Original Research Article

Experimental study on co-pyrolysis of sludge and biomass straw

Lun Ma 1,2*, Ji Xia 2, Yongjia Hu 3

1 State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, Hubei Province, China.
2 Wuhan Huazhong Sineng Technology Co., Ltd., Wuhan 430074, Hubei Province, China. E-mail: malun3g@126.com

ABSTRACT

In order to maximize the potential energy utilization of agricultural and forestry waste and sludge, the experimental research on co-pyrolysis was carried out for two kinds of sludge (urban industrial sludge, paper sludge) and a typical biomass straw. The results show that adding biomass can effectively improve sludge pyrolysis characteristics; biomass straw and sludge, there are complex interactive effects between components in the co-pyrolysis process, and the characteristic parameters show nonlinear changes. When industrial sludge is mixed with straw, with the increase of straw content, the initial temperature of pyrolysis gradually decreases, the termination temperature increases, the peak of pyrolysis reaction rate and the corresponding temperature gradually increase, and the pyrolysis index gradually increases; when paper sludge is mixed with straw, with the increase of straw content, the initial temperature of pyrolysis gradually decreases, the termination temperature increases, the peak of pyrolysis reaction rate gradually increases, while the peak corresponding temperature gradually decreases, and the pyrolysis index gradually decreases. Combined with characteristic parameters and reaction kinetics analysis, it is suggested that the straw mixing proportion should be controlled at about 25% during the co-pyrolysis of industrial sludge and straw. During the co-pyrolysis of paper sludge and straw, it is suggested to control the straw blending ratio at about 75%.

Keywords: Sludge; Biomass Straw; Pyrolysis; Reaction Dynamics Analysis

1. Introduction

With the improvement of China’s urbanization and sewage treatment level, the sludge produced in the process of sewage treatment has increased sharply[14]; Also contains heavy metals, toxic organic matter, pathogenic microorganisms and other harmful substances, its reduction, harmless treatment has aroused widespread concern[5]. Usually, the disposal methods of sludge mainly include landfill, agricultural utilization and thermochemical conversion[6]. Among them, pyrolysis is an effective thermal conversion way for sludge to obtain high value-added products[7-9]. Due to the influence of its own characteristics, sludge pyrolysis is prone to high ash content, low energy efficiency, unstable pyrolysis reactor, low added value of products and poor pyrolysis performance[10,11]. As a biomass rich in hemicellulose, cellulose and lignin, it has good pyrolysis characteristics[12,13]. Therefore, the mixed pyrolysis of sludge and biomass helps to improve the pyrolysis performance of the mixed samples[14-16]. In particular, the recycling of agricultural and forestry waste biomass and sludge can also effectively reduce carbon emissions and help carbon neutrality. Wang et al.[17] investigated ther-
mal degradation behavior and evolution of gaseous substances during sludge/rice husk co-pyrolysis using thermogravimetric analysis and mass spectrometry. The introduction of rice husk can improve the sludge pyrolysis activity and CO₂ yield and reduce the accumulation of H₂, CH₄ and C₂H₂. Lin et al. [18] found that the co-pyrolysis of oily sludge and rice husk could effectively improve the oil quality and promote the formation of H₂, CO and C₁-C₂ hydrocarbons. Huang et al. [19] studied the heavy metal content of sewage sludge and sawdust/straw co-pyrolysis for biochar production was studied. It was found that the addition of sawdust/straw could significantly reduce the heavy metal content of sludge-derived biochar. Wang et al. [20] studied and found that the synergistic effect between sludge and wheat straw would lead to an increase in gas-liquid yield but a decrease in carbon yield, and the interaction between the components was the strongest when the biomass mixing ratio was 60%. Wang et al. [21] studied the co-pyrolysis behavior and kinetic characteristics of sludge and rice husk were studied the co-pyrolysis characteristics were improved, and the two showed synergistic and inhibitory effects. The average activation energy was the lowest when 30% rice husk was mixed. This paper carried out the co-pyrolysis experiment using thermal weight of two kinds of sludge (urban industrial sludge, paper sludge) and a typical biomass straw, and the reaction kinetic analysis, in order to provide basic data for the subsequent biomass and sludge co-pyrolysis research.

2. Experimental samples and methods

2.1 Laboratory sample

Two kinds of sludge were selected: one kind of industrial sludge (MS), a kind of paper mill sludge (PS) and a typical biomass straw (ST). For industrial and elemental analysis, see Table 1. The three samples are dried, milled, and sieved into particle sizes <150 μm, and placed in a drying box at 105 °C for use before the experiment.

Table 1. Sample industry and elemental analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>Industrial analysis (dry base, wt%)</th>
<th>Elemental analysis (dry ash free base, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile component</td>
<td>Fixed carbon</td>
</tr>
<tr>
<td>MS</td>
<td>27.70</td>
<td>11.30</td>
</tr>
<tr>
<td>PS</td>
<td>81.97</td>
<td>12.23</td>
</tr>
<tr>
<td>ST</td>
<td>75.90</td>
<td>13.35</td>
</tr>
</tbody>
</table>

2.2 Laboratory equipment

The co-pyrolysis of sludge and biomass was studied by the NETZSCH thermogravimetric analyzer. For each experiment, 10 ± 0.1 mg samples were placed in a corundum dry pot, the total gas flow was controlled at 100 mL/min, the initial sampling temperature was set at 50 °C, and the termination temperature was set at 800 °C. In the continuous actual engineering operation, according to the final temperature running time from the room temperature when the material enters the pyrolysis reactor, the heating rate is generally from 10 to 40 °C/min. Therefore, the warming rate was selected for 20 °C/min in this experiment. To ensure the accuracy of the experimental results, reproducibility experiments were performed and the results were averaged.

2.3 Characteristic parameters and reaction kinetics calculation method

According to the TG curve and DTG curve, the temperature corresponding to the DTG curve reaching -1 wt%/min in the initial stage of the reaction is defined as the reaction starting temperature Tstart, and the temperature corresponding to when the DTG curve reaches -1 wt%/min in the reaction termination stage is defined as the reaction end temperature Tend [22-24].

The pyrolysis characteristic index C is determined by the maximum mass loss rate and duration of the reaction [25,26], the index indicates the difficulty of partial pyrolysis. The larger C indicates that the easier the sample is to achieve pyrolysis. The calculation equation is as follows:

$$C = \frac{|\text{DTG}_{\text{max}}| \cdot |\text{DTG}_{\text{total}}| \cdot \Delta W}{T_{\text{start}} \cdot T_{\text{peak}} \cdot \Delta T_{0.5}}$$

In equation (1), DTGmax represents the maxi-
mum reaction rate (%/min), DTG\text{mean} represents the average reaction rate (%/min), ΔW represents the total lost weight percentage of the reaction, $T_{\text{peak}}$ is the temperature (°C) corresponding to the maximum reaction rate, and Δ$T_{0.5}$ represents the temperature interval of DTG/DTG\text{max} = 0.5.

To measure whether there is an interactive influence in the mixed pyrolysis process of straw and sludge, the linear calculation value of characteristic parameters = straw characteristic parameter is defined. Straw mixing ratio + sludge characteristic parameters (1−straw mixing ratio).

In this paper, the Coats-Redfern method was used to calculate the kinetic parameters of the reaction process\textsuperscript{[27-29]}. Pyrolysis reaction rate can be described as:

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

In equation (2), $\alpha$ is the sample conversion rate. $\alpha = (m_0 - m_t)/(m_0 - m_\infty)$, $m_0$ is the initial mass of the sample, $m_t$ is the sample mass at time $t$, and $m_\infty$ is the sample mass at the end of the reaction. The reaction $f(\alpha)$ represents the mechanism function and $k(T)$ represents the Arrhenius chemical reaction rate constant.

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

(3)

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

(4)

In equations (3) and (4), $A$ is the reaction forward factor (s$^{-1}$), $E$ is the reaction activation energy (kJ·mol$^{-1}$), the ideal gas constant $R = 8.3145$ kJ·mol$^{-1}$·K$^{-1}$, and $n$ is the reaction series.

Let the heating rate $\beta = \frac{dT}{dt}$, the above equation can be reduced:

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

(5)

Further, it can be reduced:

$$n \neq 1, \quad \ln \left(\frac{1 - (1 - \alpha)^{1 - n}}{T^2 (1 - n)}\right) = \ln \left(\frac{AR}{\beta E} \left[1 - \frac{2RT}{E}\right]\right) - \frac{E}{RT}$$

(7)

During the actual reaction process, $E/RT \geq 1$, $1 - 2RT \approx 1$, it was further modified come down to:

$$n = 1, \quad \ln \left(-\frac{\ln (1 - \alpha)}{T^2}\right) = \ln \left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$

(8)

$$n \neq 1, \quad \ln \left(\frac{1 - (1 - \alpha)^{1 - n}}{T^2 (1 - n)}\right) = \ln \left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$

(9)

The reaction process can be assumed to be the first reaction, namely $n = 1$, the linear curve of $\ln| - \ln (1 - \alpha)/T^2|$ corresponding to $1/T$, through the linear slope and intercept can get the leading factor $A$ and activation energy $E$.

3. Results and discussion

3.1 Co-pyrolysis characteristics of sludge and straw

Figure 1 shows the thermogravimetric curves of sludge (MS, PS), straw (ST) pyrolysis alone and sludge and straw co-pyrolysis. Sludge (MS, PS), straw (ST) and a similar trend exists in the pyrolysis process of its mixed samples. There is a significant unimodal devolatilization process on the DTG curves, and all the mixed sample curves lie between the pure sample pyrolysis curves. After the industrial sludge MS was mixed with straw ST, with the increase of straw ST content, the DTG curve gradually shifted to the high temperature region in the initial stage of the pyrolysis reaction, and the DTG curve gradually shifted to the low temperature region in the later stage of the reaction; After the papermaking sludge PS was mixed with straw ST, with the increase of straw ST content, the DTG curve gradually shifted to the high temperature region in the initial stage of the pyrolysis reaction, and the DTG curve gradually shifted to the high temperature region in the later stage of the reaction.
Figure 1. TG curves of sludge, straw and co-pyrolysis.

Figure 2 shows the initial and end temperatures of sludge and straw for separate pyrolysis and co-pyrolysis reaction. It can be seen that the initial decomposition temperature of the mixture of pure sludge and mixed biomass straw is somewhat different, and the pyrolysis characteristics of different sludge and mixed biomass straw are also significantly different. The initial temperatures of pyrolysis of straw ST, industrial sludge MS and paper sludge PS alone were 213 °C, 243 °C and 252 °C respectively, and the pyrolysis termination temperatures were 484 °C, 475 °C, 410 °C, respectively. As far as the initial pyrolysis temperature is concerned, the initial pyrolysis temperature of the mixed samples decreased gradually after the industrial sludge MS and papermaking sludge PS were mixed with straw ST respectively. This indicates that blending biomass straw ST is beneficial to promote the pyrolysis of industrial sludge MS and paper sludge PS at lower temperature; as far as the termination pyrolysis temperature is concerned, the termination pyrolysis temperature of industrial sludge MS and papermaking sludge PS increased after blending with straw ST respectively, which was mainly due to the fact that the termination pyrolysis temperature of straw ST was higher than that of industrial sludge MS and PS, caused by paper sludge PS.

Figure 3 shows the peak and corresponding temperature of sludge pyrolysis and straw. The peak pyrolysis rate of straw ST, industrial sludge MS and paper sludge PS are 10.825%/min, 2.515%/min and 24.06%/min respectively, and the corresponding temperature is 332 °C, 312 °C and 362 °C, respectively. The peak difference in the reaction rate is mainly caused by the different volatile content of the three samples (PS > ST > MS). With the increase of straw ST content, the peak value of pyrolysis reaction rate and corresponding temperature increase gradually. With the increase of straw ST content, the peak value of pyrolysis reaction rate increases gradually, while the corresponding tem-
temperature decreases gradually.

**Figure 3.** Reaction rate and corresponding temperature of sludge, straw and co-pyrolysis.

**Figure 4** shows the pyrolysis characteristic index and half-peak temperature of single pyrolysis and co-pyrolysis of sludge and straw. The pyrolysis index C of straw ST, industrial sludge MS and papermaking sludge PS is $3.731 \times 10^{-5}/(\text{min}^{-2} \cdot \text{°C}^{-3})$, respectively, $0.058 \times 10^{-5}/(\text{min}^{-2} \cdot \text{°C}^{-3})$ and $36.32 \times 10^{-5}/(\text{min}^{-2} \cdot \text{°C}^{-3})$, which were mainly caused by the different volatile content of the three samples. The pyrolysis index C increased with the increase of straw ST content after MS was mixed with straw ST. The pyrolysis index C decreased with the increase of straw ST content after PS was mixed with straw ST.

**Figure 4.** Comprehensive pyrolysis index and half-peak temperature of sludge, straw and co-pyrolysis.

Meanwhile, it can also be seen from the above characteristic parameters that the characteristic parameters of the mixed sample deviate significantly from the linear calculated value, which indicates that there is a certain interaction between the component fuels in the mixed sample. Combined with the analysis of the above parameters, when the industrial sludge MS and straw ST are co-pyrolyzed, the mixing ratio of industrial sludge MS is controlled at about 25%, which not only has a lower reaction initial temperature and reaction termination temperature, but also has a higher thermal energy. When the papermaking sludge PS and straw ST are co-pyrolyzed, when the blending ratio of papermaking sludge PS is controlled at about 75%, it not only has a lower reaction initial temperature and reaction termination temperature, but also has a better pyrolysis index.

### 3.2 Kinetic analysis of sludge and straw co-pyrolysis reaction

Kinetics curves of single pyrolysis and co-pyrolysis of sludge and straw are shown in **Figure 5**. In order to evaluate the reaction power in the process of sludge and straw co-pyrolysis. The average activation energy $E$ and pre-exponential factor parameter $\ln A$ were calculated by stages. The calculation equation is as follows\(^{[27,30]}\):

$$E = \sum E_i \cdot F_i, \quad \ln A = \sum \ln A_i \cdot F_i,$$

where $E_i$ and $\ln A_i$ represent activation energy and pre-exponential factor param-
eters of each stage, $F_i$ represents the mass percentage for each stage. Table 2 shows kinetics parameters of single pyrolysis and co-pyrolysis of sludge and straw.

<table>
<thead>
<tr>
<th>Item</th>
<th>$T_{zone}/^\circ C$</th>
<th>$F_i/%$</th>
<th>$E_i/(kJ\cdot mol^{-1})$</th>
<th>$lnA_i/s^{-1}$</th>
<th>$lnA_i/s^{-1}$</th>
<th>$R^2$</th>
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</thead>
<tbody>
<tr>
<td>MS/ST</td>
<td>213–362</td>
<td>84.64</td>
<td>60.13</td>
<td>51.97</td>
<td>15.63</td>
<td>16.86</td>
</tr>
<tr>
<td></td>
<td>362–484</td>
<td>15.36</td>
<td>7.03</td>
<td>23.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25% MS + 75% ST</td>
<td>219–359</td>
<td>74.03</td>
<td>44.2 9.05</td>
<td>35.07</td>
<td>18.48</td>
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<tr>
<td></td>
<td>359–476</td>
<td>25.97</td>
<td>36.96</td>
<td>23.49</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>50% MS + 50% ST</td>
<td>227–356</td>
<td>73.57</td>
<td>10.91</td>
<td>30.08</td>
<td>19.78</td>
</tr>
<tr>
<td></td>
<td>356–474</td>
<td>26.43</td>
<td>33.83</td>
<td>23.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>75% MS + 25% ST</td>
<td>232–354</td>
<td>65.42</td>
<td>12.86</td>
<td>26.58</td>
<td>20.35</td>
</tr>
<tr>
<td></td>
<td>354–473</td>
<td>34.58</td>
<td>28.16</td>
<td>23.33</td>
<td></td>
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<tr>
<td>100%MS</td>
<td>243–350</td>
<td>56.85</td>
<td>18.19</td>
<td>23.86</td>
<td>21.41</td>
<td>22.06</td>
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<td></td>
<td>350–472</td>
<td>43.15</td>
<td>60.13</td>
<td>22.91</td>
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<tr>
<td>PS/ST</td>
<td>213–362</td>
<td>84.64</td>
<td>7.03</td>
<td>51.97</td>
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<tr>
<td></td>
<td>362–484</td>
<td>15.36</td>
<td>43.73</td>
<td>23.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25% PS + 75% ST</td>
<td>221–382</td>
<td>88.21</td>
<td>4.83</td>
<td>39.14</td>
<td>18.74</td>
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<tr>
<td></td>
<td>382–462</td>
<td>11.79</td>
<td>50.82</td>
<td>23.48</td>
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<tr>
<td></td>
<td>50% PS + 50% ST</td>
<td>227–386</td>
<td>93.24</td>
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<td></td>
<td>386–430</td>
<td>6.76</td>
<td>66.27</td>
<td>23.33</td>
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</tr>
<tr>
<td></td>
<td>75% PS + 25% ST</td>
<td>241–387</td>
<td>96.79</td>
<td>4.68</td>
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<tr>
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<td>3.21</td>
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<tr>
<td>100%PS</td>
<td>252–389</td>
<td>98.73</td>
<td>15.24</td>
<td>88.23</td>
<td>18.95</td>
<td>18.99</td>
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<tr>
<td>ST</td>
<td>389–410</td>
<td>1.27</td>
<td>60.13</td>
<td>22.18</td>
<td></td>
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</tr>
</tbody>
</table>

Figure 5. Kinetic analysis curves of sludge, straw and co-pyrolysis.

It can be seen that $R^2$ of all linear quasi-correlation coefficients is relatively high, indicating a good degree of fitting. During pyrolysis alone, the activation energy of PS in papermaking sludge is the highest, followed by straw ST, and MS in industrial sludge is the lowest. With the change of straw mixing ratio, the average activation energy shows a nonlinear change, which is mainly caused by the complex interaction between the samples in the mixed pyrolysis process. With the increase of straw ST content from 0% to 75%, the average activation energy increased gradually. Furthermore, when the straw ST content increased from 75% to 100%, the average activation energy increased significantly. With the increase of straw ST content from 0% to 25%, the average activation energy decreased significantly. Further, when the straw ST content increased from 25% to 75%, the average activation energy decreased gradually, and increased to 100%. In other words, when 75% ST is mixed, the average activation energy is the lowest, which is the most conducive to the pyrolysis reaction. Considering from the perspective of reactivity kinetics, during the co-pyrolysis of industrial sludge
MS and straw ST, the mixture proportion of straw ST was about 25%, and the activation energy was relatively low. During the co-pyrolysis of PS and Straw ST, the mixture ratio of straw ST was controlled at 75% and the activation energy was relatively low, which was conducive to the co-pyrolysis reaction.

4. Conclusion
In order to maximize the potential energy utilization of both agricultural and forestry wastes and sludge, this paper carried out an experimental study on the co-pyrolysis of two kinds of sludge (urban industrial sludge, papermaking sludge) and a typical biomass straw. The results show that biomass can effectively improve the pyrolysis characteristics of sludge, and there are significant differences between biomass straw and sludge pyrolysis characteristics. There are complex interaction effects between the components in the co-pyrolysis process, and the characteristics of each parameter show nonlinear variation law. When straw is mixed with industrial sludge, the initial pyrolysis temperature decreases and the termination temperature increases with the increase of straw content, and the peak pyrolysis reaction rate and corresponding temperature increase gradually, and the pyrolysis index increases gradually. When straw is mixed with papermaking sludge, the initial solution temperature decreases and the termination temperature increases with the increase of straw content, and the peak value of pyrolysis reaction rate increases gradually, while the corresponding peak temperature decreases and the pyrolysis index decreases gradually. Combined with characteristic parameters and reaction kinetics analysis, it is suggested that the straw mixing proportion should be controlled at about 25% during the co-pyrolysis of industrial sludge and straw; during the co-pyrolysis of paper sludge and straw, it is suggested to control the straw blending ratio at about 75%.

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Conflict of interest
The authors declared no conflicts.

References


