The investigation on combustion behavior of sewage sludge and duckweed blends

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Abstract: Combustion behavior of sewage sludge and duckweed blends with three different blending ratios were investigated by thermogravimetry analysis. The addition of duckweed improved the combustion characteristic of the blends at the beginning of decomposition, according to mass loss curves and kinetic analysis. The addition of duckweed could decrease the activation energy significantly, but it could be a slight decrease when a little sawdust ratio was added in. When the heating rate increased, both TG and DTG curves shifted to the high temperature region, but the combustion characteristic index increased, so there could be an optimal heating rate for different requirements and standards.

1. Introduction
The increasingly environmental problems in many aspects are endangering the survival and development of mankind. The increasing of the production of sewage due to rapid urbanization lead to the output of sewage sludge to be much higher than its processing capacity[1]. Sewage sludge that has not been treated properly has brought huge harm.

In order to reduce sewage sludge, incineration is a simple and efficient way[2], but it also causes air pollution. Therefore, the exhaust gas treatment of sludge incineration is a key step to reduce pollution. At the same time, it is necessary to fully understand the combustion properties of sludge and the kinetics of its combustion process. Co-combustion of sewage sludge and biomass could eliminate the disadvantage of the propriety of sewage sludge as fuel[3–6]. Duckweed is a common aquatic plant that grows in polluted river water and has huge yields[7–9].

This work focus on the co-combustion behavior of sewage sludge and duckweed. By analyzing the thermogravimetric parameters and kinetic parameters, the combustion behavior was assessed.

2. Experiment

2.1. samples preparation
The pulverized sewage sludge(SS) and duckweed(DW) which were sieved into the size of 75~106mm were obtained from sewage treatment factory and collected from Nanfei river, respectively, in Hefei City, Anhui Province, China. The proximate and the ultimate analyses of these samples were given in Table 1.
Table 1 The ultimate analyses, proximate analyses of SS and WS on air dry basis

| Samples | Ultimate analysis (wt.%) | Proximate analysis (wt.%) | $Q_{\text{net}, \text{d}}$ (MJ/kg) |
|---------|--------------------------|---------------------------|-------------------------------|
|         | C    | H    | O$^{a}$ | N | S | Volatile matter | Fixed carbon | Ash | Moisture |         |
| SS      | 26.33 | 4.56 | 15.59  | 4.84 | 0.87 | 48.12 | 4.07 | 44.31 | 3.50 | 9.70 |
| DW      | 46.49 | 6.35 | 46.64  | 0.10 | 0.42 | 70.62 | 18.6 | 0.3   | 10.48 | 18.63 |

$^{a}$ O, calculated by difference  
$^{b}$ $Q_{\text{net}, \text{d}}$, lower heating value on dry basis

2.2. Thermogravimetry analysis.
The mass loss, mass loss rate, and five characteristic temperatures of sewage sludge and sewage sludge blending with 10% and 20% duckweed (S9D1 and S8D2), respectively, were directly obtained from the TG and DTG curves by using thermogravimetry analysis (the Instrument type of thermogravimetric analyzer was SDT Q600). The experiment temperature was increased from room temperature to 800°C, with three heating rates of 10 °C/min, 20 °C/min and 30 °C/min, respectively, the air flow rate was set to be 100 mL/min. The comprehensive combustion performance index ($D$) was described in Eqs.(1), which could be used to compare the combustion characteristics of different samples under different conditions, for the higher $D$ value represents better combustion performance[10,11]. where $(dw/dt)_{\text{max}}$ is the maximum rate of oxidation reaction at the peak ($^\circ$C), and $(dw/dt)_{\text{mean}}$ is the average rate of SS obtained through integration of the DTG area ($^\circ$C). $T_i$ and $T_f$ are the characteristic temperature ($^\circ$C).

$$D = \frac{(dw/dt)_{\text{max}}(dw/dt)_{\text{mean}}}{T_i T_f}$$  

2.3. The combustion kinetic theory
The reaction rate of SS, WS and their blends can be generally expressed as:

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

From the Arrhenius equation:

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

$k(T)$ was the weight loss rate, only depended on the temperature. Where $E$, $A$ and $R$ was activation energy, pre-exponential factor and universal gas constant, respectively.

Where $\alpha$ in Equation 1 was the conversion degree expressed as[12]:

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

$$T = \beta t + T_0$$

Where $\alpha$ in Equation 1 was the conversion degree expressed as[12]:

$$f(\alpha) = (1 - \alpha)^n$$

$n$ referred to reaction order.

By combining the Eqs. (1), (2) and (5), the reaction rate can be expressed as:

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

By combining the Eqs. (4) and (6), the expression of reaction rate versus time Eqs. (7) can be converted into the expression of reaction rate versus temperature.

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E}{RT}\right) f(\alpha)$$

Due to the complexity of the reaction mechanism of pure SS and SS-WS blends, the model-fitting method: Coats–Redfern and Freeman–Carroll method method may not accurately depict the reaction mechanism. The appropriate reaction order $n$ should be selected with assumption firstly, which was
Intrinsic defect of model-fitting method. Therefore, in order to investigate the reaction kinetics of SS and SS-WS blends, the approaches of model-free: Flynn-Wall-Ozawa method (FWO)\cite{13–15} and Vyazovkin method (V)\cite{16,17} was applied to calculate the activation energy at any conversion degree. This iso-conversional integral method was not limited by the assumption reaction model and eliminated the compensation effect.

Integrating Eqs. (8) gave Eqs. (9):

$$\int_{\alpha}^{\beta} \frac{da}{f(a)} = g(\alpha) = \frac{A}{\beta} \int_{a_0}^{a} e^{-E/RT} dT$$  \hspace{1cm} (9)

Where $g(\alpha)$ was integral form of $1/f(\alpha)$. Flynn, Wall and Ozawa using the Doyle’s approximation of $p(x)$\cite{18} developed the FWO method, expressed as:

$$\ln(\beta) = \ln\left[\frac{AE}{Rg(\alpha)}\right] - 5.331 - 1.052 \frac{E}{RT}$$  \hspace{1cm} (10)

$E$ was obtained by the slope of the fitted straight line with plotting $\ln(\beta)$ vs. $1/T$ under at least three heating rate. The values of $E$ corresponding to each designated conversion degree can be determined. Another iso-conversional integral method was developed by Vyazovkin:

$$\ln\left[\frac{\beta}{T^2}\right] = \ln\left[\frac{AE}{Rg(\alpha)}\right] - \frac{E}{RT}$$  \hspace{1cm} (11)

$E$ was obtained by the slope of the fitted straight line with plotting $\ln(\beta/T^2)$ vs. $1/T$. The values of $E$ corresponding to each designated conversion degree can be determined.

3. Results and Discussion

3.1. Mass loss

The mass loss results of sewage sludge (SS) and the blends (S9D1 and S8D2) were shown in Fig. 1. Temperatures decreased from 125.92°C, 127.85°C and 14.23°C respectively after 10% duckweed was blended in, while only slight changes were found when the blend ratio was increased to 20%. As all the combustion processes were divided into four stages: moisture removal, gas desorption, oxygen-absorption mass gain, decomposition and combustion mass loss, and residue. The total mass loss of SS, S9D1 and S8D2 was 59.73%, 51.68% and 49.31%, it is obvious that the mass loss of SS in stage III was accounted for more than 75% of total mass loss, and that of S8D2 was about 88%, for the higher volatile content, which meant that the main combustion occurred in this stage. In stage III, only one peak was found in DTG curve of SS, while there were two peaks of S9D1 and S8D2 the emerging peak was caused by the decomposition and combustion of duckweed volatile and it appeared earlier than the second peak which represented the decomposition and combustion of sewage sludge. Actually, the main composition of duckweed was volatile, which could easily devolatilization once the temperature increased, while the volatile of SS was rather little so that the peak of volatile was negligible, thus the combination of SS and duckweed gives prominence to the peaks of volatile and the remaining blends. What’s more, the temperature at the second peak of DTG curves of S9D1 and S8D2 were smaller than that of SS, which indicated that the addition of duckweed improved the combustion of SS when the temperature was lower than 600°C, however, when the temperature was higher than 600°C, the combustion characteristics of three samples were similar. As a result, when the heating rate increased from 10 °C/min to 30 °C/min, the ignition temperatures of SS, S9D1 and S8D2 increased from 428.07°C to 452.37°C, 302.15°C to 318.31°C, and 300.48°C to 322.31°C, respectively, while the increment of the burning out temperatures Tf which were 96.96°C, 31.03°C and 50.88°C, respectively, were much larger than that of Ti, this was also ascribed to the decrease of heat transfer efficiency, for the accumulation of the negative affect increased with time. Even though, the effect of heating rate on the total mass loss of three samples was little according to table 2, this result was different from the results of previous works, and it might be caused by the relatively lack of combustible portion compared with other fuels, anyway, a decrease of total mass loss was found when the heating rate was increased.
3.2. Kinetics analysis

The iso-conversational method (Flynn–Wall–Ozawa method) was used to calculate the activation energy, and the activation energy was derived from the slope of lines by plotting lnβ versus 1/T, what’s more, this method was quite reliable and applicable for the complex co-combustion. The activation energy and the fitting corresponding correlation coefficient R² of three samples at different conversion ratios were listed in Table 4. When the conversion ratio increased, the E of SS declined because of the consume of carbon matter and the progressively formation of porous structure during the combustion, which made the combustion continued less energy, and the result was coincided with previous works[19]. While it was different for the blends, the E of S9D1 increased with the increase of conversion ratio, which could be attributed to the difference component of sewage sludge and duckweed, once the coal gangue was blended with duckweed, the volatile and carbon contents of the sample were obviously increased. The results indicated that the addition of duckweed could enormously improve the combustion characteristic of the blends at the early stage, the phenomenon of the increasing activation energy value of the S9D1 with increasing conversion ratio might be explained that the duckweed made major advantage to the combustion at first, the burning of volatile and carbon content were so effectively that the rest part of the combustible part burned out in advance, that meant the remainder samples needed more energy to maintain the combustion. The E values of S8D2 also increased with increasing conversion ratio, while compared the activation energy of S9D1 and S8D2, it could be found that the E values of S8D2 was higher than that of S9D1 at 0.2-0.4 conversion ratio, and it changed to be lower when the conversion ratio was 0.5-0.9, this might be caused by the incomplete combustion of the samples when more duckweed was added in the sewage sludge at the oxidative pyrolysis process. In general, the addition of duckweed in sewage sludge could decrease the E values at low conversion ratio, and much more duckweed could increase the upper limit of the critical conversion ratio. For SS, only one fitting line was found in the right region, and six ones was found in the middle region, while the numbers of fitting line in the right region for S9D1 and S8D2 were three and five, this difference revealed that the main combustion stage shifted from high conversion ratio time period to low conversion ratio time period. As a result, the average E of the SS, S9D1 and S8D2 were 146.30kJ·mol⁻¹, 109.34kJ·mol⁻¹ and 97.19kJ·mol⁻¹, respectively, which meant that the addition of duckweed could decrease the activation energy significant.
Table 2 Combustion kinetics parameters of SS blends at different conversion degrees calculated by FWO.

| α  | SS   | S9D1 | S8D2 |
|----|------|------|------|
|    | E(kJ/mol) | R²   | E(kJ/mol) | R²   | E(kJ/mol) | R²   |
| 0.2 | 176.63   | 0.9956 | 83.45   | 0.9732 | 97.88   | 0.9946 |
| 0.3 | 186.24   | 0.9921 | 103.52  | 0.9741 | 96.45   | 1.0000 |
| 0.4 | 177.65   | 0.9985 | 120.96  | 0.9726 | 101.25  | 0.9952 |
| 0.5 | 152.31   | 0.9976 | 140.44  | 0.9884 | 112.46  | 0.9941 |
| 0.6 | 120.53   | 0.9932 | 103.28  | 0.9999 | 83.58   | 0.9945 |
| 0.7 | 110.96   | 0.9912 | 99.03   | 0.9994 | 80.61   | 0.9956 |
| 0.8 | 109.46   | 0.9995 | 103.56  | 0.9963 | 92.42   | 0.9945 |
| 0.9 | 136.58   | 0.9923 | 120.44  | 0.9955 | 112.84  | 0.9955 |
| Average | 146.30 | 109.34 | 97.19 |

4. Conclusion
The combustion characteristics of SS, DW and their blends at β=10, 20, 30°C/min were investigated by thermogravimetric analysis. The SS and DW combustion process was divided into three stages. Combustion kinetics analysis of SS and SS-DW blends was evaluated by using an isoconversional method: FWO method. The addition of duckweed could decrease the activation energy significantly.

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