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**In-depth comparison of morphology, microstructure, and pathway of char
derived from sewage sludge and relevant model compounds**

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Abstract

Hydrothermal conversion (HTC) of sewage sludge (SS) and its relevant model compounds such as cellulose, glucose, lignin and soybean protein (substitute for protein) was experimentally conducted at moderate reaction temperature of 260 °C for 60 min. The structural properties, carbon-containing groups, and microstructure of the char were characterised by several techniques. The results revealed that more benzene rings were formed by small clusters and the C-O bond on Aryl-alkyl ether decomposed on the surface particles during the HTC process. In addition, the catalyst Zeolite Socony Mobil-5 (ZSM-5, Si/Al: 300) showed an excellent performance on the high graphite degree of the char under moderate reaction temperature of 260 °C. In particular, cellulose has the most dramatic influence on the depolymerisation of C-(C,H). As evidenced with SEM, the size of the char derived from SS with ZSM-5 catalyst is 10-15µm, which is smaller than the char without catalyst. A mechanism for derivation of char from individual model compounds is proposed. The end products of lignin are composed of polyaromatic char, while the composition of the char derived from protein suggests that polymerisation may occur during hydrothermal reaction leading to formation of structures with N-containing compounds.

1. Introduction

Sewage sludge (SS) is a combination of post-treatment water-carried residues produced in a wastewater treatment plant and is by far the largest waste component of the plant. Besides the high volume, sewage sludge may contain certain contaminants, including heavy metals, hazardous organic and inorganic substances, as well as

43 pathogenic microorganisms (He et al., 2013; Zhai et al., 2016), which can threaten the
44 environment if not disposed properly. To date, the thermochemical route has been
45 regarded as an effective way to convert the biomass into bioenergy (Ahmad et al.,
46 2018; Zhang et al., 2018), wherein the organic matter in the SS can be reused to
47 generate energy or high value products. However, the process should also enhance the
48 reduction of the toxic substances, the stability of heavy metals and the dehydration of
49 the SS as well, so that the end products could be reused with less environmental
50 consequences. For these reasons, hydrothermal conversion (HTC) of SS has emerged
51 as a promising approach to convert the SS into value-added products (Stirling et al.,
52 2018). The process involves heating the SS at 180-300 °C, and at an autogenic
53 pressure of 2-10 MPa for a short duration in an inert atmosphere (Areeprasert et al.,
54 2014; Chen et al., 2015). Previous researches have proved that various biomass
55 wastes can be treated by using HTC, especially those with high moisture content,
56 including algae, sewage sludge and digestate (He et al., 2014; Mumme et al., 2015;
57 Peng et al., 2016; Thiruvankadam et al., 2015). Patel et al. (Patel and Hellgardt, 2015)
58 investigated a novel continuous hydrothermal liquefaction reaction in microalgae
59 which conducted at 300-380 °C for a quick reaction of 0.5-4min. The highest
60 biocrude yield was 38 % and was obtained at 380 °C. Furthermore, it is possible to
61 produce high-quality biocrude by reducing the oxygen and nitrogen content in the
62 microalgae during the process. He et al. (He et al., 2013) applied HTC to SS to gain
63 fuels. They examined the hydrothermal carbonisation of SS at 200 °C for 4-12 h.
64 Their experimental results demonstrated that most of the carbon can be recovered and

HTC also has the ability to remove nitrogen and sulphur. Compared with SS, hydrochar shows a better performance on stabilisation with a high heating value (HHV). Similar results were also found by a previous study (Lu et al., 2011), that conducted a comparative research on the HTC of three types of municipal solid waste from Japan, China, and India, respectively. The researchers observed that the HTC process caused an approximately 6.4-9.0 fold enhancement in the heating value (HV) of MSW. Furthermore, HTC appears to be a clean technique that can remove the nitrogen content from SS as a pretreatment process (Shen et al., 2018). Therefore, HTC can be considered an environmentally friendly method with a bright potential.

In addition, a range of catalysts also play a crucial role during the treatment, which significantly impacts the HTC process. To achieve different corresponding end products, various catalysts, including CaO, CH₂O and Zeolite Socony Mobil-5 (ZSM-5) have been used during the treatment (Du et al., 2013; He et al., 2015; Kang et al., 2012b). Previously, He et al. (He et al., 2015) carbonised SS with CaO to produce gaseous, solid, and liquid products for energy recovery. They indicated that in high reaction temperatures, CaO as a chemical additive had a positive effect on H₂ yield and the hydrolysis process. In another study (Kang et al., 2012b), formaldehyde as a polymerization agent has been applied in the HTC of black liquor under reaction temperatures ranged of 220 to 285 °C, indicating that the char yield, HHV, and carbon recovery efficiency increased with the formaldehyde assistance. On the other hand, technically produced zeolites have been widely used in thermal chemical conversion as important catalysts (Mumme et al., 2015). It has been shown that zeolite is capable

of improving the energy and carbon recovery for char production.

Most researches have investigated the feasibility of the HTC process to produce bio-products, enhance the properties of the biochar and bio-oil, and the energy balance for the conversion system (Peng et al., 2017; Toor et al., 2011; Zhai et al., 2017; Zhao et al., 2014). Furthermore, due to the complex composition of the SS, it is reasonable to use model compounds to investigate the pathway of the char production.

However, studies on the morphology and microstructure of char derived from SS and its model compounds by using catalytic hydrothermal conversion are uncommon. Besides, few of them have explored the effect of ZSM-5 as a catalyst on the char products or performed a comparative study between SS and its model compounds, which is crucial for studying the mechanism of the treatment (Wang et al., 2013). To clearly understand the HTC process mechanism of SS-derived char in different condition, the first step is to investigate the characteristic of SS and its model compounds-derived char, respectively. The second step is to investigate the characteristic of the mixed compounds, which is composed of individual model compounds. This work focus on the first step and aims to gain an insight into the morphology and microstructure of the char derived from SS and its model compounds by employing catalytic HTC. Individual objectives of the research were (i) to analyse the morphological structure of the HTC products derived from SS and model compounds; (ii) to evaluate the surface morphology of the char during the HTC process; (iii) to comparatively describe the char properties of the SS and model compounds; (iv) to characterise and investigate the effects of ZSM-5 catalyst on the

HTC of SS; and (v) to discuss the probable pathway of each model compounds through the HTC process under 260 °C. This article will help explore further in-depth studies on the mechanisms of the char structural transformation while undergoing the HTC process on the co-pyrolysis.

2. Material and methods

2.1. Raw materials.

As a raw feedstock, dewatered SS was provided by a wastewater treatment plant in Changsha, China. Before being processed, the SS was heated in an oven at 105 °C for 24h to remove water. To homogenise raw sludge particle, they were milled and sieved into a powder, for maintaining the particle size between 0.2 and 0.25 mm. According to the previous researches on its properties, SS is composed of three main organic substances, protein, carbohydrates, and lignin (Nielfa et al., 2015; Peng et al., 2017). Therefore, protein (soybean protein), carbohydrates (cellulose and glucose) and lignin were used as the model compounds in this study. Cellulose was supplied by Whatman, glucose and soybean protein (SP) were supplied by Sinopharm Chemical Reagent Company, and lignin was obtained from Ruibio Company. Different types of ZSM-5 have different physicochemical properties. To comparatively study the catalyst, ZSM-5 with the Si/Al ratios, 38 and 300 was obtained from Kaiwei Chemical Industry company. All the raw materials were sealed in a storage bottle to avoid moisture adsorption. The predominant fractions of the organic substances in the SS were lignin (4.7%), cellulose (6.2%), glucose (7.1%), and protein (23.3%).

2.2. Hydrothermal carbonisation process

The char sample was produced in a high temperature and pressure reactor, which was connected to a temperature controller and an electromagnetic stirring module. Similar to our previous study (Wang et al., 2017; Zhai et al., 2017), the reaction temperature and the holding time for each experiment were set at 260 °C and 60 min, respectively, as optimization parameters. For a typical trial, 20 g SS and individual model compounds were mixed with 180 g deionised water in the reactor at a stirring rate of 100 r/min, respectively. A mixture of SS (20 g) and ZSM-5 (10 g) in 180 g deionised water was used as the control sample. For another control sample, cellulose (3 g), glucose (3 g), SP (8 g), and lignin (6 g) and were combined vigorously in 180 g deionised water. Each experiment was initiated with an inflow of N₂ for 5 min to remove any oxygen prior to the HTC process. After the completion of HTC, the end products were collected and separated into solid and liquid products through filtering after cooling the reactor to room temperature. The solids were oven dried at 105 °C until there was no significant change in weight and were subsequently milled into a homogeneous powder for further analysis. Each trial was named as the feedstock followed by the synthesis specifications, namely the reaction temperature and the Si/Al ratio (38 or 300). For example, the label SS-260-38 means the char was produced from the SS at 260 °C with ZSM-5, that had a Si/Al ratio of 38. Moreover, the mixture of the cellulose, glucose, SP and lignin was denoted as MC-260.

2.3. Analysis and characterisation of char

The contents of the dry matter were determined gravimetrically by heating them up at 105 °C for 24h. A CHNS analyzer, (2400 Series II PerkinElmer, USA) was used to

examine the elemental content of the samples. The oxygen content was calculated using the difference. To determine the differences among the carbon-containing groups of char produced in different trials, X-ray photoelectron spectroscopy (XPS) was performed with a K-Alpha spectrometer using an Al monochromatic X-ray anode. For C, the binding energy was corrected necessarily at 285.0 eV to the principal C1s line. The peak fitting was carried out with Gaussian peaks. A Raman spectrometer (Labram-010, JOBIN YVON, France) was employed to investigate the transformation of the carbon structure. An excitation laser beam was focused by using a charge-coupled device camera, which is equipped with a spectrometer and can record the Raman data as well. The analyser operated with a 532nm laser excitation source in a range of 1000–2000 cm collected with an acquisition time of 20 s. Each spectrum test was scanned three times to minimise the noise ratio. The morphology of the char samples were recorded using a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). Before each experiment, the samples were coated with gold.

3. Results and discussion

3.1. Raman analysis of char

Gaussian and Lorentzian profiles consist of Raman bands under a typical condition for most of the disordered materials. Quantitative parameters such as intensity, full width at half-maximum and curve-integrated area can be composed by fitting the curve for the Raman spectra (Chen et al., 2019). Based on these parameters, Figure 1 shows the Raman spectra, which is decomposed by fitting eight Gaussian curves in the region from 1000 to 1800 cm⁻¹. For the sample of SS and the char derived from

the model compounds, all the bands of the fitting curve in the spectra representing the general structures in the char, are listed in Table 1. During the HTC process of the SS, aromatic content with cross-linked structures increased significantly and small polyaromatic structures decreased in the char. G and D bands represent the degree of graphite, which can be considered as the most important feature in char (Sheng, 2007). Moreover, as shown in Figure 2, the intensity ratio of D/G as a functional parameter has a significant effect on the crystallite size or graphite-like carbon structure. Compared with the SS, the D/G ratio of char, which is related to the dehydrogenation of hydroaromatics, was dramatically enhanced, indicating the formation of six or more benzene rings during the HTC process (Brown et al., 2017). Meanwhile, the aromatic rings increased under the moderate reaction temperature (260 °C). In addition, the D/G ratio value of char derived from the model compounds rose nearly by the same degree, except for the SP. The D/G ratio of SP increased sharply, which means there was a remarkable degree of protein decomposition in the SS. According to the D/G ratios, ZSM-5 with Si/Al of 300 had a better performance on the graphite degree under 260 °C reaction temperature. The D/G tendencies of glucose, cellulose, and lignin were similar due to their molten state during the reaction and resulted in the disorder of the char due to the formation of the aromatic carbon structure (Ferrari et al., 2003). Furthermore, due to the indistinct separation between the D and G bands, an intermediate band called kekule band was formed, located at wave number values between 1320 and 1580 cm^{-1} . In the case of the char derived from the SS and model compounds, the kekule band comprises three bands, G_R , V_R , and V_L , which are

associated with the amorphous carbon and smaller aromatic rings. Accordingly, the ratio of $D/(G_R+V_R+V_L)$ represents the proportion between the large and small aromatic rings in the amorphous carbon (Zhao et al., 2016). The $D/(G_R+V_R+V_L)$ values are shown in Figure 2. The value increases after the treatment. However, both the types of ZSM-5 catalyst exert a slight reduction on the $D/(G_R+V_R+V_L)$ ratio of char, indicating that more small aromatic rings in the amorphous structure were formed during the reaction with ZSM-5. Notably, the $D/(G_R+V_R+V_L)$ intensity is the highest in the model compounds, indicating that cellulose is the most influential part in the ordering of char. Another significant transformation is in the S band, which shows a huge reduction during the HTC process. This represents the corresponding breakage in the C-C linkages on the hydroaromatic rings during the decarboxylation reaction. With the continuing hydrothermal reaction, the C-H bonds on the arene rings and C-O on Aryl-alkyl ether decomposed, resulting in formation of a graphite-like carbon structure in the char (Fushimi et al., 2009).

3.2. XPS analysis of char

XPS can identify the oxidation state of the elements on the surface (2-10 nm). The XPS C 1s spectra of the SS and the hydrothermal solid products obtained through the HTC process are shown in Figure 3. To better identify the well-defined groups in the char, curve fitting was conducted with six peaks, including several functional groups such C-H groups (282.1 -283.6 eV), C-(C,H) (284.6 eV), and -C-OR groups (285.7-286 eV) in hydrocarbons such as cellulose, lignin, and glucose (He et al., 2016). C-(O,N) (285.6 eV) can be found in proteins and alcohols. Carbonyl or

219 quinone groups R-C=O (287.6 eV) in lipids, amides, carboxylate, acetals, and
220 hemiacetals. -COOR (288.7 -289.1 eV) groups in lactones or carboxyl (Marta and
221 Fuertes, 2009; Xia et al., 2007). To understand more details about each functional
222 group, Figure 4 compares the relative intensities of the carbon-containing group of the
223 SS, and the solid products from the SS and its relevant model compounds by using
224 Gaussian–Lorentzian fitting to calculate the relative intensity of each carbon
225 functionality. For the SS, C-(C,H) and C-(O,N) are the predominant
226 carbon-containing groups (56.39% and 30.58%, respectively), followed by minor
227 contributions from R-C=O and C-H (8.47% and 4.55%, respectively). When the
228 carbon-containing groups of the char are compared with and without the ZSM-5
229 catalyst, several functional groups show a distinct change due to the catalyst effect.
230 The intensity of C-(C,H) in sample SS-260-38 reduced sharply, whereas the C-(O,N)
231 group distinctly increased during the HTC process, indicating that the ZSM-5 (Si/Al :
232 38) favoured depolymerisation of C-(C,H) during the HTC process. In addition, the
233 transformation of the internal aromatic carbon of hydroxyl groups in linear alcohols,
234 ethers, or phenols may result in high levels of C-(O,N) group (He et al., 2016). The
235 other two peaks corresponding to -C-OR and C-H maintained relative thermal
236 stability. To obtain information on the specific transformation of carbon-containing
237 groups, the carbon functionalities of char derived from SS relative model compounds
238 were compared. The COOR, R-C=O, and C-OR groups were similar and found to be
239 dominant among glucose, cellulose, and lignin-derived char. However, the main
240 carbon-containing group in cellulose was C-(C,H) whereas no C-H groups were found,

which revealed that cellulose has a dramatic influence on the depolymerisation of C-(C,H). The total intensities of COOR, R-C=O, C-(O,N), and C-OR for the char derived from the model compounds are in the range 46.37-61.96%. This means that abundant of oxygen groups were formed from glucose, cellulose, lignin, and protein on the surface of the char during the HTC process (Sevilla and Fuertes, 2009). Hydroxyl, carbonyl, and ester are the reactive groups in the model compounds and can easily degrade to molecular fragment and compete with the transformation of the aromatic compounds. It is noteworthy that the COOR group disappeared in the SS-derived char, which can be correlated with the influence of inorganic substances in their corresponding feedstocks.

3.3. Char surface morphologies

SEM was used to observe the surface morphological changes during the HTC process. Figure 5 shows the surface morphological characteristics of SS (a), SS-derived char with or without catalyst (b-d), and its relevant model compounds-derived char (e-i). It can be seen that after the HTC treatment, the char derived from SS without catalyst (b) has a size similar to the SS. However, the surface of the char is quite different according to the slits. The catalytic hydrothermal char (c and d) has homogeneous particles with a smaller size (10-15 μm) than the SS-derived char (25-30 μm), indicating that the hydrothermal reaction was conducted thoroughly with ZSM-5 assistance. The char derived from the model compounds mixture (e) forms a porous structure and several holes are apparent on the surface, which indicates a fast volatile release during the HTC process leading to the formation of several internal cavities as

open structures. Compared with the individual model compounds, SP-derived char (f) has a relative large particle size, implying that the smaller pieces of protein particles re-aggregate under 260 °C. This finding is reasonably explained by the heterocyclic-N polymerization that occurs during the high temperature reaction. Due to the properties of the lignin fragments, it is difficult to melt them into an aqueous phase under relative low reaction temperature of less than 377 °C (Fang et al., 2008). In this study, the HTC reaction temperature is 260 °C, so it results in favourable conversion from solid to solid. As shown in the lignin-derived char (g), the surface is smoother than in the other model compounds, and with no holes produced due to the emission of volatile matter. This phenomenon may be ascribed to the exposure of both dissolved and non-dissolved lignin fragments to water. Afterwards, the decomposition of lignin to phenolics due to hydrolysis and further polymerization of the phenolic char, causes its accumulation on the surface of the polyaromatic char leading to recovery of the holes or cracks (Kang et al., 2012a). The cellulose-derived char (h) decomposed into a large irregular block style structure with fewer holes and retained the fibre skeleton during the HTC process. However, compared with the earlier studies, it should have formed microspheres through the hydrothermal carbonisation of cellulose (Sevilla and Fuertes, 2009). The different operating parameters such as lower ratio of cellulose/water and less experimental duration may have caused this difference. Notably, the cellulose-derived char with aggregates of microspheres is usually formed after 4 h at approximately 220 °C. Whereas in this experiment, the cellulose-derived char shows the beginning of an abrupt morphological change under a higher reaction

temperature of 260 °C after 1 h. Similar to the glucose-derived char observation (i), it decomposed into several small particles and further formed a hydroxymethylfurfural microspherical structure. The difference in topography from the previous research can be explained by the residence time and reaction temperature. The microsphere structures are formed with an increase in the residence time and then keep growing until achieving their final size (Falco et al., 2011).

3.4. Individual model compounds pathway during HTC process

To explore further in-depth studies on the pathway of the SS-derived char structural transformation while undergoing the HTC process. Individual model compounds pathway during HTC process should be advance considered. Combining the results from numerous previous studies with ours on the transformation mechanism of model compounds, including that of cellulose (Falco et al., 2011; Fang et al., 2008; Sasaki et al., 1998; Sevilla and Fuertes, 2009), glucose (Möller et al., 2011), lignin (Pandey and Chang, 2011; Wu et al., 2017), and protein (Su et al., 2010) through HTC, the formation pathway of char from individual model compounds via HTC process can be reasonably schemed.

Figure S1 illustrates the main char formation pathway from cellulose and glucose under 260 °C hydrothermal reaction temperature. In the first step, cellulose chains are hydrolysed and subsequently converted into glucose and its isomerisation fructose in the range 180 to 240 °C. The time consumed in the first step decreases with the reaction temperature. The yield of glucose can reach its maximum value in the first 10 min under 200 °C (Nagamori and Funazukuri, 2010). In the subsequent reaction stage,

the monomers of the organic acids are decomposed into hydronium ions, which can be considered as the catalysts for the dehydration. The monomers produced from the hydrolysis of the oligomers undergo a dehydration reaction, resulting in the opening of the ring and breaking of the C-C bonds, and then subsequently form into various furans at temperatures near 130 °C (Chheda et al., 2010; Sinag et al., 2010). Acids and phenols are obtained from the decomposition of the furans with the HTC process. Simultaneously, dehydration or aldol condensation and formation of aromatic polymers occur as well. The hydroxyl groups in the monomers get dehydrated and converted into C=O groups (Bacon and Tang, 1964). Aromatic clusters appear due to the condensation of the aromatic units, which are formed due to the decomposition of the carbohydrates such as monosaccharides. As a result, more oxygen groups may get concentrated on the surface of the char particles than in the core forms.

Parameters such as temperature, duration, pH, and the use of catalysts have different effects on the conversion pathways and kinetics. For example, the pH of the liquid sharply decreased at the beginning and then either remained low or slightly increased. The inflection time point for the pH rise depends on the reaction temperature. Furfural and 5-HMF intermediates formation may be responsible for this trend, as they account for the production of various acids, as already observed elsewhere (Reza et al., 2014). Meanwhile, the pH of the liquid after the introduction of lignin to the HTC process showed a tendency contrary to the result of cellulose introduction. The pH increased with the reaction time and temperature rise, as most of the phenolic compounds are derived from lignin degradation and not from acids. According to previous tests in

different conditions, the content of hydrochar derived from lignin is more than that from cellulose because the structure of lignin is an aromatic molecule prone, which can be condensed with other polyphenolic compounds (Braghiroli et al., 2017; Selmi et al., 2018).

However, there is no obvious agreement on the kinetic parameters for cellulose conversion. Most open literatures show various E_a and K_0 values due to the wide range of reaction temperatures, durations and catalyst use (Danon et al., 2014; Kim et al., 2011; Liu et al., 2014).

Lignin is a phenyl propane biopolymer, and consists of three different phenyl propane monomer units named p-coumaryl, coniferyl, and sinapyl alcohol (Wang et al., 2018).

The structure of lignin can be randomly formed by the combination of those three monomer units. Hence, the reaction pathways of lignin are complex. Figure S2 proposes a simplified mechanism for carbon-containing substance transformation from lignin via the HTC process. In the first reaction stage, lignin quickly degraded into dissolved and non-dissolved parts. When the reaction temperature was low, a part of the lignin did not completely dissolve. The transformation of non-dissolved lignin into phenolics required more time at a relatively low reaction temperature.

Polymerisation was then seen after prolonged residence time, which led to the generation of high molecular weight polymers on the char surface. The pathway of solid-solid formation from lignin is similar to pyrolysis, which produces highly condensed char as well. On the other hand, a small amount of dissolved lignin was exposed to water. These fragments of dissolved lignin were converted to syringols,

guaiacols and catechols, and were subsequently decomposed into phenols and aromatics (Wahyudiono et al., 2010; Wahyudiono et al., 2009). Aromatic oligomers were formed through re-polymerisation on the surface of the phenolic char in the process.

The results of previous studies on the characteristics of the main experimental parameters are similar. Typically, the bio-oil yield increases with rising reaction temperatures from 250 to 350 °C (Fan et al., 2018). Furthermore, the reduction of nitrogen-containing compounds can be improved by various catalysts, however, the processing mechanism is not clear yet. Compared with this study, Figure S3 shows the typical reaction pathway of the protein model compounds through the HTC process.

The amino acids were first formed by hydrolysis where the peptide bonds (C-N) from the carboxyl and amine groups were broken (Peterson et al., 2008). Compared to cellulose and glucose hydrolysis under natural reaction conditions, the protein depolymerisation was more difficult. Due to the stability of the peptide bonds, it takes a long time to complete the depolymerisation process without changing the pH value or the catalyst. The Maillard reaction can be applied to generate several reactive intermediates under a mild reaction temperature. At higher temperatures, carbonisation and subsequent pyrolysis became more pronounced. As the hydrothermal reaction temperature increased, there was a significant cyclisation of the intermediates. Besides, the N-containing compounds were enhanced by polymerisation which is also proved by the enhancement of the C-(O,N) functional group. It is noteworthy that the hydrothermal conditions and the pH value in the

solvent have a significant effect on the decomposition of amino acids (Abdelmoez et al., 2007). The major N-containing components from the protein showed a small difference in both the middle range condition and various moderate conditions according to the previous study (Teri et al., 2014). It was also revealed that the main composition of the solid products derived from the protein showed a little variation within a certain range of reaction times and temperatures. Indeed, the total N-containing compounds after the polymerisation for the solid product from the protein were very similar.

4. Conclusions

In this paper, the morphology of the carbon-containing substances and the microstructure of char derived from SS and its relevant model compounds have been investigated. The G, D, and Kekule bands of SS and the char have been categorised according to their locations and intensities. It was revealed that these bands are almost the main aromatic vibrational bands in the whole sample. The results of the D/G ratio indicate that six or more benzene rings were formed during the HTC process. Furthermore, the dehydrogenation of the hydroaromatics and subsequent formation of aromatic rings occur at 260 °C. It is believed that ZSM-5 with a high Si/Al ratio has a positive effect on the graphite degree under a moderate hydrothermal temperature of 260 °C. Compared with the smaller Si/Al ratio of 38, the higher ratio favoured depolymerisation of C-(C,H) during the HTC process. For the model compounds, cellulose has a dramatic influence on the depolymerisation of C-(C,H). The char derived from glucose, cellulose, and lignin has several similar carbon-containing

groups, such as COOR, R-C=O, and C-OR. The char surface morphology evolution indicated that individual model compounds have different influences on the surface morphological characteristics. Smaller particles were obtained with the ZSM-5 assistance during the SS treatment. Finally, three reaction pathways from SS and its relevant model compounds to char have been proposed. This work provides insight into the morphology and microstructure of catalytic HTC process from SS and its model compounds, and may provide better understanding of the char structure and the HTC process mechanism.

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Fig.1. Raman spectra deconvolution with fitting curve (G, G_R, V_L, V_R, D, S_L, S_R) of the bands in the 1000–1800 cm⁻¹ range for the SS and its relative model

compounds derived char (MC: Model compounds mixture, SP: Soybean protein,
 L: Lignin, C: Cellulose, G: Glucose).

Table 1 Summary of typical bands for Raman spectra(Tuinstra and Koenig, 1970;
 Zhao et al., 2016)

Name	Position (cm ⁻¹)	Description
G Band	1580	Graphite; aromatic ring; C=C
	G _R 1540	Small Aromatics rings (3–5 rings)
Kekule Band	V _L 1465	C-H ₃ or C-H ₂ ; semi-circle breathing of aromatic rings;
	V _R 1380	Methyl; aromatic rings; amorphous carbon;
D Band	1310	highly ordered carbonaceous materials; C-C
S _L Band	1230	Aryl-alkyl ether; para-aromatics
S Band	1180-1100	aromatic ethers; C–C;
S _R Band	1100-1050	C–H on arene rings; benzene ring

Fig.2. Comparison of band area ratios as a functional parameter among the

hydrothermal conversion chars derived from SS and its model compounds.

Fig.3. The XPS C 1s spectra for SS, its derived char, and char derived from its model compounds

Fig.4. Percentage content of carbon-containing functional groups C-H, C-(C,H), C-OR, C-(O,N), R-C=O, and COOR during HTC process.

Fig.5. SEM micrographs of (a) SS, char produced at 260 °C from (b) SS by hydrothermal process, (c) SS with ZSM-5 catalyst (Si/Al:38), (d) SS with ZSM-5 catalyst (Si/Al:300), (e) model compounds mixture, (f) SP, (g) Lignin, (h) Cellulose, and (i) Glucose.