



Co-combustion of sewage sludge and coffee grounds under increased O₂/CO₂ atmospheres: Thermodynamic characteristics, kinetics and artificial neural network modeling

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ABSTRACT

(Co-)combustion characteristics of sewage sludge (SS), coffee grounds (CG) and their blends were quantified under increased O₂/CO₂ atmosphere (21, 30, 40 and 60%) using a thermogravimetric analysis. Observed percentages of CG mass loss and its maximum were higher than those of SS. Under the same atmospheric O₂ concentration, both higher ignition and lower burnout temperatures occurred with the increased CG content. Results showed that ignition temperature and comprehensive combustion index for the blend of 60%SS-40%CG increased, whereas burnout temperature and co-combustion time decreased with the increased O₂ concentration. Artificial neural network was applied to predict mass loss percent as a function of gas mixing ratio, heating rate, and temperature, with a good agreement between the experimental and ANN-predicted values. Activation energy in response to the increased O₂ concentration was found to increase from 218.91 to 347.32 kJ·mol⁻¹ and from 218.34 to 340.08 kJ·mol⁻¹ according to the Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa methods, respectively.

1. Introduction

Rapid growth rates of urbanization and population have increased the generation of sewage sludge (SS) to such an extent that its treatment has become an important issue across the world (Cieslik et al., 2015; Huang et al., 2018). Since SS contains large amounts of salts, nutrients, heavy metals, pathogens, and organic pollutants, public and environmental health is under significant threat unless it is treated properly (Nadziakiewicz and Koziol, 2003; Kijo-Kleczkowska et al., 2016). Compared to such methods as landfilling, composting, and agricultural recycling, the use of renewable energy sources in co-combustion has received widespread attention as it alleviates the environmental issues associated with SS disposal and allows for its efficient use for energy production (Magdziarz and Wilk, 2013). Therefore, co-combustion of SS with different biomass types has been a preferred method to increase the share of renewable solid fuels in the energy market (Niu et al., 2016; Liu et al., 2017). Coffee prepared from roasted coffee beans is a

globally popular drink with a global annual production of about 500 billion cups (Li et al., 2014). Coffee grounds (CG) as by-products are generated in vast quantities during the processing of raw coffee powder with hot water or steam for instant coffee preparation (Mussatto et al., 2011a). CG residues are rich in sugars (45.3% w/w) polymerized into cellulose and hemicellulose structures, protein (13.6% w/w) and ashes with such minerals as potassium, phosphorus, magnesium, and calcium (Mussatto et al., 2011b).

In response to the increased atmospheric emissions of greenhouse gases, O₂/CO₂ combustion appears to be a promising technology for capturing CO₂ (Wang et al., 2012a; Haykiri-Acma et al., 2010; Arias et al., 2008). Through O₂/CO₂ combustion, nitrogen is removed, with fuel burning in the mixture of pure O₂ and recycled flue gases. Most studies about the coal and biomass co-firing have been performed under air atmosphere (Roni et al., 2017; Sahu et al., 2014; Saidur et al., 2011). Also, analyses of the oxy-fuel combustion have mainly focused on pure coal or pure biomass (Scheffknecht et al., 2011; Toftegaard et al.,

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2010). However, there exists a lack of studies about the co-combustion characteristics of the SS and CG blends under increased O_2/CO_2 conditions towards the practical application of such solid fuels. For a better understanding of operating conditions of an efficient industrial system suitable for blending solid fuels such as CG under the changing O_2/CO_2 combustion, it is necessary to simulate thermal behavior based on the application of data-driven models. Among several modeling approaches are the artificial neural networks (ANNs) widely used to forecast the non-linear relationships between input-output data (Mohanraj et al., 2015; Yadav and Chandel, 2014; Witek-Krowiak et al., 2014). Since the application of ANNs still remains scarce to predict co-combustion behaviors of SS-CG blends under different O_2 concentrations, this study also attempts to explore the use potential of ANN in this field.

The main objectives of the present study were to (1) quantify impacts of the increased O_2 concentration on the (co-)combustion characteristics of SS, CG and their blends using a thermogravimetric analysis, (2) simulate yield as a function of gas mixing ratio, temperature, and heating rate using ANN and (3) estimate the kinetics of the SS-CG blends under different conditions according to the Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods.

2. Materials and methods

2.1. Proximate and ultimate analyses

SS samples were supplied from an urban wastewater treatment plant located in Guangzhou, China. CG samples were obtained from an instant coffee processing factory in China. Both materials were pulverized using a pestle and mortar after being air-dried and then passed through a sieve with a mesh size of 74 μm using a screen vibrator. The samples were dried in an oven at 105 °C for 24 h and stored in a desiccator. The proximate analyses of SS and CG were conducted in accordance with the Chinese National Standard GB/T 212-2008. The ultimate analysis (C, H, N, and S) was performed using an element analyzer (Vario EL cube, Germany), and then, O content was calculated by difference. The proximate and ultimate analyses and higher heating values (HHV) of the SS and CG samples were summarized in Table 1 (Chen et al., 2017).

2.2. Thermogravimetric analyses

SS and CG blends were prepared using the following six ratios: 100%SS, 90%SS + 10%CG, 80%SS + 20%CG, 70%SS + 30%CG, 60%SS + 40%CG, and 100%CG. The (co-)combustion behaviors of the individual and blended samples were analyzed using a thermogravimetric analyzer (TGA) (Mettler Toledo TGA/DSC 1 analyzer). (Co-)combustion was performed under the four atmospheres of 21% O_2 /79% CO_2 , 30% O_2 /70% CO_2 , 40% O_2 /60% CO_2 , and 60% O_2 /40% CO_2 in the temperature range of 30–1000 °C at the four heating rates of 5, 10, 20 and 40 °C/min⁻¹. The flow rate was kept constant at 100 mL/min⁻¹ in all experiments, and the initial weight of each sample for TGA was about 10 mg.

Table 1
Proximate and ultimate analyses of SS and CG on an air-dried basis.

Sample	Ultimate analysis (wt%)					Atomic ratio		Proximate analysis (wt%)				HHV ^a (MJ·kg ⁻¹)
	C	H	O ^f	N	S	H/C	O/C	M ^b	V ^c	A ^d	FC ^{ef}	
SS	24.13	3.94	66.69	4.50	0.74	0.163	2.764	5.50	48.80	43.38	2.32	10.67
CG	57.17	7.10	33.36	2.31	0.06	0.124	0.584	2.69	74.82	0.56	21.93	24.81

^a HHV, higher heating value on an air-dried basis.

^b M, moisture.

^c V, volatile matters.

^d A, ash.

^e FC, fixed carbon.

^f O and FC, calculated by difference.

2.3. Artificial neural network

Artificial neural network is a data-driven modeling tool to predict complex and non-linear relationships between inputs and output (Sunphorka et al., 2017a). By processing information through a complex network with sensory feedbacks, ANN learns and adjusts itself until it fits the solution (Sunphorka et al., 2017b). Feedforward Multiple Layer Perceptron (MLP) based on Levenberg-Marquardt (LM) back-propagation, an intermediate optimization algorithm between the Gauss-Newton and gradient descent methods (Fausett, 1994), was used to train ANN. MLP network has an input layer, followed by one or more neurons (nodes) with their biases (b), a weight matrix (w), and an output vector (Vani et al., 2015). Hidden layers are employed to implement complex and non-linear functions on ANN (Jorjani et al., 2008). In the present study, the three neurons of O_2 - CO_2 mixing ratios, heating rates, and temperature were used in the input layer. The numbers of hidden layers and neurons in the hidden layers, training epochs, and activation functions were chosen using a trial and error approach. Model performance was evaluated considering the root mean square error (RMSE) in Eq. (1), mean absolute error (MAE) in Eq. (2), mean bias error (MBE) in Eq. (3) and coefficient of determination (R^2) in Eq. (4) between predicted and experimental TG values. Lower RMSE, MAE and MBE values and higher R^2 values indicate more optimized ANN architecture. The ANN model was developed using the ANN toolbox in Matlab.

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (H_i - H_{i,model})^2} \quad (1)$$

$$MAE = \frac{1}{N} \sum_{i=1}^N |H_i - H_{i,model}| \quad (2)$$

$$MBE = \frac{1}{N} \sum_{i=1}^N (H_i - H_{i,model}) \quad (3)$$

$$R^2 = 1 - \frac{\sum_{i=1}^N (H_i - H_{i,model})^2}{\sum_{i=1}^N (H_i - \bar{H}_i)^2} \quad (4)$$

where H_i is the target value, $H_{i,model}$ is the network output of each pattern, and $\bar{H}_i$ is the mean of target values.

2.4. Kinetic methods

Kinetic behavior of the thermal decomposition processes of the different constituents was expressed using the following rate of conversion:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (5)$$

where t (min) is time; T is the absolute temperature; $f(\alpha)$ represents the function of reaction mechanism; and α is the degree of conversion that can be calculated thus:

$$\alpha = \frac{W_0 - W_f}{W_0 - W_i} \quad (6)$$

where W_0 , W_i and W_f refer to initial, instantaneous and final masses, respectively. $k(T)$ is a temperature-dependent rate constant and is expressed by the Arrhenius law as follows:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where A is the pre-exponential factor; E_a ($\text{J} \cdot \text{mol}^{-1}$) is activation energy of the reaction; and R is the universal gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Substituting Eq. (7) in Eq. (5) leads to the following:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (8)$$

Taking into account that the temperature is a function of time and increases with the constant heating rate β ($\text{K} \cdot \text{s}^{-1}$), β can be re-written thus:

$$\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \frac{d\alpha}{dt} \quad (9)$$

Eqs. (8) and (9) can be combined and rearranged as follows:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (10)$$

where $g(\alpha)$ is the integrated form of conversion-dependent function $f(\alpha)$, and $\int_0^T \exp\left(-\frac{E_a}{RT}\right) dT$ on the right-hand side of Eq. (10) is called the temperature integral, which does not have an analytical solution.

If it is assumed that $x = E_a/RT$, then $\int_0^T \exp\left(-\frac{E_a}{RT}\right) dT$ is reduced to $\frac{E_a}{R} \int_x^\infty \frac{e^{-x}}{x^2} dx = \frac{E_a}{R} P(x)$, where $P(x)$ is an infinite function of x . Therefore, substituting the values of temperature integral ($P(x)$) in Eq. (10) gives:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE_a}{\beta R} P(x) \quad (11)$$

As the value of E_a/R is constant, the evaluation of $\int_0^\alpha \frac{d\alpha}{f(\alpha)}$ is dependent on evaluating the function $P(x)$. In this study, the iso-conversional model based on the KAS and FWO methods was used for approximation and applied to calculate activation energy (E_a). The KAS method (Kissinger, 1957; Akahira and Sunose, 1971) based on the Coats and Redfern (1964) approximation is expressed thus:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT} \quad (12)$$

where the plot of $\ln(\beta/T^2)$ against $1/T$ resulted in a straight line whose slope can be used to determine E_a .

Doyle (1962) evaluated $P(x)$ and suggested its value to be $\log(P(x)) = -2.315 - 0.4567x$ over the range of $20 \leq x \leq 60$. Using the Doyle (1962) approximation and the logarithmic form of Eq. (10); the following linear equation of the FWO method (Ozawa, 1965; Flynn and Wall, 1966) is obtained:

$$\log(\beta) = \log\left(\frac{AE_a}{g(\alpha)R}\right) - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \quad (13)$$

Upon changing logarithm to the base 10 (log) to natural logarithm (ln), Eq. (13) can be rewritten thus:

$$\ln(\beta) = \ln\left(\frac{AE_a}{g(\alpha)R}\right) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad (14)$$

where E_a for different conversion values can be calculated from the

slope of $\ln\beta$ versus $1/T$.

3. Results and discussion

3.1. Proximate and ultimate analyses

The SS and CG samples differ in their composition as can be seen in Table 1. SS had a complex mixture of undigested organics such as plant residues, papers, inorganic materials, oil and fecal materials (Tyagi and Lo, 2013). CG biomass had high carbon content and may be used as a potential source to produce solid fuel. The molar H/C ratio as a parameter for aromaticity and carbonization degree was higher for SS than for CG (Yuan et al., 2013). At the same, the molar O/C ratio was higher for SS than for CG which meant that SS had higher hydrophilicity with more polar-groups than CG did (Chen et al., 2014).

Lower N and S contents of CG can reduce NO_x and SO_x emissions from pure SS combustion. Furthermore, CG contained higher volatile matter and HHV than did SS. The ash contents of SS and CG were 43.38% and 0.56%, respectively. Thus, blending CG with SS can be beneficial for reduction in the waste of the combustion process.

3.2. Influence of SS and CG blends on co-combustion under increased O_2/CO_2 atmosphere

Fig. 1 shows the comparison of mass loss percentages of pure SS and CG fuels and their blends under the increased atmospheric O_2 concentrations from 21% O_2 /79% CO_2 to 30% O_2 /70% CO_2 . The TG curves are given in Fig. 1a, while the DTG profiles are shown in Fig. 1b. The

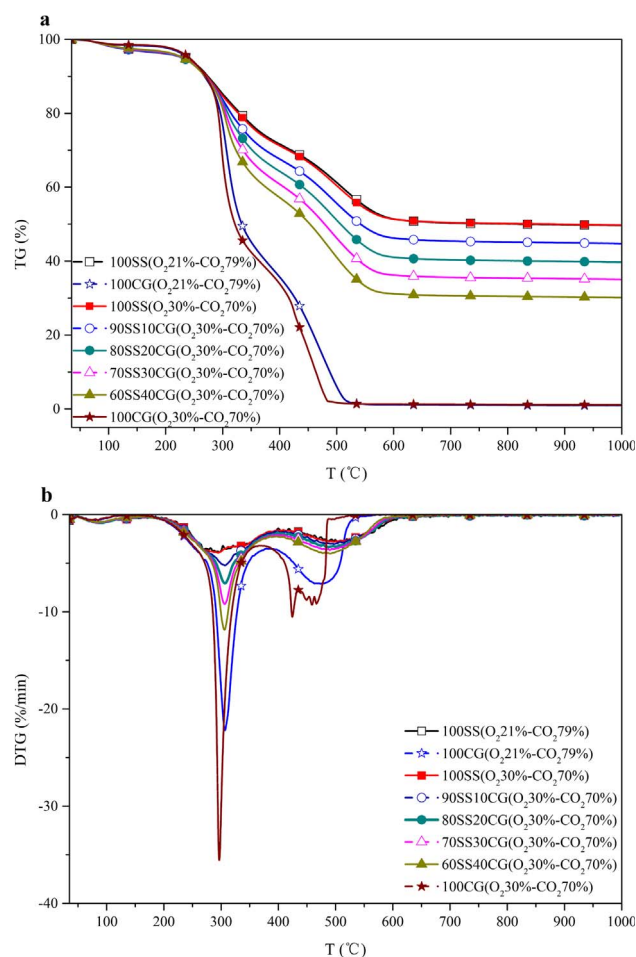


Fig. 1. The remaining mass percentages of SS, CG and their blends under the increased O_2/CO_2 atmospheres at a heating rate of $20^\circ\text{C} \cdot \text{min}^{-1}$: (a) TG and (b) DTG.

Table 2(Co-)combustion characteristic parameters of SS, CG and their blends under increased O₂/CO₂ atmosphere.

Samples	T_i^a (°C)	T_b^b (°C)	T_m^c (°C)	DTG _{max} ^d (%/min)	M_f^e (%)	S^f (10 ⁻¹¹)	Burnout time
100%SS(CO ₂ 79%-O ₂ 21%)	240.0	646.8	297.5	3.84	49.65	1.082	30.58
100%CG(CO ₂ 79%-O ₂ 21%)	280.9	511.9	306.9	22.20	0.95	11.331	23.84
100%SS(CO ₂ 70%-O ₂ 30%)	238.0	643.6	294.9	3.93	49.74	1.127	30.42
90%SS10%CG(CO ₂ 70%-O ₂ 30%)	249.2	631.1	306.9	5.22	44.72	1.534	29.79
80%SS20%CG(CO ₂ 70%-O ₂ 30%)	261.5	608.3	306.9	7.07	39.70	2.134	28.65
70%SS30%CG(CO ₂ 70%-O ₂ 30%)	264.6	591.7	306.3	9.20	35.06	2.995	27.82
60%SS40%CG(CO ₂ 70%-O ₂ 30%)	272.8	577.1	305.9	11.86	30.14	4.005	27.09
100%CG(CO ₂ 70%-O ₂ 30%)	282.0	480.5	296.7	35.56	1.13	19.150	22.27

^a T_i , ignition temperature.^b T_b , burnout temperature.^c T_m , peak temperature.^d DTG_{max}, maximum mass loss rate.^e M_f , residual mass.^f S , comprehensive combustion index in min⁻²·°C⁻³.

pure CG showed higher mass loss than did the pure SS in both environments. The two SS curves under the aforementioned conditions nearly overlapped. The maximum mass loss rate of SS was slightly higher under 30%O₂/70%CO₂ than 21%O₂/79%CO₂, with a slightly shorter burning time. As for CG, the DTG profile shifted to a lower temperature region with a remarkable higher peak value under 30%O₂/70%CO₂ than 21%O₂/79%CO₂. This can be attributed to the fact that rising O₂/CO₂ ratio enhances O₂ mass flux to the volatiles flame, thus increasing devolatilization rate. CG decomposition occurred under 30% O₂/70%CO₂ separately at ~297 and 460 °C, respectively—a shoulder ~425 °C attached to the left of the second decomposition. Peak temperature (T_m) was found to be 306.9 °C which was also similar for the different blends. All the curves of the blends lied in between those of the pure samples. With the increased CG content of the blends, the mass loss percentage and maximum mass loss rate became higher. This increase in the blend also decreased the fuel burnout temperature. The variation with the increased O₂ content was 1.1 °C in the ignition temperature (T_i) but 31.4 °C in burnout temperature (Table 2). T_i was controlled by the ejection of volatile matter from CG rather than by the O₂ concentration, whereas T_b was determined by the chemical oxidation of char (Ahn et al., 2014). The burnout time decreased was attributed to the volatile content of blends increases as the CG increases, and the heat released was increasing during the combustion (Table 1) (Wang et al., 2012b). Comprehensive combustion characteristic index (S) reflects the burning performance of the fuels defined as follows (Yu et al., 2008):

$$S = \frac{(dW/dt)_{\max}(dW/dt)_{\text{mean}}}{T_i^2 T_b} \quad (15)$$

where $(dW/dt)_{\max}$ refers to maximum mass loss rate; $(dW/dt)_{\text{mean}}$ is average mass loss rate; T_i is ignition temperature; and T_b is burnout temperature. The higher the S value is, the more vigorously the samples are burned and quicker the char is burned out. As can be seen in Table 2, under the mixed O₂/CO₂ environment, when the O₂ concentration increased from 21% to 30%, the index S of CG increased from 11.331×10^{-11} to $19.150 \times 10^{-11} \text{ min}^{-2} \cdot ^\circ\text{C}^{-3}$. The increased CG ratio caused the index S to increase. When the CG fraction of the blend was more than 30%, the value of index S was greater than in air (Chen et al., 2017). These suggest that after CO₂ replaces N₂, the decrease in the combustion performance of the SS-CG blend can be offset by the increased O₂ concentration and CG content (Wang et al., 2017).

3.3. Influence of increased O₂/CO₂ atmosphere on co-combustion

Fig. 2 shows the TG-DTG profiles of the 60%SS-40%CG blend under the increased O₂ concentrations. With the increased atmospheric O₂ volume from 21 to 60%, the overall co-combustion trend for the 60% SS-40%CG blend was consistent, and the TG-DTG profiles shifted to a

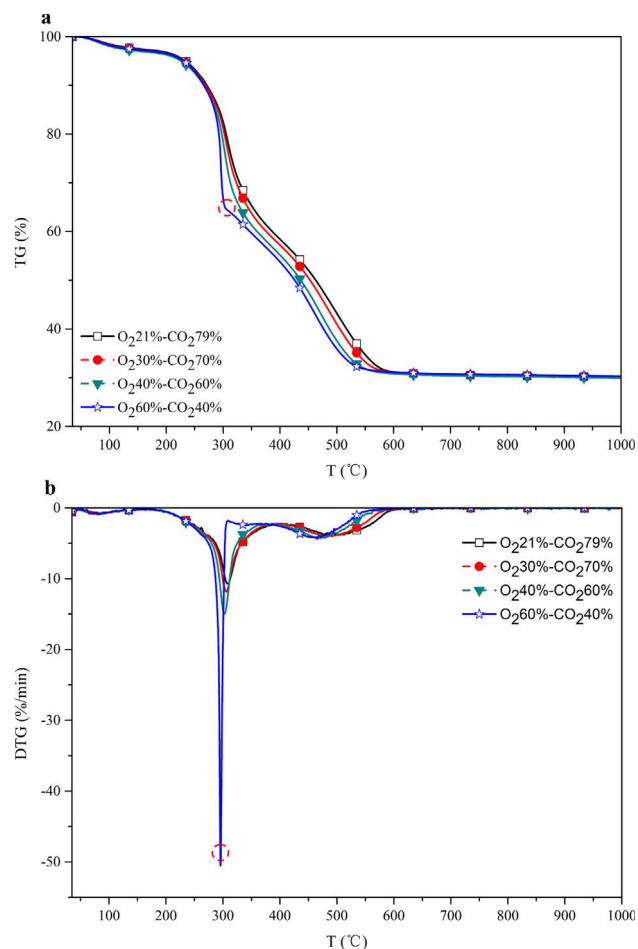


Fig. 2. The remaining mass percentages of the 60%SS-40%CG blend against T under the increased O₂/CO₂ atmospheres at the heating rate of 20 °C·min⁻¹: (a) TG and (b) DTG.

low temperature zone. When the O₂ concentration was above 60%, the TG curve decreased sharply, with the blend approaching its maximum weight loss rate immediately as indicated by the red circle in Fig. 2. According to the TG and DTG profiles given in Fig. 2, after the moisture release, the co-combustion process can be divided into the two stages. The first one occurred in the range of 185–370 °C where the 60%SS-40%CG blend burnt vigorously, and mass loss decreased significantly, with a large amount of volatile devolatilization. The second stage, mainly the char burnout stage, was in the range of 395–600 °C where the mass loss rate was relatively slow. With the increased O₂ concentration, the maximum mass loss (DTG_{max}) rate increased. As can be

Table 3Combustion characteristic parameters of the 60%SS-40%CG blend (SC64) under increased O₂/CO₂ atmospheres.

Samples	T_i^a (°C)	T_b^b (°C)	T_m^c (°C)	DTG _{max} ^d (%/min)	M_f^e (%)	S^f (10 ⁻¹¹)	Burnout time
SC64(CO ₂ 79%-O ₂ 21%)	272.7	584.7	308.5	-10.71	30.14	3.581	27.47
SC64(CO ₂ 70%-O ₂ 30%)	272.8	577.1	305.9	-11.86	30.14	4.005	27.09
SC64(CO ₂ 60%-O ₂ 40%)	273.8	562.9	302.5	-14.99	29.93	5.215	26.38
SC64(CO ₂ 40%-O ₂ 60%)	287.0	553.3	295.7	-50.54	30.29	16.073	25.90

^a T_i , ignition temperature.^b T_b , burnout temperature.^c T_m , peak temperature.^d DTG_{max}, maximum mass loss rate.^e M_f , residual mass.^f S , comprehensive combustion index in min⁻²·°C⁻³.

seen in Table 2, when the O₂ concentration increased to 60%, the DTG_{max} was 50.54 %/min. This result shows that when high concentration of O₂ was supplied, the organic substance of 60%SS-40%CG blend was combusted immediately, and a sharp loss of its mass was observed in the O₂/CO₂ mixtures (Irfan et al., 2012). T_m showed a decreasing trend as the O₂ mole fraction increased from 21 to 60%. When the O₂ volume fraction was below 40%, T_i of the blend slightly changed, whereas when O₂ increased to 60%, T_i increased to 286.2 °C. Instead, T_b of the blend showed an obvious decreasing trend. With the increased O₂ concentration to 60%, the blend T_b dropped to 553.3 °C, and the burnout time was shortened. The higher the O₂ concentration was, the higher the S index was (Table 3). When the O₂ concentration increased from 21 to 60%, the S index increased by 4.49 times. In fact, under O₂-enriched char-combustion conditions, CO oxidation in the boundary layers of char particles and the char gasification by CO₂ play an important role (Yu et al., 2013; Zeng and Fu, 1996), and the char particles burn under increased kinetic control despite the higher burning rates (Irfan et al., 2011).

At the heating rate of 20 °C·min⁻¹, the T/ α (conversion rate) relationship plot of the blend under the increased O₂ concentrations is shown in Fig. 3. With the increased O₂ concentration and temperature, α increased, while the corresponding temperature at the same α decreased. When the O₂ concentration was 21% and α reached 50%, the temperature was 351.3 °C. When the O₂ concentration increased to 40% and α remained the same, the corresponding temperature was 329.5 °C.

Fitting ignition time (τ_i) and burnout time (τ_b) led to the following equation $y = e^{a+bx+cx^2}$ (Fig. 4a and c). The fitting coefficients of τ_i and τ_b were 0.9904 and 0.9439, respectively. The first differential curves of τ_i and τ_b represented the change tendency of the blend τ_i and τ_b . The second differential curves of τ_i and τ_b reflected the change tendency of increasing τ_i rate and decreasing τ_b rate, respectively. With the

increased O₂ concentration, τ_i of the blend increased gradually (Fig. 4a and b). The two inflexion points that appeared on the second differential curve of τ_i were where the O₂ concentration reached 21 and 60%. The first inflexion point being less than the second one suggests that the change in the increasing tendency of τ_i was not obvious below 40% O₂ concentration but became apparent when the O₂ concentration reached 40%. Unlike τ_i , τ_b of the blend showed a decreasing trend with the increased O₂ concentration. The first inflexion point was higher than the second one in Fig. 4d. The rate of decline in the blend τ_b decreased gradually and flattened when the O₂ concentration was 40%.

3.4. ANNs of co-combustion of SS-CG blends

75% and 25% of the entire experimental data were used for training and testing, respectively. The performance metrics of the ANN topologies with the different numbers of hidden layers and neurons trained with LM are presented in Table 4. The total training epochs (iterations) were set to 1000, with the performance goal of 10⁻⁵. A hyperbolic tangent sigmoid function (tansig) and linear transfer function (purelin) were selected for the hidden and output layers, respectively. The architecture of ANN 18 with the three inputs, two hidden layers with 3 and 20 neurons in the first and second ones, respectively, and an output layer (mass loss percent) is shown in Fig. 5. The output was used to predict TG curves under the increased O₂/CO₂ atmospheres. ANN 18 provided the best predictive power with the highest R^2 value of 99.98% and the lowest RMSE and MAE values of 0.381 and 0.285, respectively (Table 4). The ANN 18 performed excellently to simulate the mass loss with the TG curves for the remaining gas mixing ratios (Fig. S1) and resulted in a close agreement between the experimental and predicted values (Fig. 6).

3.5. Evaluation of kinetic parameters

According to Eqs. (11) and (12), the E_a values for several α values can be determined from the slope of a straight line obtained from a plot of $\ln(\beta/T^2)$, $\ln\beta$ against $1/T$. The four different heating rates of 5, 10, 20 and 40 °C·min⁻¹ were used to calculate E_a using the KAS and FWO methods. The activation energies for $0.1 \leq \alpha \leq 0.9$ and the corresponding R^2 values under the increased O₂/CO₂ atmospheres are shown in Table 5. All the R^2 values were above 0.94, and the E_a values of each α obtained by the KAS and FWO methods varied slightly (Table 5).

Since the average E_a values estimated by the KAS and FWO models were in good agreement, the average value of the two models was taken as E_a value of the 60%SS-40%CG blend. The blend E_a values were estimated at 218.62, 236.15, 323.74 and 343.70 kJ·mol⁻¹ for the O₂ concentration of 21, 30, 40 and 60%, respectively. E_a increased with the increased O₂ concentration at the second stage of combustion. The activation energy depends on the activated molecule concentration, diffusion limitation, and organic impurities during the co-combustion process of solid samples (Fang et al., 2006). With the increased O₂ concentration, heat release from char oxidation increased, thus

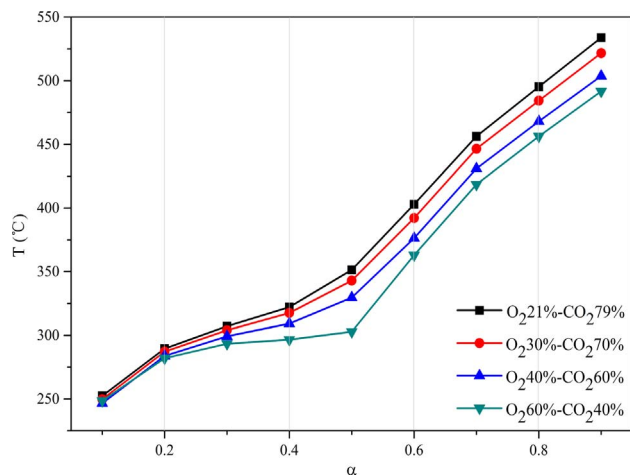


Fig. 3. Relationship between T and α under increased O₂/CO₂ atmospheres for the 60% SS-40%CG blend.

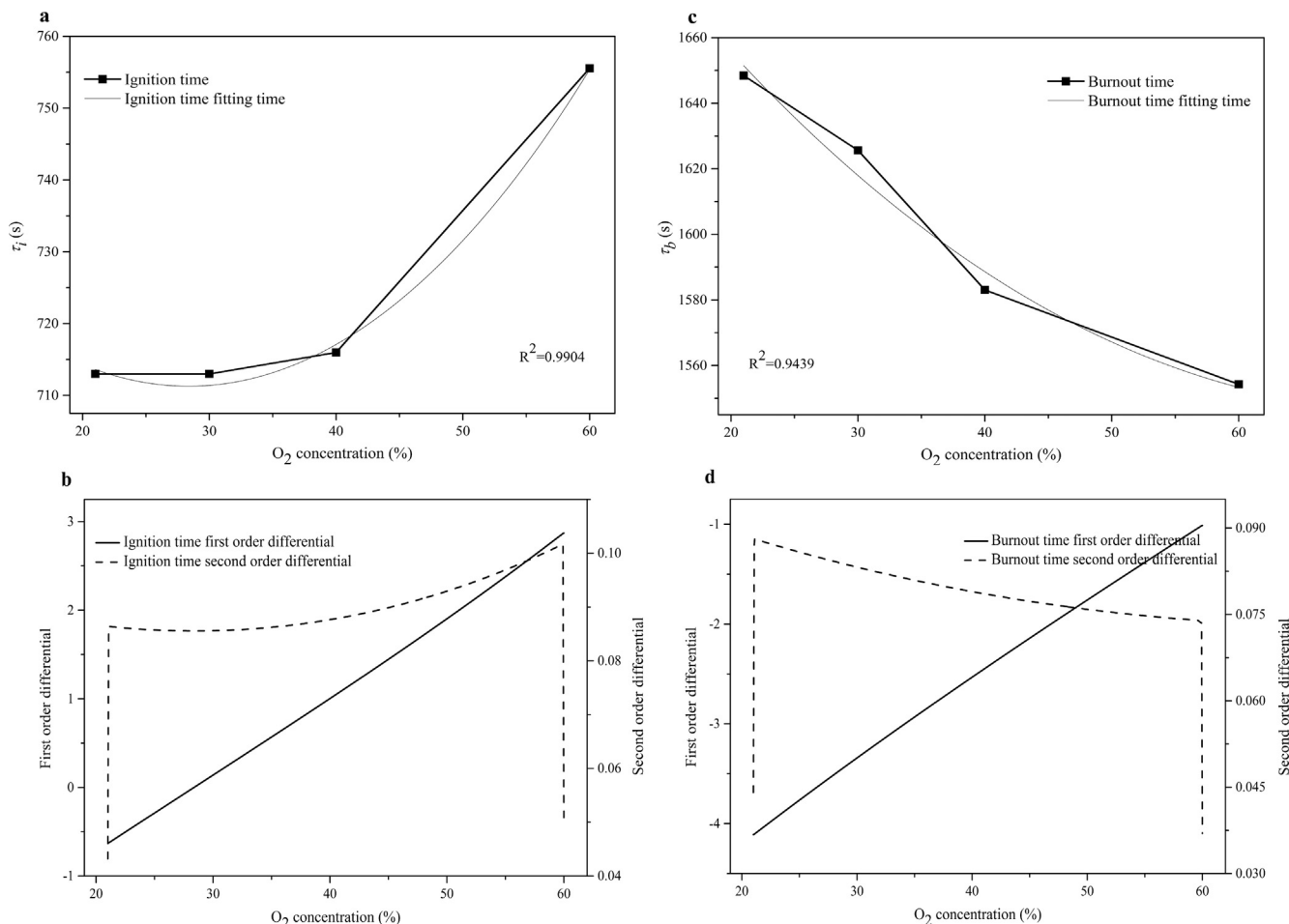


Fig. 4. Curve-fitting for (a) ignition time and (c) burnout time, and curve-fitting of differentiation processing for (b) ignition time and (d) burnout time.

Table 4
Performance comparisons of 27 ANNs.

Model	Inputs	Network topology	RMSE	MBE	MAE	R^2
ANN1	Oxygen-carbon	3*1	0.794	0.132	0.574	0.9991
ANN2	dioxide ratio,	5*1	2.432	0.142	1.717	0.9917
ANN3	heating rate,	7*1	1.046	0.187	0.750	0.9986
ANN4	temperature	10*1	1.195	0.461	0.866	0.9983
ANN5		13*1	1.395	-0.200	0.991	0.9973
ANN6		15*1	3.375	1.290	2.662	0.9863
ANN7		17*1	1.469	0.445	1.182	0.9972
ANN8		19*1	3.663	1.589	2.955	0.9843
ANN9		20*1	14.353	-4.896	11.154	0.7428
ANN10		3*3*1	0.468	0.132	0.346	0.9997
ANN11		3*5*1	0.493	0.221	0.392	0.9997
ANN12		3*7*1	1.696	0.616	1.106	0.9964
ANN13		3*10*1	0.560	0.169	0.412	0.9996
ANN14		3*13*1	1.337	0.378	0.740	0.9976
ANN15		3*15*1	0.607	0.271	0.460	0.9996
ANN16		3*17*1	1.905	0.603	0.758	0.9962
ANN17		3*19*1	4.006	-1.808	2.221	0.9815
ANN18		3*20*1	0.381	0.110	0.285	0.9998
ANN19		5*3*1	0.970	0.057	0.663	0.9986
ANN20		5*5*1	0.716	0.380	0.510	0.9995
ANN21		5*7*1	1.652	0.592	0.700	0.9966
ANN22		5*10*1	5.099	1.709	3.473	0.9709
ANN23		5*13*1	4.443	1.850	2.157	0.9766
ANN24		5*15*1	8.161	-2.695	4.426	0.9296
ANN25		5*17*1	1.260	-0.077	0.828	0.9977
ANN26		5*19*1	2.974	-0.535	1.757	0.9897
ANN27		5*20*1	2.379	0.582	1.287	0.9926

increasing the surface temperature of char. In addition, char structure expanded particle size and increased ash content with the increased final temperature (Werther and Ogada, 1999). The increase in E_a with the increased O_2 concentration was also reported by Wang et al.

The curve-fitting of E_a varied in response to the increased O_2 concentration (Fig. S2a). The calculated values agreed well with the dose-response model. The slope (R_E) of the curve-fitting (Fig. S2b) was 0.55427 at the 21% O_2 concentration and increased sharply up to 9.23068 at the 35% O_2 concentration. However, when the O_2 concentration was above 35%, R_E decreased sharply down to 1.80324 at the 45% O_2 concentration. When the O_2 concentration was above 45%, the R_E curve flattened and became 0.44731 and 0.0241 under the 50% and 60% O_2 concentrations, respectively.

4. Conclusions

During the O_2/CO_2 combustion processes, as the O_2 concentration increased, burnout temperature and combustion time of the blend tended to decrease, while ignition temperature, maximum mass loss rate and comprehensive combustion index increased. ANN model of mass loss percent as a function of O_2 - CO_2 mixing ratio, heating rate, and temperature showed very close agreement with experimental TGA values, with R^2 and RMSE values of 99.98% and 0.381, respectively. The average activation energy values of the blend were estimated at 218.62, 236.15, 323.74 and 343.70 $kJ \cdot mol^{-1}$ under the increased O_2 concentrations, respectively.

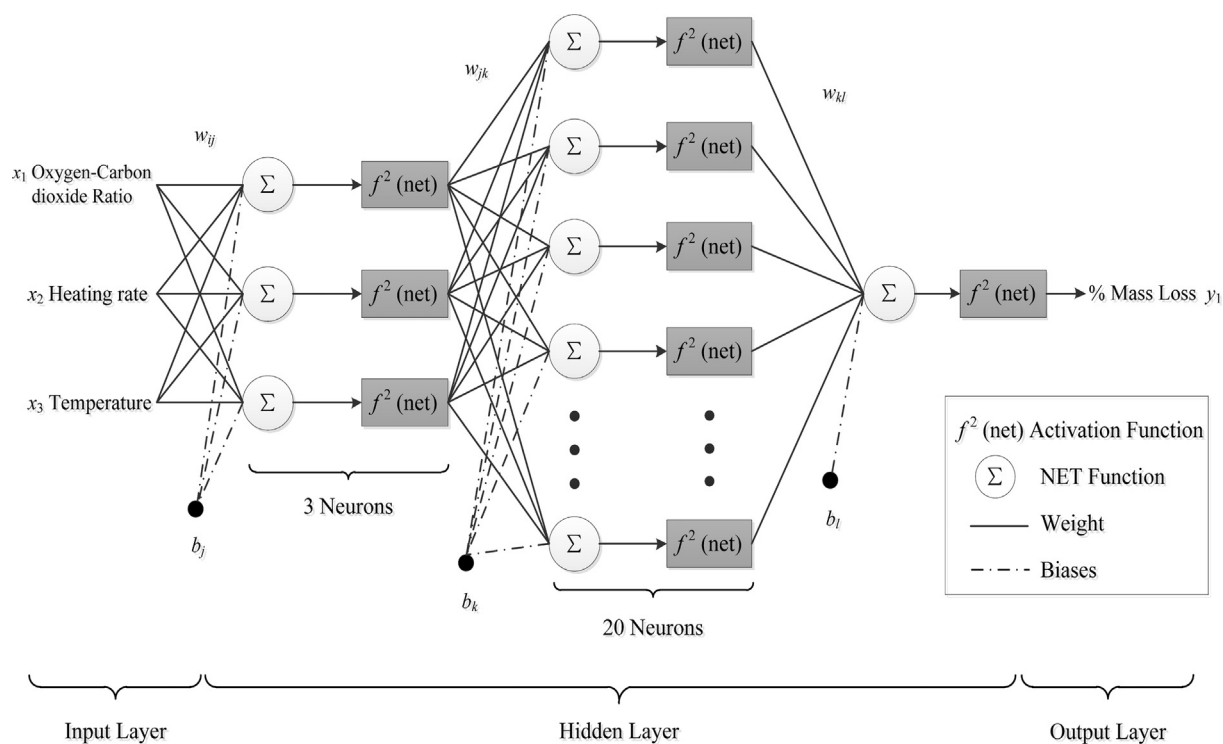


Fig. 5. Proposed ANN structure used to predict co-combustion behaviors of SS-CG blends under increased O_2/CO_2 atmospheres.

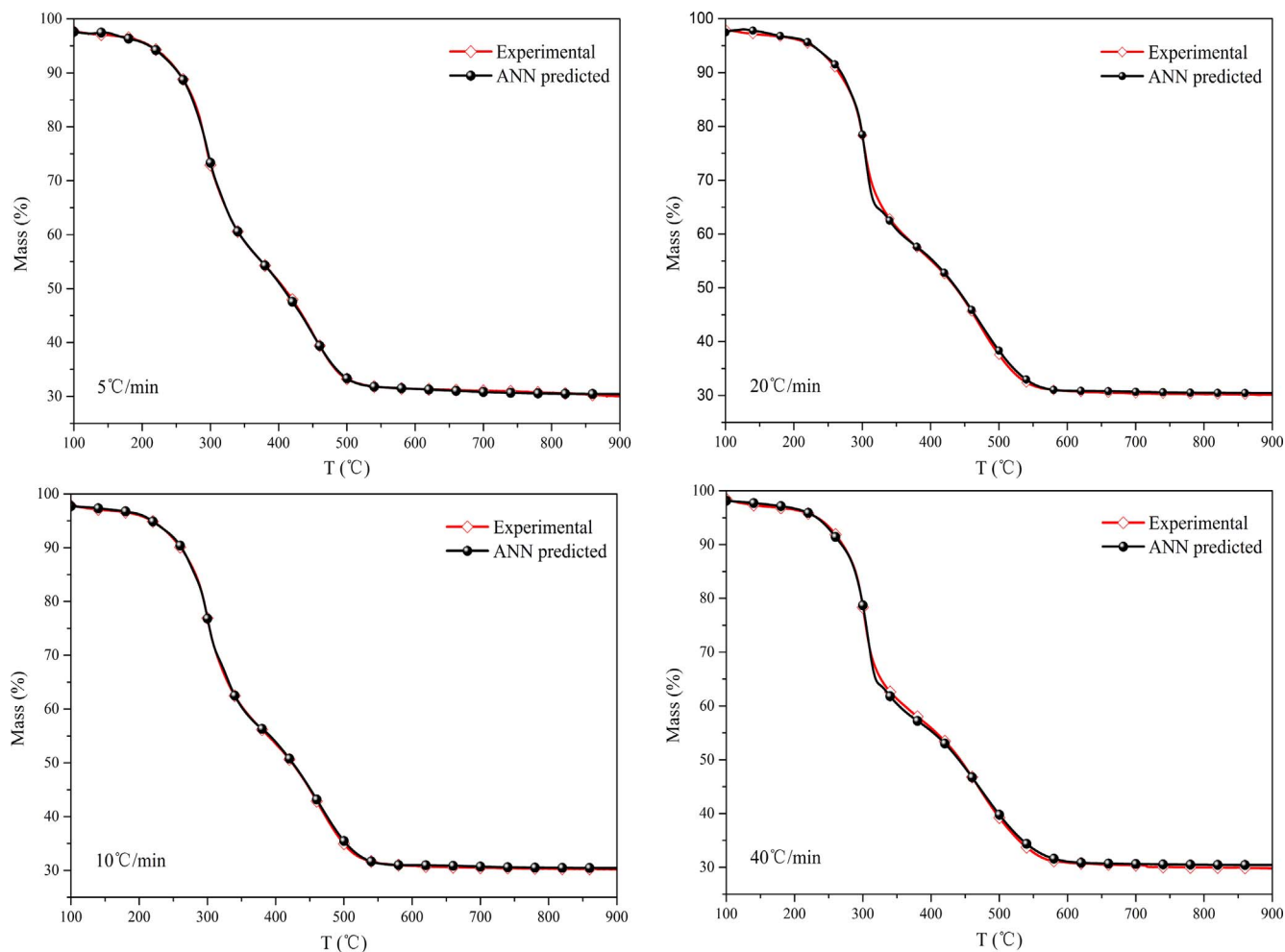


Fig. 6. Performance comparisons of ANN 18 tested for 40% O_2 -60% CO_2 mixing ratio at different heating rates.

Table 5

E_a and R^2 values based on the KAS and OFW methods for the 60%SS-40%CG blend using TG data at the different conversion rates under the increased O_2/CO_2 atmosphere.

Atmosphere	α	KAS		OFW	
		$E(kJ\cdot mol^{-1})$	R^2	$E(kJ\cdot mol^{-1})$	R^2
79%CO ₂ -21%O ₂	0.1	205.74	0.9715	203.85	0.9736
	0.2	290.99	0.9575	285.52	0.9599
	0.3	340.97	0.9418	333.33	0.9447
	0.4	323.68	0.9482	317.11	0.9510
	0.5	240.72	0.9721	238.65	0.9742
	0.6	142.53	0.9927	146.03	0.9936
	0.7	145.71	0.9950	149.90	0.9956
	0.8	144.59	0.9999	149.47	0.9999
	0.9	135.25	0.9996	141.20	0.9997
Average		218.91		218.34	
70%CO ₂ -30%O ₂	0.1	191.25	0.9876	190.05	0.9886
	0.2	281.79	0.9731	276.74	0.9747
	0.3	355.74	0.9672	347.81	0.9688
	0.4	361.93	0.9619	353.43	0.9637
	0.5	288.15	0.9747	283.66	0.9763
	0.6	160.90	0.9831	163.35	0.9850
	0.7	159.92	0.9728	163.23	0.9761
	0.8	171.21	0.9825	174.57	0.9846
	0.9	161.26	0.9916	165.69	0.9927
Average		236.90		235.39	
60%CO ₂ -40%O ₂	0.1	235.35	0.9997	231.96	0.9997
	0.2	352.76	0.9636	344.19	0.9653
	0.3	355.74	0.9206	347.26	0.9243
	0.4	473.09	0.7668	459.03	0.7739
	0.5	525.99	0.7159	509.67	0.7235
	0.6	269.63	0.9850	266.56	0.9861
	0.7	235.98	0.9814	235.38	0.9830
	0.8	260.51	0.9814	259.29	0.9830
	0.9	232.04	0.9974	232.80	0.9977
Average		326.79		320.68	
40%CO ₂ -60%O ₂	0.1	219.50	0.9883	216.89	0.9891
	0.2	260.83	0.9784	256.70	0.9798
	0.3	378.52	0.8668	368.83	0.8723
	0.4	510.84	0.8181	494.84	0.8235
	0.5	582.03	0.9767	562.87	0.9774
	0.6	349.78	0.9036	342.56	0.9086
	0.7	258.55	0.9454	256.64	0.9496
	0.8	301.57	0.9109	298.13	0.9169
	0.9	264.29	0.9813	263.26	0.9828
Average		347.32		340.08	

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.11.031>.

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