Thermodynamics and kinetics parameters of co-combustion between sewage sludge and water hyacinth in CO$_2$/O$_2$ atmosphere as biomass to solid biofuel

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HIGHLIGHTS

- Thermochemical conversion of biomass waste was carried out in oxy-fuel atmosphere.
- The performance sewage sludge combustion was improved by blending water hyacinth.
- Thermodynamic parameters ($\Delta H$, $\Delta S$, $\Delta G$) were calculated through TGA curves.
- The lowest activation energy ($E_a$) of SW was obtained in CO$_2$/O$_2$ = 7/3 atmosphere.

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ABSTRACT

Thermodynamics and kinetics of sewage sludge (SS) and water hyacinth (WH) co-combustion as a blend fuel (SW) for bioenergy production were studied through thermogravimetric analysis. In CO$_2$/O$_2$ atmosphere, the combustion performance of SS added with 10–40 wt.% WH was improved 1–1.97 times as revealed by the comprehensive combustion characteristic index (CCI). The conversion of SW in different atmospheres was identified and their thermodynamic parameters ($\Delta H$, $\Delta S$, $\Delta G$) were obtained. As the oxygen concentration increased from 20% to 70%, the ignition temperature of SW decreased from 243.1°C to 240.3°C, and the maximum weight loss rate and CCI increased from 5.70% min$^{-1}$ to 7.26% min$^{-1}$ and from 4.913% K$^{-3}$ min$^{-2}$ to 6.327% K$^{-3}$ min$^{-2}$, respectively, which corresponded to the variation in $\Delta S$ and $\Delta G$. The lowest activation energy ($E_a$) of SW was obtained in CO$_2$/O$_2$ = 7/3 atmosphere.

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1. Introduction

With the growth in the global economy and population, on the one hand, energy demands increase continuously, and fossil fuel is estimated to run out in the next few decades (Gangulya et al., 2012). On the other hand, the level of greenhouse gases in different scenarios is projected increase in the future by the Intergovernmental Panel on Climate Change (IPCC, 2011). Atmospheric pollution results in the enforcement of economic policies that encourage the use of alternative energy sources that are less harmful to the environment. Therefore, a new energy source that can replace fossil fuel is highly necessary. This necessity has resulted in an increased focus on the production of biofuel from biomass. Biomass is expected to contribute to future sustainable energy systems and sustainable development in both industrialized and developing countries (Vamvuka et al., 2009; Liu et al., 2013).

Biomass fuel can be made of many different substances, such as wood, agricultural waste, algae, sewage sludge and water hyacinth (Santos et al., 2015; Luo et al., 2011).

Sewage sludge is formed during wastewater treatment. The annual output of sewage sludge in China is $3 \times 10^7$t (moisture content of 80%), 80% of which does not reach the standards of harmlessness and stability (Liu et al., 2015). Sewage sludge is harmful for humans and the environment if it is dealt with inappropriately. The perception of sludge being an unwanted waste is changing to the view that it is a beneficial resource. Thus, developing a suitable technology or using an existing technology to reduce the environmental problem and cost of sludge treatment while utilizing it as a source of energy is important (Mountouris et al., 2008).

Highly advanced methods of sludge treatment are being developed to address the increasing amounts of sludge being produced. Such
techniques usually include thermal sludge treatment, which is mainly involves sludge incineration, pyrolysis and gasification. Sludge incineration treatment mainly includes combustion and co-combustion. Given that co-combustion entails a low cost and mature equipment and technology, it has become the main method of sludge incineration (Madjzdar and Wilk, 2013).

Water hyacinth (Eichhornia crassipes), one of the world’s “top ten evil grasses”, has a wide geographic distribution and rich reserves because of its rapid proliferation and lack of natural control mechanisms (Villamagna and Murphy, 2010). Uncontrolled growth of this plant has negatively affected many bodies of water, but the rapid growth rate of water hyacinth makes it a potential biomass source (Zimmels et al., 2009). Water hyacinth presents attributes that are considered ideal for bio-fuel production. These attributes include a culture that is composed of natural growth vegetation, preferably “perennial” (with a fast production rate), that does not compete in terms of space, light and nutrients with crops; pest-resistance and being easily degradable. Furthermore, it is not prone to genetic pollution by crossbreeding with other cultures (Bhattacharya and Kumar, 2010). Current studies on water hyacinth focus on bioremediation (Gangulya et al., 2012), bio-ethanol and gas production (Aswathy et al., 2010; Mishima et al., 2008), feed production and adsorbent preparation (Guerrero-Coronilla et al., 2015). A few studies have investigated water hyacinth co-combustion.

Given that traditional combustion results in only approximately 15% CO2 in the flue gas, capturing CO2 from the flue gas is difficult and costly (Mondal et al., 2012). Combustion in a CO2/O2 atmosphere is one of the several promising new technologies that are associated with CO2 capture and storage (Li et al., 2009). Notably, a large amount of nitrogen results in minimal radiation in exhaust gas but consumes a large amount of heat, which causes a loss of energy in the process of energy transfer. Combustion in a CO2/O2 atmosphere has the following features: (1) reduces the available energy loss in the process of converting chemical energy into thermal energy, (2) decreases the concentration of organic pollutants in the exhaust gas, and (3) reduces the thermal energy of the exhaust gas to the minimum (Yu et al., 2008). Implementation of oxy-fuel atmosphere combustion has been proven to achieve effective and environmental benefits (Habib et al., 2011).

The combustion of sewage sludge in air, pyrolysis in an N2 atmosphere and co-combustion with coal and biomass in air have already been studied (Liao and Ma, 2010; Xie and Ma, 2013; Madgizdar and Wilk, 2013). However, sewage sludge co-combustion with water hyacinth in an oxygen-enriched atmosphere and CO2/O2 atmosphere, especially when thermogravimetric analysis is involved, has not been studied in a prior study. Improved understanding of the kinetic characteristics and thermodynamic parameters in oxy-fuel combustion needs to be obtained.

Blending water hyacinth with sludge could provide a useful means to solve the environmental problems and could result in a certain amount of energy supply. The quality and quantity of the obtained bioenergy depend not only on the chemical composition of the original biomass but also on the reaction conditions. Thus, understanding the chemistry of this alternative biomass is vital to determine the thermochemical process of conversion into biomass-derived fuel (Lee et al., 2014).

This paper examines thermochemical conversion of sewage sludge (SS) blended with water hyacinth (WH), including the oxy-fuel combustion characteristics of their blends in different CO2/O2 atmospheres and the thermodynamic parameters for non-isothermal analyses using the Ozawa-Flynn-Wall (OFW) kinetic isovolumetric model. Then, the values of the apparent activation energy (Ea), the pre-exponential factor (A) in the Arrhenius equation, as well as the changes in the entropy (∆S), enthalpy (∆H) and free Gibbs energy (∆G), were calculated.

### 2. Methods

#### 2.1. Materials

The biomasses considered in this study were sewage sludge (SS) and water hyacinth (WH). SS samples were collected at intervals of 0.5 and 8 h through continuous acquisition from a terminal conveyor belt in a wastewater treatment plant in Guangzhou, Guangdong Province, China. WH samples were collected from the canals that surround Guangzhou University Mega Center, Guangzhou, Guangdong Province, China. In the laboratory, the biomass allowed to dry naturally at room temperature for one week. Afterward, it was milled and sieved with a 74 μm sieve. It was then subjected to oven drying at 105 °C to constant weight and stored in a desiccator for testing. The ultimate analysis and proximate analysis of the SS and WH are presented in Table 1.

#### 2.2. Apparatus and procedure

Thermogravimetric analysis was conducted at three different heating rates, 10, 20 and 40 °C min⁻¹, with a flow rate of 50 ml min⁻¹, using simultaneous DSC–TGA equipment, NETZSCH STA 409 PC, from 25 to 1000 °C. Approximately (10 ± 0.5 mg) of the biomass was used in alumina crucibles in each analysis. Before the start of the experiment, several experiments without samples were conducted to obtain the baseline, which was deducted when the experiments with samples started, to eliminate the systematic errors of the instrument itself. Furthermore, the samples selected randomly in the same batch were repeated three times in an experiment to confirm the repeatability and authenticity of the generated data and the errors were within ±2%. The NETZSCH–T 4–Kinetic2 software provided the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves. A Vario EL–II chons elemental analyzer (Elementar Analysen Systeme GmbH, Germany) and a Parr 6300 Oxygen Bomb Calorimeter (Parr Instrument
Company, United States) were used for the ultimate analysis, proximate analysis and lower heating values of the samples.

The apparatuses used were the following: (1) Thermogravimetry analyzer (NETZSCH STA 409 PC); (2) Vario EL–II chons elemental analyzer (Elementar Analysen Systeme Gmbh, Germany); (3) Parr 6300 Oxygen Bomb Calorimeter (Parr Instrument Company, United States); (4) The muffle furnace (SX2–4–13); (5) Electronic balance (sartorius CAP2P); and (6) The pulverizer (PW177); (7) Electrothermal (DHG–9140A).

2.3. Kinetic theory

2.3.1. Ozawa-Flynn-Wall methods

The one-step global model assumes that the degradation processes result in a single reaction, below.

Biomass $\rightarrow$ Volatiles + Biochar

Here, $k$ is defined as the rate constant of the reaction, whose temperature dependence is expressed by the Arrhenius equation:

$$\ln k(T) = \frac{-E_a}{R} \cdot \frac{1}{T} + \text{ln} A$$

where $x$ is the conversion degree, $t$ is the time, $T$ is the reaction temperature, $A$ is the pre-exponential factor, $E_a$ is the activation energy, and $R$ is the universal gas constant $8.314 \text{ J/K mol}^{-1}$.

The rate of transformation from a solid-state to volatile product is described by the following expression:

$$\frac{\text{d}m}{\text{d}t} = k(T)f(x)$$

The conversion degree $x$ is expressed as (Xie and Ma, 2013)

$$x = \frac{m_0 - m_t}{m_0 - m_{\infty}}$$

where $m_0$ and $m_{\infty}$ are the initial mass and the final mass of the samples, respectively. Here, $m_t$ is the mass of the samples at time $t$.

Eqs. (1) and (2) could be combined into the following equation:

$$\frac{\text{d}x}{\text{d}t} = A \cdot e^{-\frac{E_a}{RT}}f(x)$$

When the heating rate $\dot{\beta}$ is introduced, Eq. (4) is transformed to

$$\dot{\beta} \cdot \frac{\text{d}x}{\text{d}t} = A \cdot e^{-\frac{E_a}{RT}}f(x)$$

Kinetic analysis is essential to design and establish efficient, safe and reasonable processes. The determination of the thermo-kinetic behavior of the biomass allows control of the decomposition mechanism of the biomass. The kinetic parameters of reaction are necessary for accurate prediction of the reaction behaviors and optimization of the process toward products during thermal degradation (Amanda and Leandro, 2016). Non-isothermal thermogravimetric analysis is the most popular and simplest method to study the kinetics and thermodynamics properties of the biomass. An isoconversional integral method appears to be a safer alternative for the calculation of meaningful activation energy values for certain prerequisites, without knowing the kinetic model of the reaction mechanism.

The Ozawa-Flynn-Wall kinetics isoconversional method in Eq. (7) is applied (Kim et al., 2010).

$$\ln(\beta) = C_s - \frac{E_a}{R \cdot T}$$

where $\beta$ is the heating rate; $E_a$ is the activation energy; $C_s$ is the function of the conversion degree $x$; $R$ is the universal gas constant $8.314 \text{ J/K mol}^{-1}$; and $T$ is the reaction temperature.

2.3.2. Kinetic and thermodynamic parameters

We applied at least three values of the heating rate ($\beta$) for the same and different values of the different reaction temperatures obtained in the thermogravimetric curves. This approach allows us to investigate whether the mechanism of the conversion changes with the conversion degree, while estimating the respective activation energy $E_a$ at a conversion degree of $x$. To calculate the kinetic parameters, we used an intermediate value of $\beta$ ($20 \text{ °C min}^{-1}$).

The thermodynamic parameters using the OFW isoconversional method for analysis of the kinetic and thermodynamic parameters, including the pre-exponential factor ($A$) in the Arrhenius equation as well as the enthalpy ($\Delta H$), free Gibbs energy ($\Delta G$) and the changes in the entropy ($\Delta S$), can be expressed by Eqs. (8)–(11) (Kim et al., 2010; Xu and Chen, 2013).

$$A = \dot{\beta} \cdot E_a e^{-\frac{E_a}{RT}} / R \cdot T_m^2$$

$$H = E_a - RT$$

$$G = E_a + R \cdot T_m \cdot \ln \left( \frac{k_b \cdot T_m}{h \cdot A} \right)$$

$$S = \frac{\Delta H - \Delta G}{T_m}$$

where $k_b$ is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J/K}$); $h$ is the Plank constant ($6.626 \times 10^{-34} \text{ J s}$); and $T_m$ is the DTG peak temperature.

To make the research acceptable and applicable in practice with respect to using SW as a fuel, the combustion characteristic parameters for SW under various oxy-fuel conditions, including the ignition temperature ($T_i$), peak temperature ($T_p$), burnout temperature ($T_b$), maximum weight loss rate ($R_{pk}$), and average weight loss rate ($R_w$), are required. They can be directly determined from the TG–DTG curves. Furthermore, the combustion performance parameters, the comprehensive combustibility index (CCI), are recommended to evaluate the combustion performance of SW under different conditions. The CCI index can be calculated as a function.
of the characteristic temperatures and reaction rates (Liu et al., 2013).

\[ CCI = \frac{(-R_p) \times (-R_v)}{T_i^2 \times T_b} \]  

(12)

3. Result and discussion

3.1. Co-combustion characteristics of blend fuels

The influence of SS blended with WH at the ratio of 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% was investigated. Fig. 1 shows the mass loss (TG) and weight loss rate (DTG) curves of the blended fuels in a CO₂/O₂ = 7/3 atmosphere at the heating rate of 20 °C min⁻¹, and the characteristic parameters of SW are given in Table 2.

As shown in Fig. 1, all of the TG and DTG curves of the blends lay between the individual fuels in the CO₂/O₂ atmosphere and varied with the proportion of the individual fuels but, overall, had the combustion characteristics of the SS and WH. As the blending ratio increased, the maximum weight loss rate that corresponds to the main decomposition process was gradually reduced (Table 2), the temperature that corresponds to this rate was reduced, and the trends in the curves shifted to a lower temperature range. The residual weight of the pure SS, their blends of 10 wt.%, 20 wt. %, 30 wt.%, 40 wt.% and pure WH corresponded to 46.36%, 43.74%, 39.71%, 37.63%, 34.65%, 6.55%, respectively. This finding could be

![Fig. 1. TG(a)-DTG(b) curves of co-combustion of sludge blends with water hyacinth.](image-url)
caused by the weight loss rate of the WH being better than that of the sludge, which causes some advantageous influence for SS combustion. It was worthwhile to note that the reductions in $R_p$ and $T_p$ were not linearly related to the amount of WH blend and that the curves of the blends appeared in the third peak, which varied from the SS and WH combustion curve. The maximum weight loss rate of both the SS and WH occurred in the stage of volatile combustion, but the maximum weight loss rate of WH (16.57% min$^{-1}$) was greater than that of SS (4.01% min$^{-1}$), which illustrated that the WH in SS can make up for the inadequacy of the SS combustion and made the SS evaporation and combustion phase release more vigorously. After adding 40% WH, the combustion temperature, which corresponds to the mass loss of SS of 75%, 65% and 55%, was lowered by approximately 43.4°C, 112.7°C and 82.9°C, respectively, and the reaction time was advanced. This finding could arise because the atomic ratio of O/C in the WH was high. The oxygen that contained functional groups such as hydroxyl, carboxyl, and carbonyl had a higher content and were more activated. Adding WH can cause the SS to contact the oxygen around it and decompose into relatively easy burning material, enhancing the activity of the combustion reaction and accelerating the combustion of volatiles (Xie and Ma, 2013).

To evaluate the combustion characteristics of SS, WH and SW in a CO$_2$/O$_2$ atmosphere, the comprehensive combustion index (CCI) was calculated. The larger the index CCI was, the more vigorously the samples burned and the faster the char burned out. Table 2 showed the results of TGA for the samples. It was found that in CO$_2$/O$_2$ atmosphere, the combustion performance of SS added with 10–40 wt.% WH was improved obviously represented as CCI gained by 1–1.97 times.

3.2. The interaction between sewage sludge and water hyacinth

In order to illustrate the co-combustion mechanism of SS and WH, the interaction of these two fuels was studied. The interaction between fuels is a concern in many co-combustion applications. To investigate whether there is an interaction between SS and WH, the theoretical TG–DTG curve of the mixture is calculated by the average weight of the individuals (Deng et al., 2016).

$$Y_{mixture} = X_{SS}Y_{SS} + X_{WH}Y_{WH} \tag{13}$$

where $X_{SS}$ and $X_{WH}$ are the percentage of sewage sludge and water hyacinth in the mixture, respectively, and $Y_{SS}$ and $Y_{WH}$ are the mass loss or weight loss rate of sewage sludge and water hyacinth respectively.

The experimental thermogravimetry–derivative thermogravimetry (TG–DTG), calculated TG–DTG, and deviation curves of the SW sample are presented in Fig. 2 with the S/W = 8/2 mixture as an example. The greater degree of separation of the experimental and calculated TG–DTG curves was, the stronger the interaction between the burnt mixtures was. As shown in Fig. 2a, the experimental TG curve lagged behind the calculated TG curve when the temperature was 260°C–380°C and 480°C–580°C but exceeded it when the temperature was 380°C–480°C. This result indicates that some degree of interaction occurred between SS and WH during the co-combustion process. The calculated DTG curve almost coincided with the experimental DTG curve at the temperature range of 170°C–260°C. However, in the temperature ranges of 260°C–305°C and 455°C–500°C, the experimental DTG curve lagged behind the calculated DTG curve. The maximum weight loss rates of the experimental DTG curves were 10.67% min$^{-1}$ lower than those of the calculated DTG curves. This result suggests that some degree of interaction occurred between the components of SS and WH at low temperatures. This interaction slowed down the combustion process of SW. At 305°C–455°C and 500°C–650°C, the experimental DTG curves were higher than the calculated DTG curves. This result confirms that an interaction occurred between the components of SS and WH at high temperatures, and this interaction accelerated the combustion process. The experimental DTG curve shifted at a high temperature compared with the calculated DTG curve, and the shapes of the curve indicated a significant interaction among the components of SW during combustion. As shown in Fig. 2a, the peak value and shape revealed large differences. These differences are attributed to the chemical interactions between the components of SS and WH during decomposition and combustion (Deng et al., 2016). SS had a high ash content of 43.38% as shown in Table 1, and the ash inhibited its combustion. Several studies have found that when the mineral matter in sludge is removed, the combustion rate increases significantly (Vamvuka et al., 2009). The interaction at a low temperature range of 260°C–380°C might be interpreted as resulting from the release of volatile matter from WH reacting with SS residues. For this reason, the experimental DTG curve lagged behind the calculated DTG curve. In the high temperature range of 305°C–455°C and 500°C–650°C, the interaction appeared to accelerate the combustion process of SW. After WH was added to SS, much heat was released to promote the combustion reaction. This scenario improved the decomposition depth of the sludge residues (Liao and Ma, 2010).

Based on the calculated and the experimental TG value, deviation of the SW from the calculated TG values was calculated using following equation (Haykiri-Acma and Yaman, 2010):

$$\text{Deviation (\%)} = \frac{T_{Gexp} - T_{Gcal}}{T_{Gcal}} \times 100 \tag{14}$$

As shown in Fig. 2b, the highest deviation in TG values were up to 5.5%. This value was greater than the statistical significance of 5% (Haykiri-Acma and Yaman, 2010). Thus, it can be concluded that the synergetic effect on mass loss of the SW was obviously during co-combustion.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_r$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$R_p$ (% min$^{-1}$)</th>
<th>$R_m$ (% min$^{-1}$)</th>
<th>$M_c$ (%)</th>
<th>$T_p$ (°C)</th>
<th>$CCI$ (10$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>243.1</td>
<td>298.5</td>
<td>0.41</td>
<td>1.13</td>
<td>46.36</td>
<td>661.14</td>
<td>3.080</td>
</tr>
<tr>
<td>S/W = 9/1</td>
<td>240.3</td>
<td>295.1</td>
<td>0.72</td>
<td>1.19</td>
<td>43.74</td>
<td>656.08</td>
<td>3.760</td>
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<tr>
<td>S/W = 8/2</td>
<td>242.4</td>
<td>292.8</td>
<td>0.63</td>
<td>1.27</td>
<td>39.50</td>
<td>644.59</td>
<td>5.169</td>
</tr>
<tr>
<td>S/W = 7/3</td>
<td>242.0</td>
<td>292.3</td>
<td>0.65</td>
<td>1.33</td>
<td>37.63</td>
<td>670.86</td>
<td>5.742</td>
</tr>
<tr>
<td>S/W = 6/4</td>
<td>230.8</td>
<td>291.3</td>
<td>0.74</td>
<td>1.40</td>
<td>34.65</td>
<td>789.38</td>
<td>6.064</td>
</tr>
<tr>
<td>WH</td>
<td>258.5</td>
<td>282.9</td>
<td>1.65</td>
<td>2.04</td>
<td>65.55</td>
<td>953.90</td>
<td>14.363</td>
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<tr>
<td>SS</td>
<td>234.1</td>
<td>298.5</td>
<td>0.41</td>
<td>1.13</td>
<td>46.36</td>
<td>661.14</td>
<td>3.080</td>
</tr>
<tr>
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<td>1.33</td>
<td>37.63</td>
<td>670.86</td>
<td>5.742</td>
</tr>
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<td>291.3</td>
<td>0.74</td>
<td>1.40</td>
<td>34.65</td>
<td>789.38</td>
<td>6.064</td>
</tr>
</tbody>
</table>

$^a$ $T_r$ is onset temperature for volatile release.  
$^b$ $T_p$ is the temperature associated to $R_p$. 
$^c$ $R_p$ is maximum weight loss rate. 
$^d$ $R_m$ is the average mass loss rate. 
$^e$ $M_c$ is residual mass at 1000°C. 
$^f$ $T_p$ is the temperature of 98% conversion. 
$^g$ CCI is the comprehensive combustion index, unit is % 2 K $^{-1}$ min$^{-2}$. 

\( CCI = \frac{\left(\frac{T_p}{T_r} - 1\right) \left(\frac{T_r}{T_p} - 1\right)}{\left(\frac{T_p}{T_r} - 1\right) \left(\frac{T_r}{T_p} - 1\right) + 1} \)
3.3. Oxygen-enriched combustion of blend fuels

3.3.1. Effects of oxygen concentration on the co-combustion of blend fuels

In this work, the effect of the oxygen concentration on the combustion characteristics of SW (S/W = 8/2 sample) was evaluated at a heating rate of 20 °C/min in different CO₂/O₂ atmospheres (CO₂/O₂ = 8/2, CO₂/O₂ = 7/3, CO₂/O₂ = 5/5, CO₂/O₂ = 3/7 atmosphere). Fig. 3 shows that three stages could be distinguished for SW during the oxy-enrich combustion process. Step I (<170 °C) was moisture exhalation, and the weight loss rate is approximately 7.13%; step II (170–650 °C) was corresponded to the release and combustion of organic volatile matter and fixed carbon, including the decomposition of hemicelluloses, cellulose and lignin, during which the mass of SW was rapidly lost (approximately 86.23%) (Luo et al., 2011); step III (>650 °C) was the residue decomposition.

![Fig. 3](image-url)
In this step, the carbonaceous residuals continue burning at a very low rate, and a slight mass loss is observed.

As shown in Table 3, in the CO₂/O₂ atmospheres, with increasing oxygen concentration, ignition became easier, a lower temperature \( T_{p1} \) was needed to reach that maximum peak of the DTG curves, and the curves gradually shifted to a lower temperature range. For example, with the increase in the oxygen concentration from 20% to 70% in the CO₂/O₂ atmosphere, \( T_{p1} \) decreased from 243.1 to 240.3 °C, \( T_{p3} \) decreased from 293.0 to 289.1 °C, and the maximum weight loss rate \( (R_{p1}) \) increased from 5.70 to 7.26% \( /\text{min} \). Similar findings were also reported in previous investigations on the co-combustion between microalgae and textile dyeing sludge (Peng et al., 2015). The increase in the maximum mass loss rate was perhaps due to the force of the fusion layer being reduced in the presence of oxygen and the quick release of volatiles (Liu et al., 2009). As the oxygen concentration increased, the peak that corresponds to biochar combustion \( (R_{p2}) \) also became more apparent, and the corresponding temperature \( T_{p2} \) decreased, while the third peak \( (R_{p3}) \) acted in the opposite fashion. As shown in Table 3, \( M_r \) increased in the following order: CO₂/O₂ = 7/3 < CO₂/O₂ = 8/2 < CO₂/O₂ = 3/7 < CO₂/O₂ = 5/5. \( M_r \) was the best (39.50%) in the CO₂/O₂ = 7/3 atmosphere, while it was the worst (42.10%) in the CO₂/O₂ = 5/5 atmosphere. In the oxy-fuel combustion, the \( M_r \) of the SW was not linearly related to the amount of oxygen concentration.

![Fig. 3. TG(a)-DTG(b) curves of S/W = 8/2 in different oxygen concentration atmospheres at 20 °C min⁻¹.](image-url)
Table 3
Characteristic parameters obtained from TG-DTG curves of samples in CO$_2$/O$_2$ atmospheres.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>$T_1$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_p$</th>
<th>$T_p$</th>
<th>$T_p$</th>
<th>$R_\alpha$</th>
<th>$R_\beta$</th>
<th>$R_\gamma$</th>
<th>$M_r$ (%)</th>
<th>$T_b$ (°C)</th>
<th>$CCI$ (10$^{-8}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/O$_2$ = 8/2</td>
<td>243.1</td>
<td>293.0</td>
<td>498.1</td>
<td>555.1</td>
<td>5.70</td>
<td>2.59</td>
<td>2.68</td>
<td>1.268</td>
<td>39.71</td>
<td>637.86</td>
<td>4.913</td>
</tr>
<tr>
<td>CO$_2$/O$_2$ = 7/3</td>
<td>242.4</td>
<td>292.8</td>
<td>497.2</td>
<td>560.4</td>
<td>6.03</td>
<td>3.12</td>
<td>2.23</td>
<td>1.274</td>
<td>39.50</td>
<td>644.59</td>
<td>5.169</td>
</tr>
<tr>
<td>CO$_2$/O$_2$ = 5/5</td>
<td>241.2</td>
<td>289.3</td>
<td>479.5</td>
<td>549.3</td>
<td>6.97</td>
<td>2.94</td>
<td>2.09</td>
<td>1.230</td>
<td>42.10</td>
<td>620.93</td>
<td>6.039</td>
</tr>
<tr>
<td>CO$_2$/O$_2$ = 3/7</td>
<td>240.3</td>
<td>289.1</td>
<td>477.4</td>
<td>545.9</td>
<td>7.26</td>
<td>2.92</td>
<td>2.08</td>
<td>1.272</td>
<td>40.21</td>
<td>636.78</td>
<td>6.327</td>
</tr>
</tbody>
</table>

Fig. 4. TG–DTG (a) and T–α (b) curves of S/W = 8/2 at different heating rates in oxygen concentration atmosphere.
3.3.2. Effect of heating rate on the co-combustion characteristics of blend fuels

To investigate the effect of the heating rate on the co-combustion characteristics of the SW, the combustion process of the SW sample in the CO$_2$/O$_2$ = 7/3 atmosphere was randomly selected for analysis in this section. Fig. 4(a) and (b) showed the TG–DTG and T–$\alpha$ curves of SW at the heating rates of 10, 20, and 40 °C min$^{-1}$ in the CO$_2$/O$_2$ = 7/3 atmosphere. It can be seen that between 200 and 650 °C, the TG curves shifted to a higher temperature when $\beta$ increased (Fig. 4(a)), which was due to heat transfer limitations. As $\beta$ increased, the DTG curves also shifted toward the higher temperatures, and the values heightened obviously. This relationship occurred because a lower heating rate would induce a higher heat transfer efficiency during heating. A greater temperature gradient across the poor heat conductor of the SW particle would be generated by raising the heating rate, which ultimately increases the thermal oxidative degradation rate (Chen et al., 2013). Similar findings have also been reported from research on the pyrolysis and oxy-fuel combustion characteristics and the kinetics of petrochemical wastewater sludge (Chen et al., 2015).

For the purpose of designing new combustion facilities or retrofitting existing plants that employ SW as fuel feedstock under oxy-fuel conditions, data for SW, including the effect of the heating rate on the co-combustion characteristic parameters of SW at the heating rate of 10, 20, and 40 °C min$^{-1}$, are required. As shown in Table 4, $T_a$, $T_p$ ($T_{p1}$, $T_{p2}$, and $T_{p3}$), and $T_b$ shifted to higher temperatures when $\beta$ increased. The $R_p$ of all of the steps ($R_{p1}$, $R_{p2}$, and $R_{p3}$) and $R_b$ markedly increased as $\beta$ increased from 10 to 40 °C min$^{-1}$. As shown in Fig. 4(b), when the temperature increased, the mass conversion ($\alpha$) gradually rose. As $\beta$ increased, the mass conversion ($\alpha$) curves moved toward a higher temperature region. Thus, the residual mass $M_r$ and $T_a$ was better at a lower $\beta$. In addition, the combustion performance of SW was evaluated by the combustion index of CCI. When $\beta$ increased from 10 to 40 °C min$^{-1}$, the CCI was increased from 1.325 to 20.197 × 10$^{-8}$ kg$^{-1}$ K$^{-2}$ ·min$^{-2}$. This relationship illustrates that although increasing the heating rate did not favor burnout, it was beneficial to the separation and combustion of the volatiles. Although the effects that were caused by increasing $\beta$ were common for various solid samples in the TGA experiments, data for SW combustion under oxy-fuel conditions have not yet been reported.

### 3.4. Evaluation of combustion parameters

$E_a$ was an important kinetic parameter for revealing the activation energy that is required to keep the chemical reaction going (Amanda and Leandro, 2016). According to Eq. (7), the plots for the determination of $E_a$ calculated by OFW at the second stage with $\beta = 10, 20$ and 40 °C min$^{-1}$ under different oxygen concentration atmospheres are depicted in Fig. 5(a) and (b), and the thermodynamic parameters of combustion of SW in the CO$_2$/O$_2$ atmospheres were gathered in Fig. 6(a)–(d). $E_a$ has high linear correlation coefficients ($R^2$) in the range of 0.9242–1.0000 at 0.1 < $\alpha$ < 0.99, which illustrate the calculated value of $E_a$ is reliable. The differentiation of the date obtained at different mass conversions in different atmospheres could be appropriately reflected at the date obtained for the maximum weight loss rate in Table 5.

As shown in Fig. 6a, the variation in the values of $E_a$ was not similar at different constant extents of conversion because the reaction of SW was not simple one-step mechanisms and instead followed a complex multi-step reaction (Xu and Chen, 2013). It was clear that the activation energy varied with increasing conversion and the $E_a$ value of the SW did not increase all the way with the mass conversion ($\alpha$). However, the $E_a$ value calculated in different atmospheres had almost the same tendency, which was similar to an “N” shape. Taking the CO$_2$/O$_2$ = 7/3 atmosphere as an example, the $E_a$ varied with increasing conversions. It increased steeply from approximately 19.24 to 155.16 kJ mol$^{-1}$ at the mass conversion ($\alpha$) at 0.1 < $\alpha$ < 0.35, followed by a decline at 0.35 < $\alpha$ < 0.65, and thereafter, it showed a quick increase at $\alpha$ > 0.65 and drying and thermal decomposition and volatile degradation at approximately $\alpha$ = 0.1–0.6, with fixed carbon combustion at approximately $\alpha$ > 0.65 (Xu and Chen, 2013). The initial activation energy value was considered to be low due to cleavage of some of the weak bonds and elimination of the volatile components from the biomass because at the beginning of the process, all of the strong bonds are not cleaved (Gašparović, 2012). The SW presented two small values of the activation energy in the range $\alpha$ = 0.1 and 0.65 between 24.04 kJ mol$^{-1}$ and 61.47 kJ mol$^{-1}$.

Additionally, the $E_a$ values at maximum weight loss rate shown in Table 5 were 163.54 kJ mol$^{-1}$ in CO$_2$/O$_2 = 8/2$, 116.26 kJ mol$^{-1}$ in CO$_2$/O$_2 = 7/3$, 165.48 kJ mol$^{-1}$ in CO$_2$/O$_2 = 5/5$ and 230.19 kJ mol$^{-1}$ in CO$_2$/O$_2 = 3/7$. As shown in Fig. 6a, with an increasing oxygen concentration from 20 to 30%, the $E_a$ of SW in CO$_2$/O$_2$ atmosphere curves move toward a lower region. However, with an increasing oxygen concentration from 30 to 70%, the $E_a$ of SW curves move toward the opposite fashion. Similar findings were also reported in previous investigations (Chen et al., 2013). The $E_a$ of SW was affected by a decreased concentration of activated molecules, diffusion limitations and organic impurities during the process of sample combustion. As the oxygen concentration increases, the heat release from semicoke oxidation increases, and thus, the surface temperature of the semicoke increases. Additionally, the semicoke structure expands the grain size and increases the ash content, which corresponds to an increase in the final temperature (Chen et al., 2011). Therefore, the $E_a$ increased with an increased oxygen concentration from 30 to 70%, which revealed that it is not the more oxygen concentration the easier to response in the combustion. The lowest activation energy of SW was obtained in CO$_2$/O$_2$ = 7/3 atmosphere.

### Table 4

Co-combustion characteristic parameters of SW at the heating rate of 10, 20, and 40 °C min$^{-1}$.

<table>
<thead>
<tr>
<th>$\beta$ (°C/min)</th>
<th>$T_a$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_b$ (°C)</th>
<th>$R_{p1}$ (%/min$^{-1}$)</th>
<th>$R_{p2}$ (%/min$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$M_r$ (%)</th>
<th>$T_b$ (°C)</th>
<th>CCI ($10^{-8}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>234.0</td>
<td>286.1</td>
<td>477.0</td>
<td>551.2</td>
<td>2.56</td>
<td>1.55</td>
<td>0.68</td>
<td>39.42</td>
<td>627.24</td>
</tr>
<tr>
<td>20</td>
<td>242.4</td>
<td>292.8</td>
<td>497.2</td>
<td>566.4</td>
<td>6.03</td>
<td>3.12</td>
<td>2.23</td>
<td>39.50</td>
<td>644.59</td>
</tr>
<tr>
<td>40</td>
<td>252.2</td>
<td>304.3</td>
<td>539.0</td>
<td>/</td>
<td>12.03</td>
<td>6.25</td>
<td>2.62</td>
<td>40.88</td>
<td>652.21</td>
</tr>
</tbody>
</table>
Table 5, lower heat energies were required for the CO$_2$/O$_2$ = 7/3 atmosphere than for the CO$_2$/O$_2$ = 3/7 atmosphere and CO$_2$/O$_2$ = 5/5 atmosphere to oxidate the reagents. The change in $\Delta H$ shown in Fig. 6b also showed the energy differences between the activated complex and the reagents. If this difference was small, then the formation of activated complex was favored because the potential energy barrier is low (Vlaev et al., 2007). The $\Delta H$ variation of SW was between 16.19 and 123.40 kJ/C$_1$mol/C$_0$ in CO$_2$/O$_2$ = 7/3, 35.75 and 161.04 kJ/C$_1$mol/C$_0$ in CO$_2$/O$_2$ = 5/5 and 20.95 and 225.79 kJ/C$_1$mol/C$_0$ in CO$_2$/O$_2$ = 3/7, respectively. Thus, the formation of activated complex was more favored in CO$_2$/O$_2$ = 7/3.

The entropy ($\Delta S$) is associated with the formation of complex activated species, and it is also a measure of disorder. The varied $\Delta S$ showed that the biomass has a high degree of arrangement and had a physical and/or chemical process. Changes in the entropies shown in Fig. 6c had positive and negative values, which was consistent with the variation in the values of $E_a$. A positive $\Delta S$ demonstrates that the reaction will increase the disorder of the system and, thus, is favorable. The $\Delta S$ values indicated that the disorder of the system decreased in the CO$_2$/O$_2$ = 7/3 atmosphere, while those of the CO$_2$/O$_2$ = 5/5 atmosphere and CO$_2$/O$_2$ = 3/7 atmosphere increased. In terms of the disorder, the reaction tendency order was the following: CO$_2$/O$_2$ = 3/7 atmosphere, CO$_2$/O$_2$ = 5/5 atmosphere, and CO$_2$/O$_2$ = 7/3 atmosphere. In addition, a low $\Delta S$ means that the material has just passed through some type of physical or chemical aging process, bringing it to a state that is near to its own thermodynamic equilibrium. In this situation, the material shows little reactivity, which increases the time taken to form the activated complex. On the other hand, when high $\Delta S$ values are observed, the material is far from its own thermodynamic equilibrium. In this case, the reactivity is high, and the system can react faster to produce the activated complex, which results in the short reaction times and fast mass loss rate that were observed (Turmanova et al., 2008). Thus, it was favored when $\alpha = 0.3–0.5$ during the co-combustion process.

The change in the Gibbs free energy ($\Delta G$) revealed the total energy increase of the system at the approach of the reagents and the formation of the activated complex. It is a comprehensive evaluation of the heat flow and disorder change, and a higher value of $\Delta G$ indicates a lower favorability of reaction. The co-combustion reaction of SW in the CO$_2$/O$_2$ = 3/7 atmosphere had a $\Delta G$ of approximately 157.18 kJ/C$_1$mol, while the CO$_2$/O$_2$ = 8/2, CO$_2$/O$_2$ = 5/5 and CO$_2$/O$_2$ = 7/3 atmosphere had values that were higher than that. The combustion reaction limit of SW in the CO$_2$/O$_2$ = 3/7 atmosphere was the highest. Thus, the favorability order of co-combustion was the following: CO$_2$/O$_2$ = 3/7, CO$_2$/O$_2$ = 5/5, CO$_2$/O$_2$ = 8/2 and CO$_2$/O$_2$ = 7/3 atmosphere. In terms of the $\Delta G$, co-combustion in the CO$_2$/O$_2$ = 3/7 atmosphere had the lowest energy barrier and absorbed the least amount of heat during the process, and yet, it decreased the disorder of the system, and hence, it had the lowest favorability. In contrast, co-combustion in the CO$_2$/O$_2$ = 3/7 atmosphere had the highest energy barrier and required the highest amount of heat, but it had the highest favorability of reaction because it greatly increased the disorder of the system.
4. Conclusions

The combustion performance of SS added with 10–40 wt.% WH was improved 1–1.97 times, as revealed by CCI. As the oxygen concentration increased from 20% to 70%, the ignition temperature of SW decreased from 243.1°C to 240.3°C, and the maximum weight loss rate and CCI increased from 5.70%/min to 7.26%/min and from 4.913% to 6.327%, respectively, which corresponded to the calculated variation in DS and DG.

The lowest activation energy (Ea) of SW was obtained in CO2/O2 = 7/3 atmosphere.

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References


