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Thermogravimetric study for the co-combustion of coal and dried sewage sludge

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Abstract−The co-combustion of dried sewage sludge with coal is a promising method to dispose of and treat sewage sludge waste. Because sewage sludge has a different elemental composition than coal, the co-combustion of sewage sludge with coal may have different combustion characteristics than the single combustion of coal. In this study, the co-combustion of dried sewage sludge with coal was tested varying heating rates and mixing ratios of the dried sewage sludge. The results were analyzed using thermogravimetric (TG) and derivative thermogravimetric (DTG) curves and modeled using Ozawa-Flynn-Wall and Vyazovkin models. The mixed samples of coal and dried sewage sludge showed similar TG curves to the coal sample. The co-combustion showed activation energies close to that of the single coal combustion. This suggests that the co-combustion of coal and dried sewage sludge has similar combustion behavior to the single combustion of coal for mixing percentages of dried sewage sludge up to 20%.

Keywords: Dried Sludge, Co-combustion, TGA, Kinetics, Secondary Fuel

INTRODUCTION

The amount of sewage sludge generated from municipal wastewater treatment plants has been increasing. Because ocean dumping is limited by the Ocean Dumping Act, an alternative method of disposal needs to be considered. Co-combustion of sewage sludge with coal is one of the most promising methods for sewage sludge disposal [1]. In addition, the heat generated from the combustion of sewage sludge can be recovered and converted into energy [2]. Because sewage sludge has a different elemental composition than coal, the co-combustion of sewage sludge with coal may have different combustion characteristics than the single combustion of coal.

Many studies have been conducted to gain a better understanding of the characteristics of the co-combustion of sewage sludge with coal. Kang et al. suggested that co-combustion of sewage sludge and coal is economically feasible [3]. Yang et al. conducted co-combustion of sewage sludge and coal gangue [4]. They found reduction in sulfur dioxide (SO_2) emission by alkali and alkaline earth elements of sewage sludge and reduction in nitrogen monoxide (NO) emission by char content of coal gangue. They also suggested sewage sludge as an alternative cement clinker material [5]. Wang et al. suggested that heat generated from combustion of volatile content of activated sludge increased the efficiency of co-combustion with lignite [6]. Kim et al. conducted thermogravimetric analysis of the co-combustion of sewage sludge with coal by changing the mixing ratio of sewage sludge [7]. They found that a large number of volatile components in sewage sludge influenced the combustion characteristics when the percentage of sewage sludge exceeded 20%. Otero et al. conducted kinetic analysis and modeled the co-combustion using the Ozawa-Flynn-Wall and Vyazovkin models [8]. The mixing percentages of sewage sludge used were 2, 5 and 10%. The activation energy required for co-combustion was similar to that of the single combustion of coal, but was significantly lower than that required for the combustion of sewage sludge. Compared to coal, sewage sludge can be burned at a lower and wider temperature range because it contains a greater number of volatile components [9]. This may result in different combustion behavior than the co-combustion of sewage sludge with coal.

As discussed, it has been suggested that co-combustion of sewage sludge with coal is technically and economically feasible. This study was designed to gain a better understanding of its combustion behavior with a wide range of mixing ratios of dried sewage sludge and heating rates. Thermogravimetric study analysis was conducted. Sewage sludge samples were obtained from two different wastewater treatment plants to investigate the effects of sewage sludge composition on its combustion behavior. The results were presented as thermogravimetric (TG) and derivative thermogravimetric (DTG) curves and modeled using Ozawa-Flynn-Wall and Vyazovkin models.

MATERIALS AND METHODS

1. Materials

Dried sewage sludge samples were obtained from two different wastewater treatment plants. Bituminous coal was pre-mixed with each sewage sludge sample using a lab spoon and placed in a sample pan for thermogravimetric analysis. It was heated at various heating rates using a thermogravimetric analyzer (Q600, TA Instruments Inc., balance sensitivity: 0.1 μg, DTA sensitivity 0.001 °C, USA). Table 1 shows the ultimate and proximate analysis results. As reported in other studies, the sewage sludge samples contain higher volatile components and significantly lower fixed carbon than coal. Because the sewage sludge samples were pre-dried, they have similar moisture content to that of coal. In addition, the fixed carbon

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Table 1. Results of ultimate and proximate analysis (unit: %)

	C	H	N	S	Moisture	Volatile	Fixed C	Ash
Coal	74.4	4.4	1.4	0.5	5.8	30.4	55.7	8.2
Sludge 1 (S1)	35.2	5.4	5.6	0.6	3.2	46.4	5.7	44.7
Sludge 2 (S2)	28.9	4.8	4.7	1.0	6.3	47.1	8.1	38.5

and ash content differed, while the volatile matter content was similar between the sludge samples.

2. Methods

Each sewage sludge sample was pre-mixed with coal at a different mixing ratio and then heated to 1,000 °C in the thermogravimetric analyzer injecting 100 ml/min air at a heating rate of 5, 10, 25, 40, and 100 °C/min, respectively. The weight of the sample was recorded continuously as the temperature increased. The results were presented as TG and DTG curves and modeled using the Ozawa-Flynn-Wall and Vyazovkin models. Both models used a non-isothermal and isoconversional integral method. Using this method, the activation energy can be obtained without determining the reaction order.

2-1. Ozawa-Flynn-Wall Model

In the Ozawa-Flynn-Wall model, the activation energy for combustion can be obtained using the weight loss of the sample with temperature using the following equations:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = (1-\alpha)^n A\exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

$$\ln(\beta) = \ln\left[\frac{AE_a}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E_a}{RT} \qquad (2)$$

where β=dT/dt is the heating rate, t is the time, A is the pre-exponential factor as Arrhenius parameters, E_a is the activation energy, R is the gas constant, α is the weight loss ratio of the sample and T is the absolute temperature corresponding to the value of α. g(α) is a power series expansion for the integration of the exponential term of Eq. (1).

The activation energy can be determined via the slope −1.052 (E_a/R) of the straight line obtained from ln(β) vs 1/T plots [10,11].

2-2. Vyazovkin Model

The Vyazovkin model determines the activation energy via the slope −(E_a/R) of the straight line obtained from ln(β/T^2) vs 1/T plots using the following equation:

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{RA}{E_a g(\alpha)}\right] - \frac{E_a}{R}\frac{1}{T} \qquad (3)$$

Using this model, the activation energy (E_a) for combustion can also be obtained from the temperature (T) at a certain weight loss ratio (α) [12,13].

RESULTS AND DISCUSSION

1. Single Combustion

Each sample of coal, sludge 1 and sludge 2 was combusted at different heating rates. Figs. 1-3 show the TG curves obtained from the single combustion at a heating rate of 5, 10, 25, 40 and 100 °C/min, respectively. The coal sample shows a sudden weight reduction at approximately 400 °C due to the combustion of its fixed carbon content and a decrease in the weight reduction rate as the

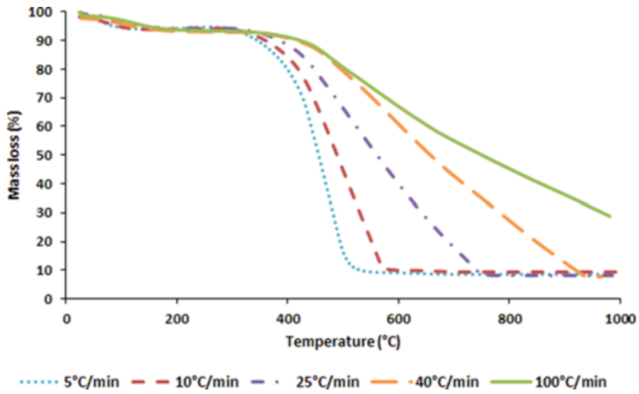

Fig. 1. TG curves for the single combustion of coal the heating rates of 5, 10, 25, 40 and 100 °C/min [14].

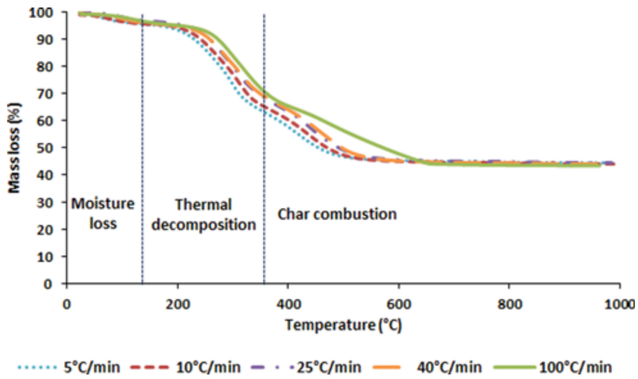

Fig. 2. TG curves for the combustion of sludge 1 at the heating rates of 5, 10, 25, 40 and 100 °C/min [14].

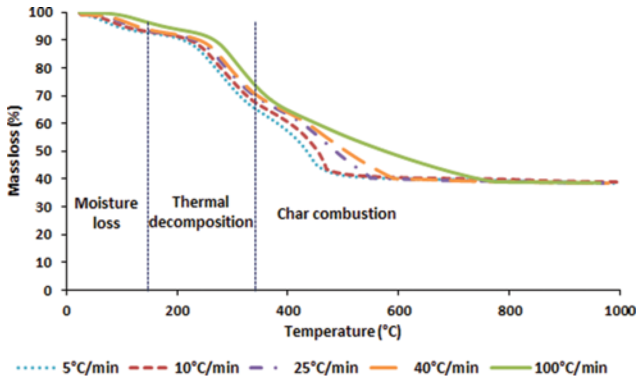

Fig. 3. TG curves for the combustion of sludge 2 at the heating rates of 5, 10, 25, 40 and 100 °C/min [14].

heating rate increases, as shown in Fig. 1. The dried sludge samples showed a gradual weight reduction over a wide range of temperature because they contain higher volatile matter content and lower fixed carbon amounts, as shown in Figs. 2 and 3. In addition, both dried sludge samples had similar TG curves at the various heating rates. A detailed discussion of single combustion behavior with TG and DTG curves can be found in our previous publication [14].

2. Co-combustion

2-1. Effect of Mixing Ratio

Co-combustion of coal and dried sludge was tested varying the percentage of dried sludge to investigate the effect of the mixing ratio on the combustion behavior. Figs. 4 and 5 show TG curves at the slowest heating rate, 5 °C/min while Figs. 6 and 7 show those at the fastest heating rate, 100 °C/min. For both dried sludge samples, the co-combustion showed very similar combustion behavior to that of the single combustion of coal for all mixing percentages of dried sludge. Changing the mixing percentage, a slightly different TG curve was found around the temperature of 350 °C, and a different residual amount was found due to the change in ash content. Although dried sludge was mixed with coal up to 20%, a sudden weight reduction was not found at approximately 200 °C, as found in the combustion of dried sludge. Comparing Figs. 4 and 5, both dried sludge samples show very similar TG curves.

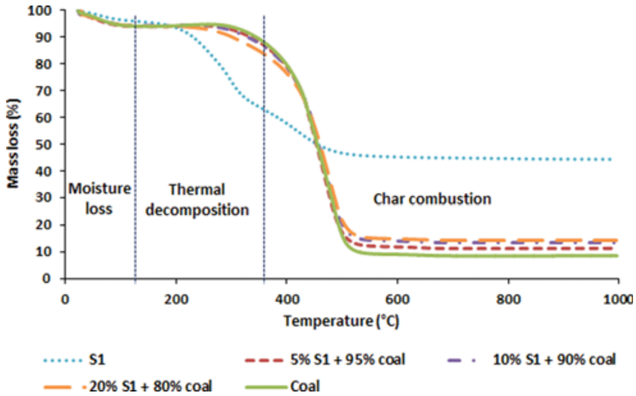

Fig. 4. TG curves for the single combustion and co-combustion of coal and sludge 1 with different mixing percentages at a heating rate of 5 °C/min.

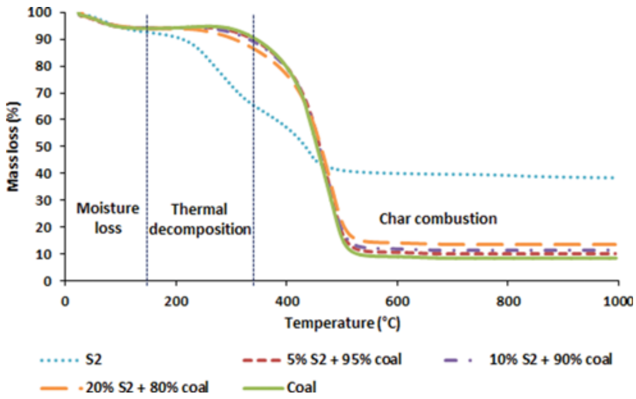

Fig. 5. TG curves for the single combustion and co-combustion of coal and sludge 2 with different mixing percentages at a heating rate of 5 °C/min.

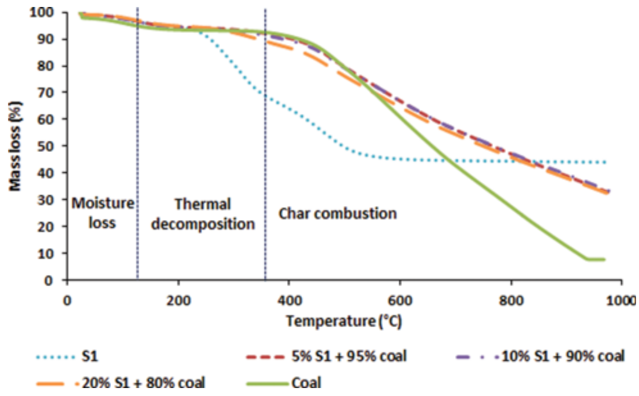

Fig. 6. TG curves for the single combustion and co-combustion of coal and sludge 1 with different mixing percentages at a heating rate of 100 °C/min.

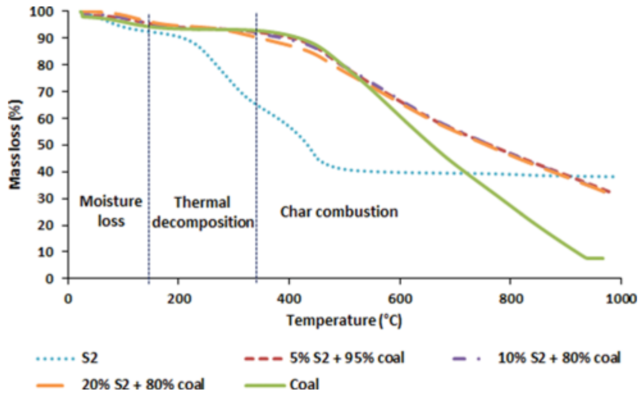

Fig. 7. TG curves for the single combustion and co-combustion of coal and sludge 2 with different mixing percentages at a heating rate of 100 °C/min.

In the single combustion results shown in Figs. 1-3, the coal sample had significantly different TG curves with respect to the heating rate, while both dried sludge samples showed similar TG curves for all heating rates. The mixed samples of coal and dried sludge also had significantly different TG curves with respect to the heating rate by comparing Figs. 4 and 6 or Figs. 5 and 7 as the coal sample shown in Fig. 1. This result shows that co-combustion has very similar combustion behavior to that of the single combustion of coal. This result also suggests that the effect of addition of sludge to coal on combustion behavior is minimal up to the mixing percentage of 20%. In addition, both dried sludge samples had very similar TG curves with changes in the heating rate and the mixing percentage even though those samples had different fixed carbon contents.

Figs. 8 and 9 show DTG curves for single combustion and co-combustion while changing the mixing percentage of dried sludge at a heating rate of 5 °C/min. The combustion of dried sludge had relatively low two peaks at approximately 300 and 420 °C, while the single combustion of coal had a very high peak at approximately 420 °C. This indicates that dried sludge combustion undergoes

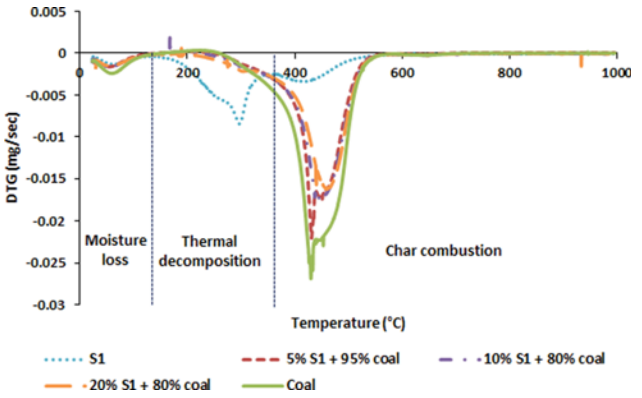

Fig. 8. DTG curves for the single combustion and co-combustion of coal and sludge 1 with different mixing percentages at a heating rate of 5 °C/min.

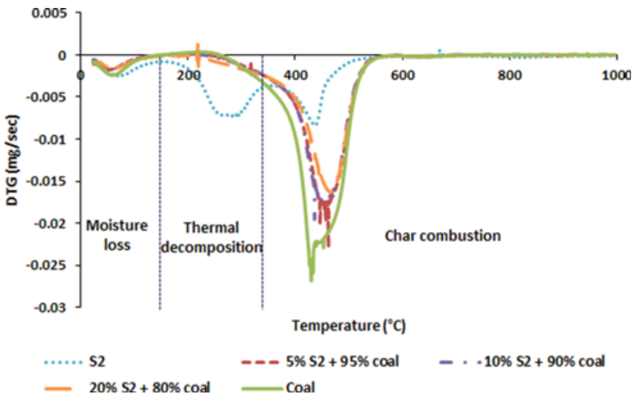

Fig. 9. DTG curves for the single combustion and co-combustion of coal and sludge 2 with different mixing percentages at a heating rate of 5 °C/min.

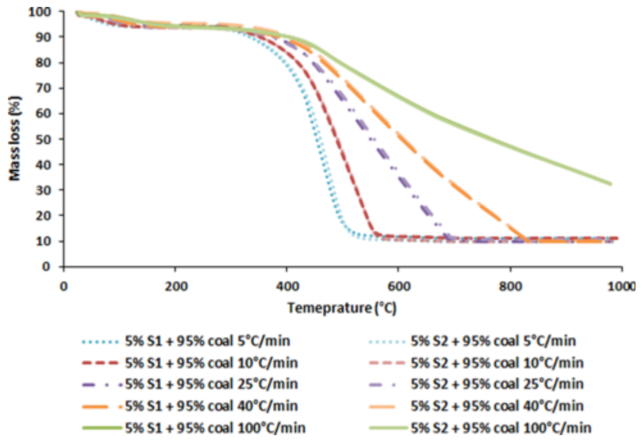

Fig. 10. TG curves for the co-combustion of coal with 5% sludge 1 and 5% sludge 2 at different heating rates of 5, 10, 25, 40 and 100 °C/min.

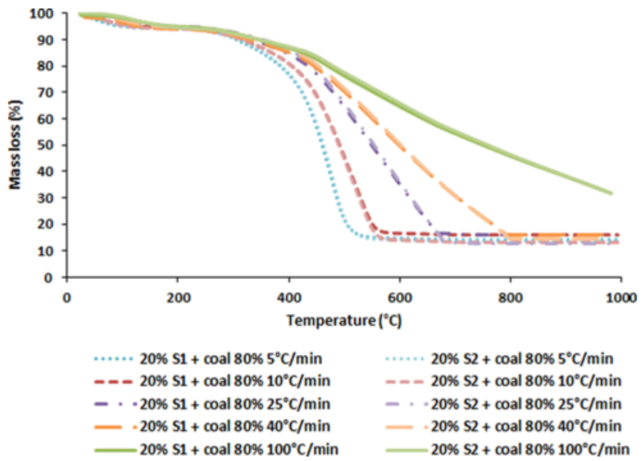

Fig. 11. TG curves for the co-combustion of coal with 20% sludge 1 and 20% sludge 2 at different heating rates of 5, 10, 25, 40 and 100 °C/min.

two distinct steps such as thermal decomposition and char combustion, while char combustion is dominant for the single coal combustion. In other studies, the combustion of dried sewage sludge and biomass which have high volatile matter content also showed two distinct peaks while the single coal combustion showed one high peak [15-19]. The co-combustion of coal and dried sludge samples also show similar DTG curves to the single combustion of coal for all mixing percentages of dried sludge, except for a decrease in the height of the peak. This decrease in the peak at approximately 420 °C may be attributed to a decrease in the fixed carbon content caused by adding dried sludge to the coal.

2-2. Effect of Heating Rate

Single combustion and co-combustion tests were conducted at heating rates of 5, 10, 25, 40, and 100 °C/min to investigate the effect of the heating rate on the combustion behavior. Figs. 10 and 11 show TG curves for the co-combustion of coal and dried sludge with the lowest mixing percentage, 5%, and the highest mixing percentage, 20%, respectively, at heating rates of 5, 10, 25, 40, and 100 °C/min. Similar to the single combustion of coal shown in Fig. 1, both samples had noticeably different TG curves as the heating rates increased. With a lower heating rate, the weight of the sample decreased faster at approximately 400 °C. With a higher heating rate, the weight of the sample decreased more gradually, which shows thermal lag effect of the sample. This was commonly found in the single combustion and co-combustion of coal and dried sewage sludge samples used in this study. The TG curves for the co-combustion of the samples shown in Figs. 10 and 11 are almost identical to the TG curve for the single combustion of coal shown in Fig. 1. This suggests that the co-combustion of coal and dried sludge has similar combustion behavior to that of the single combustion of coal for the mixing percentages of dried sludge up to 20%.

3. Kinetic Analysis

The plots of ln(β) and 1/T and the plots of ln(β/T^2) and 1/T are shown for the single combustion of coal in Figs. 12 and 13, respectively, using the Ozawa-Flynn-Wall and Vyazovkin models. As seen in the figures, both methods accurately modeled the combustion results for coal. In addition, the modeling results for the combustion of the other samples are summarized in Table 2. Considering the high coefficients of determination (R^2) obtained from the plots of the Ozawa-Flynn-Wall and Vyazovkin models, both methods

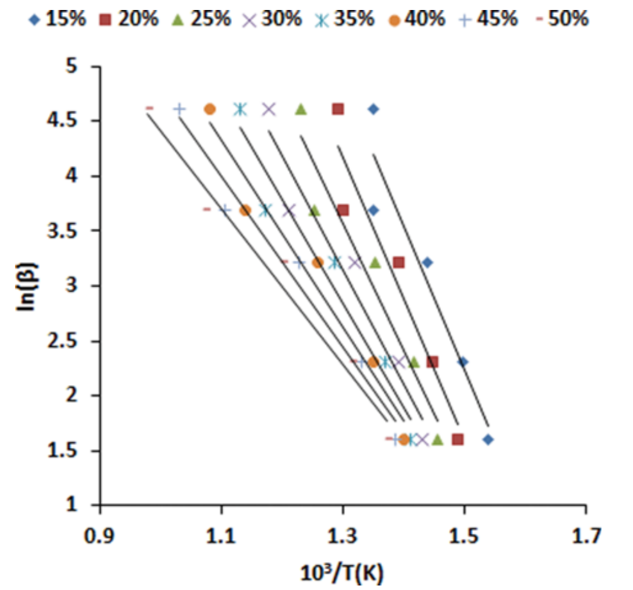

Fig. 12. Plots of ln(β) and 1/T in the Ozawa-Flynn-Wall model for the single combustion of coal.

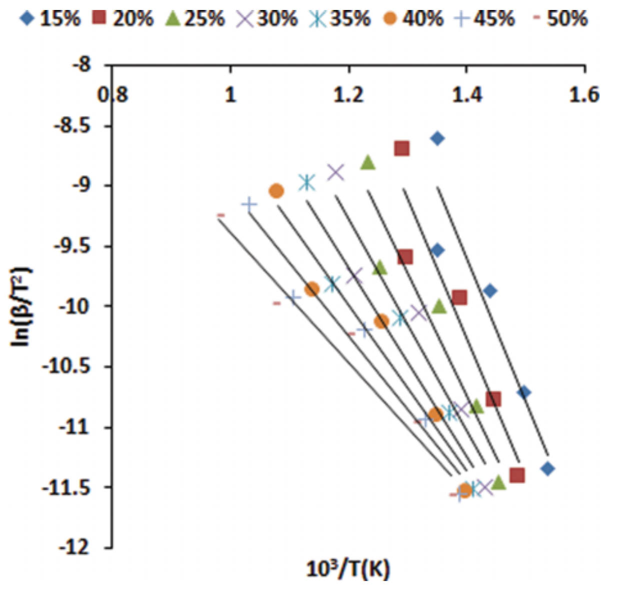

Fig. 13. Plots of ln(β/T²) and 1/T in the Vyazovkin model for the single combustion of coal.

accurately modeled the single combustion and co-combustion of coal and dried sludge. As described in Eqs. (1) and (2), activation energy for the combustion of each fuel sample was determined from the slope of the straight line for the plots of ln(β) and 1/T for the Ozawa-Flynn-Wall model and from the plots of ln(β/T^2) and 1/T for the Vyazovkin model. The activation energy for the single combustion and co-combustion of coal and dried sludge with different mixing percentages are summarized in Table 3. As seen in the table, the activation energy for co-combustion is similar to that for the single combustion of coal, although it increases slightly with an increase in the mixing percentage of dried sludge. Therefore, in addition to the TG and DTG curves, the Ozawa-Flynn-Wall and Vyazovkin model results also show that the co-combustion of coal

Table 2. The values of slope and the coefficient of determination (R^2) from the plots in the Ozawa-Flynn-Wall and Vyazovkin models

Sample	Weight loss (%)	Ozawa-Flynn-Wall		Vyazovkin	
		Slope	R^2	Slope	R^2
Coal	15	−13.25	0.9142	−11.86	0.8947
	20	−12.94	0.9263	−11.49	0.908
	25	−11.53	0.938	−10.04	0.9193
	30	−10.35	0.945	−8.81	0.9251
	35	−9.39	0.954	−7.81	0.9341
	40	−8.48	0.9644	−6.86	0.9458
	45	−7.75	0.9722	−6.09	0.9545
	50	−7.07	0.9762	−5.36	0.9573
S1	15	−24.51	0.9938	−23.41	0.9932
	20	−27.28	0.9897	−26.14	0.9888
	25	−26.19	0.9915	−25.01	0.9908
	30	−22.43.	0.9896	−21.21	0.9886
	35	−19.19	0.983	−17.89	0.9808
	40	−18.89	0.992	−17.49	0.9905
	45	−17.31	0.9418	−15.83	0.9303
	50	−15.12	0.8818	−13.54	0.8554

Table 2. Continued

Sample	Weight loss (%)	Ozawa-Flynn-Wall		Vyazovkin	
		Slope	R^2	Slope	R^2
5% S1+95% coal	15	−15.74	0.9892	−14.37	0.9874
	20	−15.38	0.9967	−13.94	0.9962
	25	−13.67	0.9964	−12.18	0.9951
	30	−11.86	0.9885	−10.33	0.9838
	35	−10.32	0.9836	−8.74	0.9755
	40	−9.024	0.9812	−7.40	0.9694
	45	−7.97	0.9755	−6.29	0.9565
	50	−7.12	0.9702	−5.39	0.9416
10% S1+90% coal	15	−16.63	0.9991	−15.26	0.9988
	20	−15.89	0.9963	−14.46	0.9954
	25	−13.99	0.9838	−12.50	0.979
	30	−12.05	0.9746	−10.52	0.9654
	35	−10.48	0.9702	−8.90	0.9567
	40	−9.17	0.9671	−7.54	0.9485
	45	−8.02	0.9602	−6.33	0.932
	50	−7.17	0.9553	−5.43	0.9163
20% S1+80% coal	15	−17.32	0.9955	−16.00	0.9948
	20	−16.63	0.995	−15.24	0.9943
	25	−15.44	0.9997	−13.99	0.9996
	30	−13.20	0.9941	−11.69	0.9919
	35	−11.34	0.9869	−9.78	0.9812
	40	−9.87	0.979	−8.25	0.9678
	45	−8.62	0.9721	−6.96	0.9537
	50	−7.61	0.9658	−5.89	0.9375

Table 2. Continued

Sample	Weight loss (%)	Ozawa-Flynn-Wall		Vyazovkin	
		Slope	R^2	Slope	R^2
S2	15	−20.82	0.9941	−19.74	0.9934
	20	−23.15	0.9936	−22.02	0.9929
	25	−25.73	0.9921	−24.56	0.9913
	30	−25.48	0.9841	−24.27	0.9827
	35	−22.00	0.8821	−20.72	0.8693
	40	−20.93	0.9503	−19.56	0.9439
	45	−18.03	0.9945	−16.57	0.9934
	50	−13.23	0.9756	−11.69	0.9677
5% S2+95% coal	15	−15.55	0.9815	−14.18	0.978
	20	−15.60	0.9935	−14.17	0.9923
	25	−14.12	0.9978	−12.63	0.9972
	30	−12.15	0.994	−10.61	0.9914
	35	−10.64	0.9866	−9.06	0.9801
	40	−9.32	0.9809	−7.69	0.9695
	45	−8.20	0.9829	−6.52	0.9697
	50	−7.11	0.9492	−5.39	0.9089
10% S2+90% coal	15	−16.02	0.9815	−14.18	0.9976
	20	−15.64	0.9935	−14.17	0.9988
	25	−13.75	0.9978	−12.63	0.9947
	30	−11.99	0.994	−10.61	0.9886
	35	−10.50	0.9866	−9.06	0.9784
	40	−9.26	0.9809	−7.69	0.9702
	45	−8.20	0.9829	−6.52	0.9568
	50	−7.36	0.9492	−5.39	0.9421
20% S2+80% coal	15	−16.39	0.9564	−15.07	0.949
	20	−15.91	0.9865	−14.51	0.9841
	25	−15.73	0.9984	−13.27	0.9981
	30	−12.71	0.9946	−11.19	0.9925
	35	−11.02	0.9866	−9.45	0.9806
	40	−9.68	0.9805	−8.06	0.9697
	45	−8.54	0.9724	−6.87	0.9539
	50	−7.56	0.9659	−5.83	0.9376

and dried sludge is similar to the single combustion of coal.

CONCLUSION

This thermogravimetric study was conducted for the co-combustion of dried sewage sludge with coal to gain a better understanding of its combustion behavior by comparing it with the single combustion dried sewage sludge and coal. The experiments were conducted by varying the heating rate and the mixing percentage of the dried sewage sludge within a range of 0-20%. The results were analyzed using TG and DTG curves and modeled using the Ozawa-Flynn-Wall and Vyazovkin models. The coal sample shows a sudden weight reduction at approximately 400 °C due to the combustion of its fixed carbon content, while the dried sludge samples show a gradual weight reduction over a wide range of temperature due to their high volatile matter content. The mixed samples of coal and dried sludge show a gradual weight reduction regardless of the mixing ratio similar to the coal sample. The co-combustion of coal and dried sludge have significantly different TG curves with respect to the heating rate similar to the coal sample. In addition, similar TG curves are found for all mixing percentages of dried sludge applied in this study. The co-combustion of coal and dried sludge had a very high peak at approximately 420 °C in its DTG curve similar to the single combustion of coal. The kinetic analysis results obtained using the Ozawa-Flynn-Wall and Vyazovkin models show that co-combustion has activation energies close to that of the single combustion of coal. This finding suggests that the co-combustion of coal and dried sewage sludge has very similar combustion behavior to that of the single combustion of coal for the mixing percentages of 0-20%. This can also be applied to sewage sludge samples generated from different sources.

Table 3. Activation energy values obtained from the Ozawa-Flynn-Wall and Vyazovkin models

Sample	Activation energy (E)	
	Ozawa-Flynn-Wall model	Vyazovkin model
Coal	79.79	70.99
S1	168.84	166.83
5% S1+95% coal	89.98	81.74
10% S1+90% coal	92.29	84.13
20% S1+80% coal	98.84	91.24
S2	167.32	165.39
5% S1+95% coal	91.57	83.39
10% S1+90% coal	91.58	83.41
20% S1+80% coal	95.38	87.56

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