

Study on the co-pyrolysis behavior of sewage sludge and water hyacinth

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Abstract. The purpose of this study is to investigate the thermal behavior and their interaction patterns of SS and WH co-pyrolysis. The mixture was non-isothermally heated at different heating rates (20,30,40°C/min) using a thermogravimetric analyzer under N₂ atmosphere and reaction temperature range of 20 – 800°C. The study found that both SS and WH pyrolysis can be divided into three parts, in order of water release zone, major volatile fraction release zone, and slow carbonization zone. The individual pyrolysis performance of WH(CPI=26.17) was significantly better than that of SS (CPI=6.22), and the co-pyrolysis of samples with different mixing ratios showed inhibition or promotion, with W7S3 showing the strongest promotion interaction. From the viewpoint of thermal behavior and kinetics, co-pyrolysis of SS and WH is highly feasible, and the proportion of WH should be appropriately increased in practical engineering applications to achieve more effective utilization of waste.

Keywords: sewage sludge、Water hyacinth、co-pyrolysis、TG

1. Introduction

sewage sludge(SS) is a by-product produced in the process of urban sewage treatment. According to Chinese environmental statistics, the annual sludge generation has reached 76.36 million tons as of 2019. Sludge mainly contains a large amount of water, organic matter, trace elements and biological elements (such as nitrogen, phosphorus, etc.), but also contains a large number of heavy metal elements (Cu, Pb, Zn, Cd, Cr, Ni, Mn, etc.). It is extremely easy to decay and emit bad odor, so the treatment of sludge has become an urgent environmental problem. Water hyacinth(WH) is one of the ten most invasive species in the world. At present, its lack of natural enemies has caused flooding, which has seriously affected waterway transportation and caused economic losses of more than 10 billion dollars every year.

Sludge pyrolysis technology refers to the process of cracking solid waste into tar, char and gas under a certain temperature and pressure in the absence of oxygen or anoxia, which has the characteristics of low energy consumption, large treatment capacity and short time consumption, and is suitable for large-scale application, and is one of the most promising sludge treatment methods at present. However, sludge has high water content, high ash content and low calorific value, which makes it difficult to be used as a high-quality fuel alone. Also, if the combustion ratio is too large, a large amount of CO₂ will be produced, which affects the calorific value of the produced gas. Therefore, it is necessary to add other auxiliary materials to the sludge pyrolysis process for co-pyrolysis.

Therefore, this paper uses a thermogravimetric analyzer to study the thermal behavior of the co-pyrolysis of SS and WH, mainly to explore the interaction law, and determine the best mixing ratio of co-pyrolysis.

2. Materials and methods

2.1 Materials preparation

2.1.1. Raw materials and properties.

The SS used in this experiment was taken from a wastewater treatment plant in Nanjing. After compressed and dewatered, it was placed in a cool and ventilated place to dry. Then placed in a grinder and sieved into 80 mesh powder, placed in a drying oven at 105°C for 24h, and stored in a drying container for backup. WH was collected from a water area in Nanjing, Jiangsu Province, washed and roots were removed, natural air-drying treatment was performed. Then crushed and sieved into 80 mesh powder and placed in a drying oven at 105°C for 24h, and stored for backup. The ultimate and proximate analysis of feedstocks are shown in Table 1.

Table 1. The ultimate and proximate analysis of feedstocks

Samples	Ultimate analysis(wt.%)				Proximate analysis(wt.%)				
	Car	Har	Oar	Nar	Sar	Var	FCar	Aar	Mar
SS	10.39	7.56	17.25	6.88	4.04	42.26	3.86	50.51	3.37
WH	35.92	8.47	9.33	1.76	1.48	52.05	4.91	35.90	7.14

2.1.2. Experimental methods.

In order to study the co-pyrolysis behavior and interaction law of SS and WH with different mixing ratios, WH and SS were divided into five groups according to the different mixing ratios, named W0S1, W3S7, W5S5, W7S3, W1S0. Taking W3S7 as an example, it represents the weight ratio of WH to SS of 3 : 7.

The experiment was carried out on a thermogravimetric analyzer (Germany NETZSCH 449F3). The mass of the sample was weighed at 10mg each time, the carrier gas was N₂, the carrier gas flow was 50ml/min, the initial temperature was 20°C, and the termination temperature was 800°C. According to the different heating rate, it is divided into 3 groups, followed by 20°C/min, 30°C/min, and 40°C/min. In order to ensure the accuracy of the experiment, a group of samples were randomly selected for 3 repeated experiments to monitor the experimental data.

2.2 Thermogravimetric analysis and interaction of Co-Pyrolysis

2.2.1. Thermogravimetric analysis of Co-Pyrolysis.

The thermogravimetric analyzer can obtain TG and DTG data, and the analysis of the images can obtain parameters such as the initial temperature of pyrolysis (Ti), the termination temperature of pyrolysis (Tf), the mass loss rate (Mf), the peak temperature at the maximum weight loss rate (Tmax), the maximum weight loss rate (Dmax), and the half-peak width temperature range (ΔT1/2). The pyrolysis process is quantitatively evaluated and the pyrolysis characteristic parameter CPI is introduced. The value of CPI reflects the pros and cons of pyrolysis performance. The larger the CPI value, the better the pyrolysis performance. Its formula is as follows[1]:

$$CPI = \frac{D_{max} D_{ave} (1 - M_f)}{T_i T_{max} \Delta T_{1/2}} \quad (1)$$

where D_{ave} denotes the average weight loss rate and the half-peak width temperature range (ΔT1/2) denotes the temperature range within D/D_{max}=0.5.

2.2.2. Synergistic effects in the WH/SS blends Co-Pyrolysis.

In order to study the interaction of SS and WH co-pyrolysis, the following formula is introduced[2]:

$$\Delta Diff_i = E_i - C_i \quad (2)$$

In the formula, E_i represents the data obtained from the experiment, i represents a certain pyrolysis parameter, and C_i represents the data obtained by theoretical calculation. It is based on the assumption that the co-pyrolysis process is regarded as a linear superposition of the pyrolysis of a single raw material, That is, no interaction, its calculation formula is as follows:

$$C_i = \eta_{ss}E_{i, ss} + (1 - \eta_{ss})E_{i, WH} \quad (3)$$

Where η_{ss} denotes the proportion of SS in the blends, and $E_{i,ss}$ and $E_{i,WH}$ denote the experimental data for parameter i when SS and WH are pyrolyzed separately.

The magnitude of $\Delta Diff_i$ can reflect the interaction between SS and WH. Taking the residual mass at time t as an example, $\Delta Diff_i = EM - CM$, if $\Delta Diff_i > 0$, the experimental value is greater than the theoretical calculation, which means that the co-pyrolysis of the two slows down the process of weight loss. That is to say, inhibition may be dominant between the two, and vice versa, promotion is dominant.

3. Results and discussion

3.1 Thermogravimetric analysis

3.1.1. Separate pyrolysis characterization of SS and WH.

Figure 1 shows the TG and DTG curves of the pyrolysis of SS and WH when the heating rate is 20°C/min. The SS pyrolysis residue was more, reaching 49.33%, while the WH residue was 34.93%. The composition is the most important reason for the difference. The more aromatic compounds in the raw material, the easier the pyrolysis process is to coke, and the higher the carbon residual rate. SS is rich in protein, and there are a lot of aromatic compounds in the amino acid side substitutions of protein, which is easier to coke. While WH is mainly cellulose and hemicellulose with low residual carbon rate (more than 60% of the total), lignin that is easy to coke is less (6%), so the residue in the pyrolysis product is less than SS. Another reason for the difference is the existence of ash, which does not participate in the pyrolysis reaction, and the mass of ash does not change due to pyrolysis. It is also evident from the industrial analysis of the material that the ash content of SS is 50.51%, which is higher than that of WH. The value is close to the specific gravity of its respective pyrolysis residues and supports this view.

The SS pyrolysis process was mainly divided into 3 stages. The first stage was 69.9 – 118.6°C, with a mass change rate of 3.16%, accounting for 6.24% of the total change rate (50.67%), which was mainly the dehydration stage of the raw material, with less weight loss and close to the moisture content in the industrial analysis. The second stage is 329 – 413.1°C, and the mass change rate is 27.3%. In this stage, the maximum weight loss rate occurs at about 381°C. This stage is mainly for the removal of volatile fractions and the depolymerization of organic matter, such as proteins (peak at 330°C), fats and oils (peak at 423.5°C), and starch (peak at 335.3°C)[3]. This stage is the main weight loss stage of the pyrolysis process and governs the sludge pyrolysis process. The third stage is mainly the slow carbonation with solid phase rearrangement releasing small molecule gas, which leads to the mass reduction[4]. From Figure 1, it can be seen that the TG curve is almost parallel to the horizontal axis at the end of the third stage, indicating that the pyrolysis reaction is basically completed.

For WH, the same is divided into three parts. The mass loss in the first stage is mainly due to the removal of water, the temperature range is 75.7 – 121.3°C, and the mass change rate is 6.25%. The second stage is mainly the decomposition of hemicellulose and cellulose[5], the temperature range is 281.4 – 369.5°C, the mass change rate is 38.08%, and the peak temperature is 331.5°C, which is consistent with the pyrolysis characteristics of cellulose and hemicellulose. It was also noticed that the weight loss rate was basically constant in the range of 266 – 295°C, and a rapid weight loss region existed after exceeding 295°C, which might be related to the inconsistent temperature range of hemicellulose and cellulose decomposition[6]. The decomposition temperature range of hemicellulose is 203 – 464°C and cellulose is 314 – 373°C, After 300°C, cellulose starts to decompose a lot thus leading to a rapid increase in weight loss rate. Therefore, the second stage can be divided into two parts, the first part is 281.4 – 295°C, which is mainly the decomposition of hemicellulose. And the second part is 295 – 369.5°C, which is mainly the decomposition of

cellulose and hemicellulose. The third stage is mainly a secondary reaction with continuous slow carbonization, which includes tar cracking and coke formation. Meanwhile, due to the continuous decomposition of lignin in the range of 194 – 534°C, a wide and blunt weight loss peak was observed due to the presentation of a wide and blunt weight loss peak[6]. But the lignin content in WH was low (about 6%), so the effect of lignin decomposition in the third stage was less and no significant weight loss peak was observed.

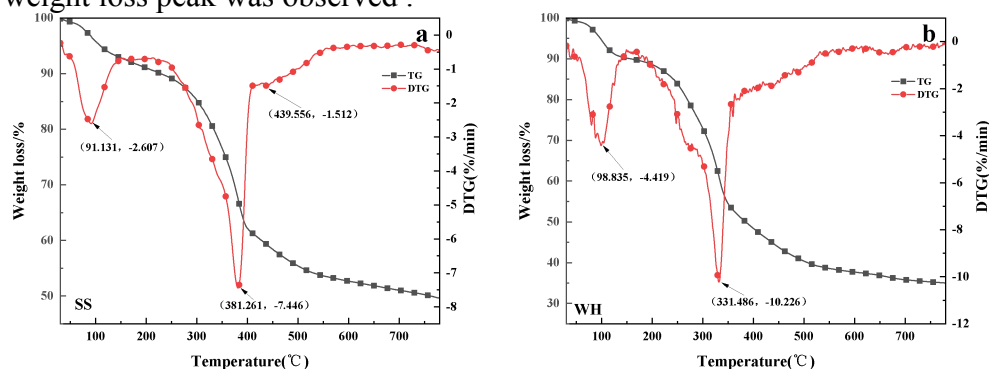


Figure 1. TG-DTG curves of SS and WH

3.1.2. Analysis of pyrolysis properties of blend.

Under the condition of a heating rate of 20°C/min, investigate the co-pyrolysis characteristics when the mixing ratio of WH and SS is 0 : 1, 3 : 7, 5 : 5, 7 : 3, 1 : 0. The objective was to investigate the effect of WH addition on SS pyrolysis. The TG-DTG curves are shown in Figure 2. Comparing the TG-DTG curves of separate pyrolysis and mixture pyrolysis, it can be seen that the curve of the blend is between the SS and WH separate pyrolysis curves, combining the characteristics of the two substances pyrolysis separately, and varying with the mixing ratio.

With the increase of SS ratio, the weight loss rate of the co-blends gradually decreased, it may be due to the weight loss rate of WH being greater than that of SS, thus improving the overall pyrolytic properties of the blends. The maximum weight loss rate of both WH and SS occurred in the release phase of the main volatile fraction. The maximum weight loss rate of WH was 10.23 %/min, while SS was 7.45 %/min, which was obviously smaller than the value of WH. This reflects that the co-pyrolysis of WH and SS can make up for the deficiency of SS when it is pyrolyzed separately, promoting the release of volatile fraction and making the pyrolysis reaction more intense.

From the perspective of T_{max} , significant differences exist between WH and SS, the T_{max} of WH is 331.49°C, while SS is 381.26°C, obviously higher than the value of WH. This may be due to the difference in their composition, WH is mainly composed of cellulose and hemicellulose, SS is mainly composed of protein, oil and starch, etc. Hemicellulose has abundant thermally unstable side branches, which are connected by α -1,4-glycosidic bonds, so they are most easily broken down. Starch consists of repeating glucose units ($C_6H_{10}O_5$) connected by β -1, 4-glycosidic bonds. This connection facilitates the formation of hydrogen bonds, resulting in a strong fibrous substance in cellulose, leading to more difficult decomposition. Meanwhile, the oil in SS is mainly composed of long aliphatic triglycerides, which contain more stable C-C and C-H bonds and are more difficult to decompose. Due to the difficult decomposition of starch and oil, the easy decomposition of hemicellulose and cellulose, which leads to the difference in T_{max} values between WH and SS. With the increase of WH incorporation in SS, T_{max} showed a gradual decrease, which indicated that the incorporation of WH could promote the decomposition of the mixture and increase the pyrolytic activity of the mixture.

The larger value of CPI indicates the better pyrolysis performance, which proves that the incorporation of WH can improve the pyrolysis performance of SS. Meanwhile, from the CPI data, we found that the CPI values are significantly lower than those of pure WH pyrolysis when the WH ratio is 30% and 50%. The underlying reason is that WH is a macromolecular structure composed of cellulose, hemicellulose, and lignin, etc. In the main decomposition zone of volatile fraction

release, WH starts to decompose earlier than SS, resulting in the weight loss peaks of SS and WH do not correspond to the same temperature.

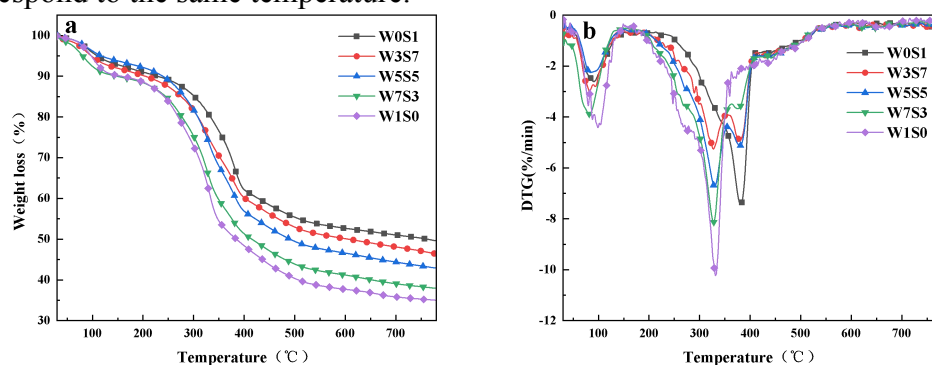


Figure 2. TG-DTG curves of SS co-pyrolysis with WH

Table 2. Mixture pyrolysis characteristics parameters and interactions

Sample	$T_i(^{\circ}\text{C})$	$T_{max}(^{\circ}\text{C})$	$D_{max}(\%/min)$	$D_{ave}(\%/min)$	$M_f(\%)$	$T_f(^{\circ}\text{C})$	$\Delta T_{1/2}(^{\circ}\text{C})$	CPI(10^{-7})
W0S1	329.00	382.50	7.45	1.34	49.33	788.99	64.42	6.22
W3S7	275.30	331.49	5.26	1.42	46.11	789.03	110.91	3.97
W5S5	274.20	329.62	6.71	1.51	42.74	789.00	106.31	6.06
W7S3	277.40	327.62	8.13	1.64	37.83	789.11	58.75	15.49
W1S0	281.40	327.26	10.23	1.71	34.93	789.01	47.27	26.17

3.2 Synergistic analysis of co-pyrolysis.

Figure 3 shows the calculated TG curves of the 3 samples compared with the experimentally obtained ones. As shown in Figure 3a, the experimental TG curve lags behind the calculated TG curve when the temperature is 30 – 140°C, but the experimental TG curve exceeds the calculated TG curve when the temperature is in the range of 335 – 800°C. However, the calculated TG curves and experimental TG curves nearly overlap in the temperature range of 140 – 335°C. This result suggests that there is some kind of interaction during the co-pyrolysis of SS and WH. When the temperature range is 30 – 140°C, it is for promoting effect, but the interaction strength is not large. These differences are attributed to the chemical interaction between SS and WH components during the decomposition process. When the temperature range is 335 – 800°C, it is mainly inhibition, and the interaction strength is significantly greater than that of the low temperature section. From the industrial analysis, we can know that the ash content in SS is as high as 50.51%. When in the high temperature zone, the ash melts and adheres to the surface of WH and SS particles, preventing its decomposition process[7]. Figure 3(b) and (c) show the images of W5S5 and W7S3 samples, respectively. Compared with the images of W3S7 samples, both of them show strong interactions in the high-temperature and low-temperature sections, but the two interactions show opposite trends.

Figure 4(d) shows the TG deviation images of the 3 mixtures. $\Delta \text{Diff}_i = \text{EM} - \text{CM}$, which represents the residual mass at time t , the larger the value, the stronger the interaction. If $\Delta \text{Diff}_i > 0$, the experimental value is greater than the calculated value, which means that the co-pyrolysis slows down the process of weight loss. That is to say, the inhibition between the two may be dominant. If $\Delta \text{Diff}_i < 0$, the promotion effect is promotion. As shown in Figure 4(d), the mixtures with different WH ratios have different interaction patterns. The samples with 50% WH showed mutual inhibition during the whole pyrolysis process, while the samples with 70% WH showed promotion.

In the region 400 – 800 °C, with the decrease of SS content, the pyrolysis reaction showed a change of inhibition to promotion in general. Among the three samples, W3S7 showed the strongest inhibition, W5S5 showed slightly lower inhibition than W3S7, while W7S3 showed a strong promotion. WH pyrolysis releases heat, which provides heat for SS to overcome the resistance of pyrolysis, so more WH will play a role in promoting the process. Meanwhile, SS contains a large

amount of Fe_2O_3 , Al_2O_3 , P_2O_5 , SiO_2 and other metal oxides, which can promote the decomposition of organic materials and have the effect of in situ catalysis[8]. Therefore, when WH ratio was 70%, under the combined effect of metal oxide catalysis and heat provided by WH, the inhibition caused by SS ash adhesion was overcome, and the overall effect was presented as promotion. In contrast, when WH ratios were 30% and 50%, the high ash content brought by the presence of large amounts of SS had a stronger inhibitory effect on pyrolysis production and was significantly higher than the promoting effect, showing an overall inhibitory effect.

However, it is noteworthy that in the region 30 – 400 °C, the 30% proportion of WH is essentially free of interaction, while the WH proportion of 50% shows inhibition, which is inconsistent with the high-temperature region. This may be due to the fact that the ash in the low temperature section does not reach the melting temperature, and its melting is less, which has a weak effect on pyrolysis. However, the pyrolysis of WH will produce porous biochar, which can adsorb the volatiles released during the pyrolysis process. This region is also the main stage of volatiles release, thus providing some inhibition.

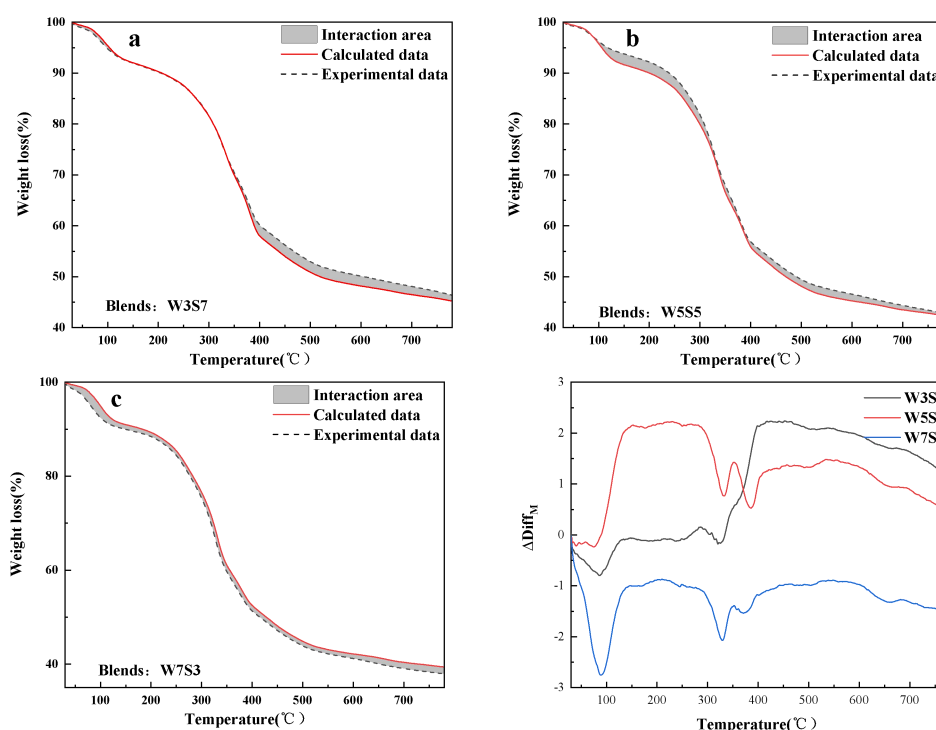


Figure 3. Experimental, calculated and TG deviation curve of 3 blends

3.3 Analysis of pyrolysis characteristics at different heating rates.

In order to study the effect of the heating rate on the pyrolysis characteristics, W0S1 and W1S0 samples were selected for analysis in this section. Figure 6 (a) and (b) show the TG-DTG curves for W0S1 and W1S0 heating rates of 20, 30, and 40°C/min, respectively. It is obvious from Figure 6 (a) that when the heating rate is 20°C, 30°C and 40°C/min, the maximum weight loss rate is 7.45%, 9.66% and 10.70%/min respectively. With the increase of heating rate, the maximum weight loss rate increases significantly. Meanwhile, the DTG curve gradually moved toward the high temperature region with the increase of the heating rate, and T_{max} also increased with the increase of the heating rate, which were 381.26, 390.19, and 396.89°C in order. This indicates that the increase in heating rate helps to accelerate the pyrolysis process. This may be because the increase in heating rate enlarges the temperature gradient inside the SS particles. According to Fourier's law, the increase in temperature gradient will lead to an increase in heat transfer, thus accelerating the pyrolysis rate.

It can be seen from Figure 4(b) that the heating rate also has a large effect on the residual mass of the SS pyrolysis process. The residual mass of SS was 49.33%, 50.55% and 53.62% when the

heating rate was 20, 30 and 40 °C/min. The increase of heating rate led to the increase of residual mass, which might be due to the fact that more ash in SS melted and sintered on the surface of the particles at higher heating rate, which caused an obstruction to the pyrolysis reaction. Some studies have shown that the removal of minerals from SS results in a significantly higher pyrolysis rate. The weight loss process of WH is less affected by the heating rate, which confirms that the high ash content is the reason for the higher residual mass of SS at high heating rates.

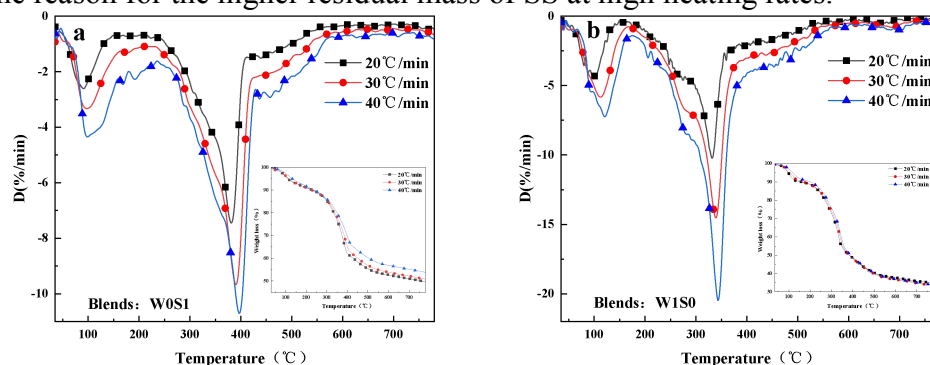


Figure 4. Effect of heating rate on co-pyrolysis properties

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References

- [1] Zhao B, Xu X, Li H, Chen X, Zeng F (2018) Kinetics evaluation and thermal decomposition characteristics of co-pyrolysis of municipal sewage sludge and hazelnut shell. *Bioresour Technol* 247:21-29. doi:10.1016/j.biortech.2017.09.008
- [2] Wang C, Bi H, Lin Q, Jiang X, Jiang C (2020) Co-pyrolysis of sewage sludge and rice husk by TG-FTIR-MS: Pyrolysis behavior, kinetics, and condensable/non-condensable gases characteristics. *Renewable Energy* 160:1048-1066. doi:10.1016/j.renene.2020.07.046
- [3] Naqvi SR, Hameed Z, Tariq R, Taqvi SA, Ali I, Niazi MBK, Noor T, Hussain A, Iqbal N, Shahbaz M (2019) Synergistic effect on co-pyrolysis of rice husk and sewage sludge by thermal behavior, kinetics, thermodynamic parameters and artificial neural network. *Waste Manag* 85:131-140. doi:10.1016/j.wasman.2018.12.031
- [4] Naqvi SR, Tariq R, Hameed Z, Ali I, Naqvi M, Chen W-H, Ceylan S, Rashid H, Ahmad J, Taqvi SA, Shahbaz M (2019) Pyrolysis of high ash sewage sludge: Kinetics and thermodynamic analysis using Coats-Redfern method. *Renewable Energy* 131:854-860. doi:10.1016/j.renene.2018.07.094
- [5] Luo G, Strong PJ, Wang H, Ni W, Shi W (2011) Kinetics of the pyrolytic and hydrothermal decomposition of water hyacinth. *Bioresour Technol* 102 (13):6990-6994. doi:10.1016/j.biortech.2011.04.048
- [6] Zong P, Jiang Y, Tian Y, Li J, Yuan M, Ji Y, Chen M, Li D, Qiao Y (2020) Pyrolysis behavior and product distributions of biomass six group components: Starch, cellulose, hemicellulose, lignin, protein and oil. *Energy Conversion and Management* 216. doi:10.1016/j.enconman.2020.112777
- [7] Wang T, Chen Y, Li J, Xue Y, Liu J, Mei M, Hou H, Chen S (2020) Co-pyrolysis behavior of sewage sludge and rice husk by TG-MS and residue analysis. *Journal of Cleaner Production* 250. doi:10.1016/j.jclepro.2019.119557
- [8] Chen J, Zhang J, Liu J, He Y, Evrendilek F, Buyukada M, Xie W, Sun S (2020) Co-pyrolytic mechanisms, kinetics, emissions and products of biomass and sewage sludge in N₂, CO₂ and mixed atmospheres. *Chemical Engineering Journal* 397. doi:10.1016/j.cej.2020.125372