to 56.5%, respectively, while the mass yields of biochar produced with the maximum sewage sludge mixing ratio (75%) decreased from 83% to 77%, respectively. The addition of sludge increased mass yields of biochar because of having low volatile matter (48.62%), cellulose (1.99%), and lignin (16.33%) content of sludge compared with that of sawdust. Herein, the volatile matter fraction of pine sawdust undergoes thermal degradation at relatively high temperatures resulted in a decrease in weight yield [7]. In Figure 2a, it can easily be seen that the interaction of temperature and mixing ratio is a key factor for the weight yield of biochar. Similar findings were reported by [46], who investigated the co-torrefaction of sewage sludge and leucaena through microwave. These authors also found that the mass yield improved with increasing sewage sludge mixing ratio. They identified that the mass yield decreased with the microwave power level. The study indicated that the mass yields of SS25% and SS50% were 36% and 44% at 100 W, respectively. [47] investigated the effects of the pinewood sawdust mixing ratio on the mass yield and hydrochar ash content. The hydrochar yields were 49.67%, 58.11%, and 65.61% for 3:1, 1:1 and 1: 3 of sewage and sawdust. On the contrary, when the pinewood sawdust mixing ratio was increased, the ash content of hydrochar reduced from 22.73% to 4.36%.

Previous research has found that the ash of biochar went up with rising temperature and the sewage sludge mixing ratio [25,48]. For example, [49] investigated the torrefaction of sewage sludge derived from anaerobic digestion to improve the thermochemical properties in the lab-scale system. Their results showed that when the temperature went up from 220 to 300°C, the ash of sewage sludge biochars climbed from 37.70 to 45.90 wt%. The results of the present study indicated that the ash content climbed from 17.80 to 21.93% with temperature from 250 to 280°C at a minimum sewage sludge mixing ratio (25%). Furthermore, biochar with a high sewage sludge mixing ratio (75%) had a maximum ash content of 55.33%.

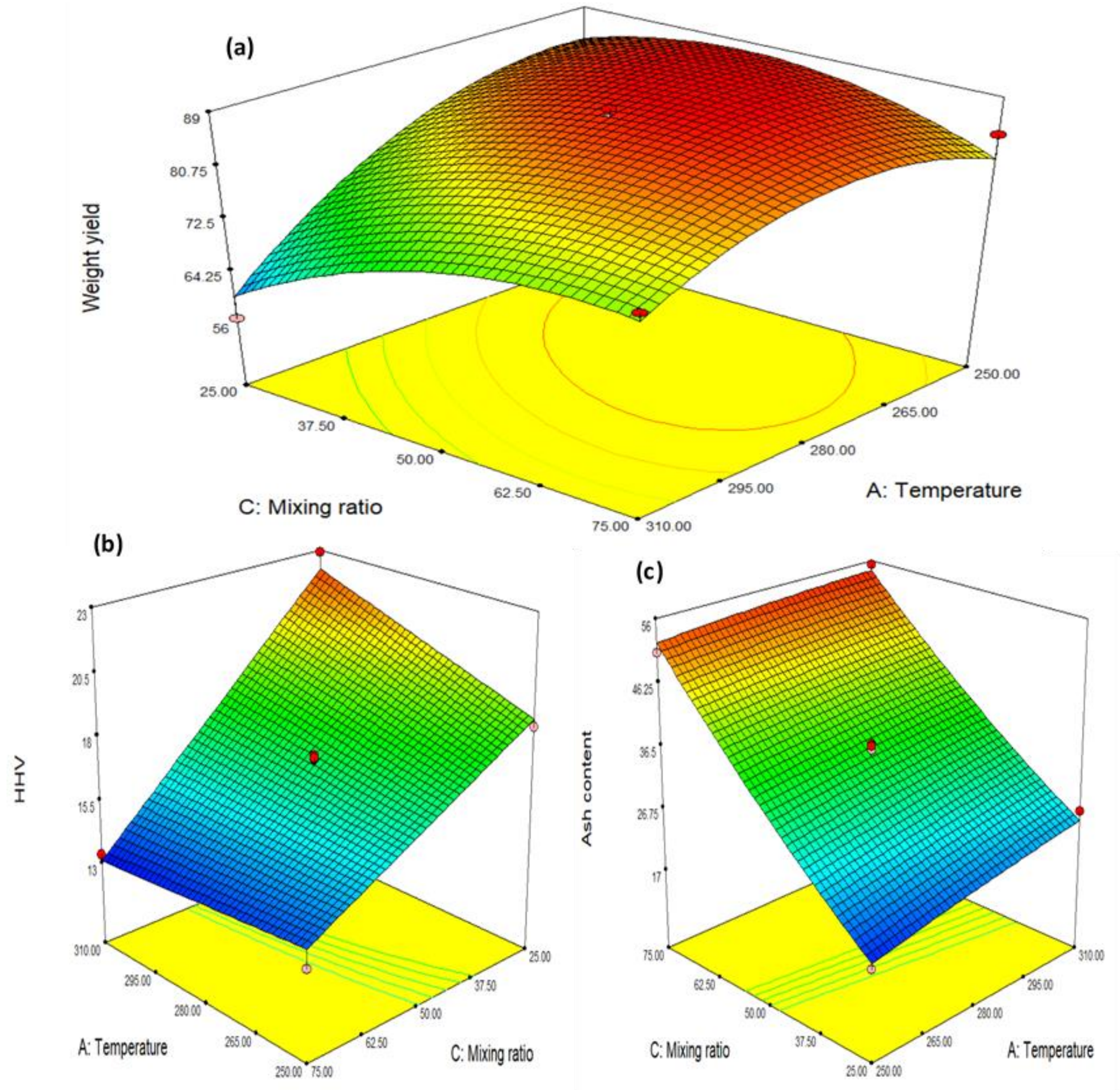

Figure 2. *Response surface plots of the temperature and mixing ratio*

It is well-known that the reduction in the HHV of biochar with rising temperature is linked to the excessive ash in biomass during torrefaction. As can be seen in Figure 2b, HHV decreased with increasing sewage sludge mixing ratio**.** Maximum HHV (22.92 MJ kg^{-1}) was obtained at 310 ° C for 40 minutes at a minimum sewage sludge mixing ratio (25%), while minimum HHV was obtained at 280 ° C for 60 minutes at the maximum sewage sludge mixing ratio (75%). Similarly, [50] reported that the HHV of hydrochars. The HHV of 22.87 MJ kg^{-1} and 13.80 MJ kg^{-1} was obtained at sludge mixing ratios of 30% and 70% at 230°C, respectively. They found that elevating the proportion of sludge resulted in a diminish in HHV because the high ash content of raw materials had an adverse effect on HHV. In another study, [51] investigated the impact of temperature on the physicochemical properties of biochar obtained from sewage sludge. The hydrothermal carbonization above 220 °C significantly increased the HHV of the sewage sludge.

The HHV rises as the carbon content increases, a consequence of removal of oxygen and hydrogen-containing volatiles with increasing temperature [52]. For a constant residence time (40 min) and mixing ratio (25%), the weight yield and HHV were determined as 82.75% and 18.63 MJ/kg at 250°C, while the weight yield and HHV were determined as 56.50% and 22.92 MJ kg^{-1} at 310°C, respectively.

Consequently, compared to lignocellulosic biomass in terms of combustion properties, sewage sludge has some disadvantages like dimmer flame and having a prolonged ignition delay during incineration due to its low holocellulose and high ash. To solve these disadvantages, the co-torrefaction of sludge and sawdust is a feasible and effective thermochemical conversion process [53].

Determination of Optimal Conditions

Temperature, residence time, and mixing ratio were optimized to minimize ash content and maximize the weight yield and HHV. As depicted in Table 5, optimization criteria were adjusted at "the range option". The optimum were obtained at a temperature of 310°C, the time of 20 minutes, the mixing ratio of 25%, respectively. Accordingly, the estimated response values for the weight yield, HHV, and ash content at optimal condition were 60.82%, 21.58 MJ kg^{-1}, and 18.78%, respectively. Furthermore, trials were performed to confirm the results of the model and consequently the average value of the experiments was 56.4%, 22.9 MJ kg-1 and 21% for the weight yield, HHV, and ash content, respectively. The results indicated that the experimental findings agreed with the predicted values.

Table 5. *Optimization variables for biochar mixing of sewage sludge and pine sawdust*

Variables	Goal	Lower	Upper
Temperature (°C)	is in range	250	310
Time (min)	is in range	20	60
Mixing ratio (%)	is in range	25	75
Weight yield (%)	is in range	56.5	88.25
HHV (MJ kg^{-1})	maximize	13.15	22.92
Ash content (%)	minimize	17	55.33

Moreover, the results of the elemental analysis indicated that the C, H, N, and S of biochar produced at optimum conditions were by 52.05%, 4.40%, 1.19%, 0.19%, respectively. Depending on the carbon content, biochars are classified as Class 1 (<60%), Class 2 (≥30% and <60%), Class 3 (≥10% and <30%) by IBI. According to EBC, biochar should have a minimum carbon content of 50%. The results showed that the biochar produced under optimum conditions had qualified them as premium grade according to EBC or Class 2 according to IBI depending on the carbon content. The nitrogen and sulfur of biochar was significantly lower than that of sewage sludge. Furthermore, when the sludge was converted to biochar, approximately 66% of the nitrogen and 80% of the sulfur were removed during torrefaction. In view of physicochemical properties, the biochar can meet the requirements for coal and coke substitution. [54] stated that the nitrogen and sulfur content of Tunçbilek lignite was 2.65% and 1.45%, respectively. Owing to having lower nitrogen and sulfur of biochar than coal, the NO_X and SO_X during co-combustion can be reduced [55,56].

3.3. Thermogravimetric Analysis

Thermogravimetric analysis of SS25%, SS50%, SS75%, biochar produced under optimized conditions, sewage sludge, and pine sawdust was conducted from 30 °C to 1200 °C are shown in Figure 3. Table 6 includes the ranges of decomposition temperature, mass loss, maximum weight loss rate.

Table 6. *Thermogravimetric analysis results for feedstocks and biochar*

	1. decomposition zone (30-150°C)		**2. decomposition zone (150-800°C)**		**3. decomposition zone (800-1200°C)**		
	-DTG_{max} (% min^{-1})	**Weight loss (%)**	**-DTG_{max} (% min^{-1})**	**Weight loss (%)**	**-DTG_{max} (%min^{-1})**	**Weight loss (%)**	**Total weight loss (%)**
Sewage sludge	1	2.3	7.6	37.2	2	7.6	47.1
Pine sawdust	2.3	8.2	18.6	71.7	-	5	84.9
SS%25	0.7	3.5	2.5	36.4	1.45	11.9	51.8
SS%50	0.05	2.5	0.3	35.9	0.2	8.5	46.9
SS%75	0.5	2.6	2.5	33.3	2.5	8.9	44.8

Biochar under optimized conditions	0.5	1.1	2.5	34.8	2.25	11.4	47.3

TG and DTG curves of pine sawdust differing from that of raw sewage sludge and biochars can be seen in Figure 3. The reason for this difference is the main components of raw sewage sludge and pine sawdust [57,58]. Sewage sludge typically consists of 25–30% protein, 6–35% fats and 8–15% carbohydrates, whereas primarily structural components of the lignocellulosic are largely cellulose, hemicellulose, lignin [59].

Weight loss during the decomposition process was observed in three main stages. At the beginning of the thermogravimetric analysis, the mass loss is associated with the removal of moisture. Firstly, mass loss of all samples except pine sawdust was below 5% between 30 and 150°C. As shown in Figure 3, the most important weight loss in curve occurred from 150 to 800 ° C. This could be attributable to volatile fraction of samples degraded during decomposition [60]. Due to the decomposition of the mineral content of the samples, there was a slight decrease in weight loss between 800 and 1200 ° C [32].

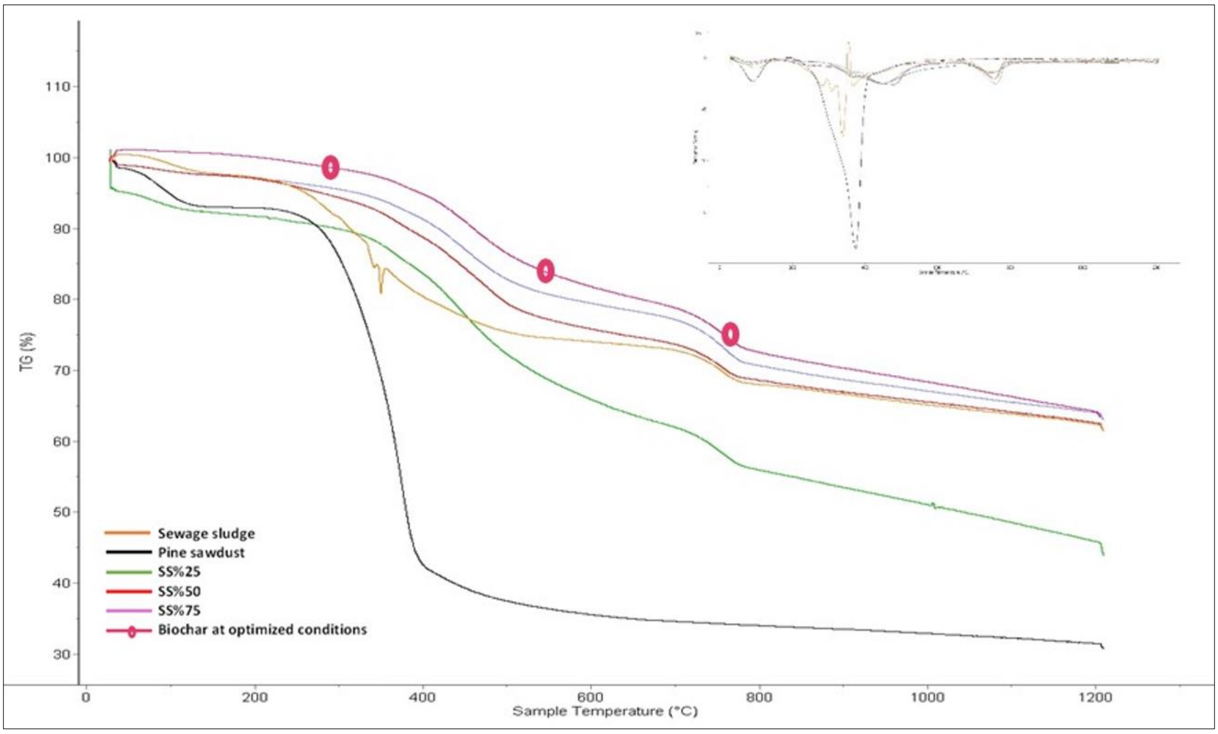

Figure 3. *TG and DTG curves for feedstocks and biochar*

It is obvious in Figure 3 that the maximum weight loss rate occurred at 83.99, 86.54, and 91.82 °C from the TG and DTG curves in the first decomposition zone for SS25%, SS50% and SS75%, respectively. Appeared endothermic peak is related to absorbed heat during the removal of water. At the same time, two weight loss rates occurred at different temperatures for all biochars in the second decomposition zone. The main reason could be ascribed to the existence of different volatiles in the sludge. Similarly, the formation of an exothermic peak in this zone was related to the heat released during the decomposition of proteins and carboxyl groups (Figure 3) [60].

Furthermore, weight loss after the completion of the TGA for sawdust was 84.9%, while weight loss for all biochar produced ranged between 44.8 and 51.8%. The thermal behavior of the biochar produced under optimized conditions was nearly that of SS25%, SS50%, SS75%.

The maximum weight loss rate was determined at 450, 477, 451, and 457 ° C for SS%25, SS%50, SS%75 and biochar produced under optimized conditions, respectively. Similar findings were reported by [58], who experienced the pyrolysis of sludge. The maximum weight loss rate carried out at 340.25 and 373 ° C for sewage sludge and pine sawdust, respectively.

3.4. Ash Fusion

Understanding the AFT of fuels is important to prevent ash fouling and slagging problems on the heating surfaces of boilers [61,62]. Table 7 and Figure 4 depict the AFT of raw sludge and biochar produced under optimization conditions and the changes in cone shape during ash fusion analyzes. The results indicated that morphological transformations of sludge and biochar started above 1000°C. Compared to lignite, raw sludge and biochar has low AFT, as presented in Table 7. The difference between the deformation and fluid temperature of the sewage sludge was greater than 100°C, significantly higher than those of biochar and lignite.

Table 7. *AFTs of sewage sludge and biochar produced under optimization conditions*

	DT (°C)	ST (°C)	HT (°C)	FT (°C)	Reference
Sewage sludge	1121	1215	1250	1269	-
Biochar produced	1184	1198	1213	1232	-
Lignite*	1405	1420	1440	1460	[63]

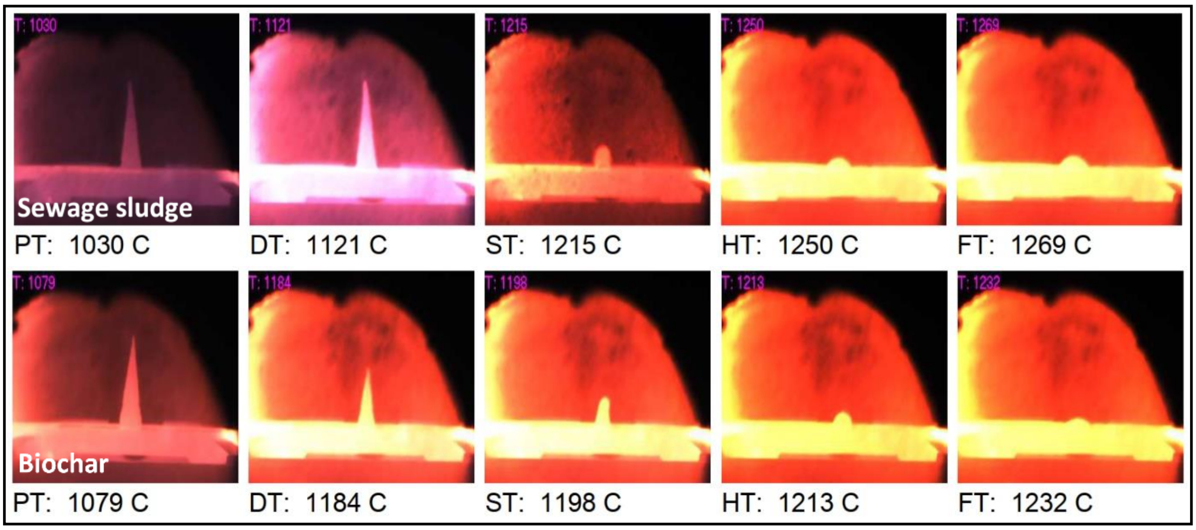

Figure 4. *Morphological changes in cone shape during ash fusion analyzes*

Several studies examined the occurring of ash sintering, agglomeration, and slagging during gasification of sludge and coal. Similar findings were reported by [64], who studied the influences of the addition of municipal sludge on the AFT for coal. These authors also observed that sewage sludge had low AFT compared to that of coal. They stated an increase in the sewage sludge mixing ratio led to reducing the AFT of mixed samples [64]. Similarly, [63] found that the DT, ST, HT and FT of the sewage sludge ash were 1165°C, 1200°C, 1235°C, 1285°C, respectively, which is similar to the results of the AFT values obtained from the sewage sludge in this paper. [61] determined ash fusion behavior of the pine sawdust and coal mixtures during co-firing. They found that the optimal coal and pine sawdust ratio should be 30% and 70% to prevent ash agglomeration, respectively. Additionally, pine sawdust had a low DT value around 1150 ° C and flowed at around 1200 ° C compared to coal. In another study, DT and FT values of peanut hull ash was found as 1098°C and 1173°C, respectively [65]. The study indicated that ash fusion behavior of biochar produced at optimum conditions showed similarities to other research.

In conclusion, to operate gasification systems without ash fouling and slagging problems, the operating temperature should be lower than ash fusion level. For example, preferred ash melting temperature is <1298.8°C for commercial gasification systems such as fixed bed and entrained flow [66,67]. As given in

Figure 4, since the ash melting temperature of biochar produced under optimum conditions is below 1298.8°C, biochar produced under optimum conditions is a suitable candidate as solid fuel in gasification systems.

3.5. Determination of Biochar Safety: Heavy metal and Nutrients

When sewage sludge is used in the soil for agronomic practices, the highly poisonous metals in the sewage sludge could be absorbed by plants and subsequently enter the food chain [68,69,70]. When sewage sludge is converted to biochar, nonvolatile elements (Fe, Co, and Cu) accumulate in biochar and some heavy metals, including Cd and Pb, convert to volatile forms with increasing temperature [71,72]. Table 8 shows the limits of the heavy metal content in biochar established by the EBC and IBI standards. In Table 8, the concentrations of Cd, Cr, Cu, Ni, Pb in biochar produced under optimal conditions were within the allowed limits of IBI and EBC. According to EBC, biochar produced under optimal conditions can be qualified as a premium grade in terms of heavy metal. The heavy metal content in sewage sludge and biochar were in the order of: Zn>Cu>Cr>Mn>Pb>Ni>Cd. Table 8 showed that the total amounts of heavy metals in the pine sawdust were relatively lower compared to those of the sewage sludge. Among these heavy metals, Zn in pine sawdust was negligible, although Zn was found at the highest level in sewage sludge (1112.5 mg kg^{-1}) and biochar (439.5 mg kg^{-1}) as presented in Table 8. The Pb concentration of biochar produced under optimal conditions (61.8 mg kg^{-1}) was within the allowed limits of IBI and EBC after co-torrefaction of sewage sludge and pine sawdust. This result was attributed to the lower amount of Pb concentration in pine sawdust (0.997 mg kg^{-1}) than in sewage sludge (176.8 mg kg^{-1}). [73] studied the pyrolysis of sludge and sawdust and confirmed that biochar produced through co-pyrolysis had potential for metal immobilization. Furthermore, [74] reported that the mixing of cotton stalks with sewage sludge reduced the amounts of heavy metals of biochar. [75] showed that the total heavy metals in blended biochars were lower than that of sludge biochar.

Table 8. *Heavy metal and metalloids*

(mg kg^{-1})	Sewage sludge	Pine sawdust	Biochar produced under optimized conditions	Biochar Standards		
				IBI	EBC (basic grade)	EBC (premium grade)
Ca	74570	1560	25103.5	-	-	-
Cd	2.04	-	0.626	1.4-39	<1.5	<1
Cr	221.5	0.238	81.5	64-1200	<90	<80
Cu	282	0.61	98.5	63-1500	<100	<100
Fe	8266.5	308	4212.5	-	-	-
K	2421.5	798	1445	-	-	-
Li	12.8	0.764	4.2	-	-	-
Mg	7831.5	253	2427	-	-	-
Mn	211.5	43	123.5	-	-	-
Mo	12.5	0.348	2.3	5-20	-	-
Na	2613	233	945	-	-	-
Ni	76	-	26.3	47-600	<50	<30
P	13117.5	51	4416	-	-	-
Pb	176.8	0.997	61.8	70-500	<150	<120
Zn	1112.5	-	439.5	200-700	<400	<400

Sewage sludge consists of essential macronutrients and micronutrients including K, P, Ca, Mg [76]. The concentrations of Ca, K, Mg, P in biochar produced under optimized conditions were found to be 25103, 1445, 2427 and 4416 mg kg^{-1}, respectively. Similar results were reported by [77] and [32]. Studies found that biochar obtained from sewage sludge was rich in nutrients such as Ca, P, and K [78,79]. [80] found that sewage sludge biochar served as fertilizer by improving the levels of nutrients in the tomato plant. These authors stated that the Ca, Mg, Na, and Fe concentrations in roots of tomato plants were increased through biochar addition, whereas biochar promoted the P, K, and Ca concentrations in leaves of tomato plant compared with the control. In another study, [81] converted sludge to biochar at 300 ° C and used for corn growth. The study showed that the concentrations of P, K, Ca, and Mg in corn were at 41100, 1600, 6700, and 1800 mg kg^{-1}, respectively. The biochar from sewage sludge increased N, P, K in leaf of the corn plant [81].

4. RESULTS

This study investigated the torrefaction of dried sludge and pine sawdust. Temperature, time, and the mixing ratio was carried out to maximize the HHV and weight yield of biochar and to minimize ash content of biochar using Box-Behnken design. A quadratic model for weight yield, HHV, and ash content was developed using a set of experimental data and ANOVA. Optimal values were obtained with 60.82%, 21.58 MJ kg-1 and 18.78% for weight yield, HHV and ash at 310 ° C for 20 min with a 25% sewage sludge mixing ratio. The experimental results show that the average values of the experiments were 56.4%, 22.9 MJ kg^{-1}, and 21% for the weight yield, HHV and ash content, respectively. The impact of temperature and mixing ratio was higher than that of the residence time for the three response variables. Moreover, DT, ST, HT, FT of biochar ash was 1184°C, 1198°C, 1213°C, 1232°C, respectively. It indicates that the interaction of sewage sludge and pine sawdust is suitable for co-torrefaction. Moreover, achieving the IBI and EBC established values, these findings showed that biochar produced from co-torrefaction enhance plant growth and soil health.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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