Suppression of tar and char formation in supercritical water gasification of sewage sludge by additive addition

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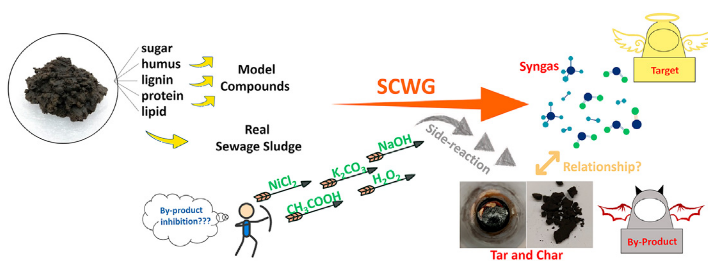
HIGHLIGHTS

- Char yields were inhibited with ad ditives, tar yields were still reached 13.3 18.8%.
- The effect of additives on char/tar formation from different components was different.
- Carbon distribution in products was changed by additives.
- The use of additives will affect the gasification efficiency at same time.

GRAPHICAL ABSTRACT



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ABSTRACT

This study explored the feasibility of char and tar formation inhibition during supercritical water gasi fication of sewage sludge (SS) by additive addition. Experiments were conducted in autoclave with 5 wt% additives at 400 °C for 30 min. The non additive gasification of SS resulted in a higher char yield (12.6%) and tar yield (16.4%). In contrast, the five additives reduced the char yield (3.4 11.2%), the inhibition of char yield by additives was in the order of NaOH > K_2CO_3 > H_2O_2 > acetic acid > $NiCl_2$. The inhibition of tar formation was limited, tar yield were 13.3 18.8% with additives. Fourier transform infrared spec troscopy was used to determine the functional groups of char/tar, and it was observed that the spectra of char were more similar to those of hydrochar obtained in a low temperature experiment. Model com pounds of potential precursors was also tested to study the mechanism of action of additives, the results reveal that additives have different effects on char/tar formation from various components, the inhibitory effects of additives on the yield of char from humus and tar from lignin were limited. Finally, the effects of additives on gasification were also studied. The addition of additives will have an impact on the hydrogen yield and gasification efficiency, which also needs to be considered when use additive to reduce the by products yield.

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1. Introduction

Sewage sludge (SS) is an inevitable by product of wastewater treatment. Owing to its high moisture content and complex organic composition, it can easily cause secondary environmental pollution if it is not treated properly. At the same time, SS also has high potential for use in the bioenergy field owing to its high organic matter content of approximately 50 wt% on a dry basis. The use of SS as a resource has increasingly attracted the interest of researchers (Shi et al., 2019; Wei et al., 2020). Supercritical water gasification (SCWG) of wet biomass such as SS is a promising method of using biomass energy (Qian et al., 2016), as it allows SS to be treated without needing to be dried and transforms the organic matter in SS into syngas, which can be used as clean energy through further purification (Chan et al., 2019a, 2019b; Dou et al., 2019).

Tar and char formation, as an unwanted side reaction during SCWG, is a bottleneck in this technological development. The terms char and tar mainly refer to the solid organic substances and residual viscous oily substances with a high carbon content, respectively; they have no clear molecular formulae or definitions. The formation of tar and char has negative effects on the SCWG of SS, such as reducing the efficiency of syngas production (Chuntanapum and Matsumura, 2010), deactivating heterogeneous catalysts (Wang et al., 2018), blocking the continuous reactor (Molino et al., 2016; Lu et al., 2006), and reducing the heat transfer efficiency. However, few studies have focused on the inhibition of tar/char formation, although the formation of char and tar during SCWG of some types of biomass (either of model compounds or real biomass) has been widely reported (Peng et al., 2017; May et al., 2010; Titirici et al., 2008; Asghari and Yoshida, 2006; Antal et al., 2000). As a waste biomass with a very complex organic composition, SS is more likely to produce tar and char during SCWG.

The hydrothermal processes can be directed differently by reaction conditions. In all cases, gas, liquid, and solid products are formed, but with a very different product distribution. The most important reaction parameter is temperature. A large amount of hydrothermal char and a small amount of hydrogen will be generated in the range of 200 °C–300 °C; this temperature range is used to obtain biochar materials (Kruse, 2008). At 300 °C to the critical temperature, the tar yield is higher. This is the temperature range for hydrothermal treatment of algae to obtain biocrude. Free radical reaction is promoted under supercritical water conditions while organic matter is largely converted into gaseous products. With the increase in the reaction temperature, the gasification efficiency (GE) will be greater. Kruse (2008) pointed out that hydrogen is the main product when the temperature is above 600 °C. Müller and Vogel (2012) tested the tar/char yield from SCWG of glycerol with different concentrations at a temperature range between 300 °C and 430 °C, and found that no char or less char is produced at a temperature close to 400 °C and the tar yield also decreases with the increase in temperature. Our previous study also found that a higher reaction temperature and longer retention time are beneficial to reducing the char/tar yield (Wang et al., 2019).

To inhibit the formation of tar and char by changing the reaction conditions, the operation cost will be greatly increased. Another more economical way to solve this problem is by using an additive during SCWG, but only a few studies have focused on tar and char suppression using additives. Matsumura et al. (2018) reported that char is inhibited by adding organic acid as a free radical scavenger in SCWG of guaiacol and shochu residue at 580–620 °C. Oxidants such as H_2O_2 can destroy the structure of ring compounds (Zhang et al., 2020), while tar contains many nitrogen heterocyclic compounds and aromatic compounds (Wang et al., 2020). The small molecular organic matter after ring opening will be more easily gasified and may reduce the tar yield. In addition, Gong et al. (2017) reported that Lewis acid can improve the GE of humic acid, thereby promoting the disintegration of char derived from humic acid. However, whether organic acids, oxidants, and Lewis acid can inhibit the formation of tar and char during SCWG of SS requires further verification. Muangrat et al. (2010) showed that by adding alkaline additives and nickel based catalysts, the char deposition on the surface of the catalyst can be reduced, thereby slowing the deactivation of the catalyst.

At present, the mechanism of tar and char formation is still unclear, which also hinders the research progress of tar and char inhibition. The most unified understanding is that carbohydrates are the precursor of char formation. Many experiments have been conducted using polysaccharides (Karayıldırım et al., 2008; Fang et al., 2008), monosaccharides (Chuntanapum and Matsumura, 2010; Knezevic et al., 2009), and other intermediates of carbohydrate gasification (Chuntanapum and Matsumura, 2010) as reactants to verify this conclusion, and intermediate product 5 Hydroxymethylfurfural (5 HMF) is considered to be closely related to the formation of char. In addition to carbohydrates, SS contains a variety of other organic components, which are mainly humus, proteins, lipids, and lignin. In our previous work (Wang et al., 2020), the model compounds of five typical organic components in SS were tested in subcritical and supercritical water. It was found that in addition to that of carbohydrates, the char yield of humus was also very high. Udayanga et al. (2019) also reported that humic acid in SS increased the carbon content in the derived char to 35.2% compared to that in the char derived from the raw sludge (31.0%). The contents of different organic components in SS are also very different. According to the statistical results of 18 types of SS, the proportion of carbohydrates is only approximately 10%, and the proportion of humus is approximately 20–40%. Therefore, the contribution of humus to char formation was even greater than that of carbohydrates in SCWG of SS. Besides, due to chemical vapor deposition, hydrocarbon gas in syngas product is also one of the possible ways to form char. However, Xu et al. (2011) studied the gas composition of SCWG of SS at 400 °C for 30min, the proportion of hydrocarbon gas in total gas was only 8.32%. Moreover, higher temperature is needed for vapor deposition, but hydrothermal conversion temperature is not enough to achieve this condition, so the influence of this pathway on char formation is usually ignored.

Müller and Vogel (2012) determined the char and tar yield from SCWG of phenol and hydroquinone, which usually serve as the model compounds of lignin, and no char or solid residues were found. Therefore, lignin can be ruled out as a precursor for the formation of char, but some studies have reported biocrude produced by hydrothermal conversion of lignin and lignin rich biomass (Breunig et al., 2018; Arturi et al., 2017). In addition, tar formation has also been found in the SCWG of protein containing biomass (zoo mass) (Kruse et al., 2007) and model compounds of lipids (glycerol) (Müller and Vogel, 2012). Our previous study of model compounds also found that proteins and lignin tend to produce tar (Wang et al., 2020). Therefore, lignin, proteins, and lipids may all be precursors of tar.

In summary, it can be seen that it is more economical to use appropriate additives than to change the reaction conditions for char/tar inhibition. Therefore, the effects of additives on tar and char formation in the SCWG of SS were systematically examined in this study. NaOH, K_2CO_3, acetic acid, $NiCl_2$, and H_2O_2 were selected as additives, which were used as representatives of a strong base, weak base, organic acid, Lewis acid, and oxidant, respectively. Gasification experiments of real SS and model compounds were then conducted in a micro autoclave at 400 °C for 30 min with the aim to (1) clarify the effects of different types of additives on char/tar yield; (2) clarify the effects of additives on char/tar yield of various organic components; (3) clarify whether additives for char/tar inhibition will simultaneously affect the gasification reaction.

2. Materials and methods

2.1. Materials

The SS sample was collected from a wastewater treatment plant in Karlsruhe, Germany. The main source of wastewater is domestic sewage and rain water, and the SS dewatering method utilized in this wastewater treatment plant is centrifugation. The sample was stored in a refrigerator at a temperature below 4 °C. Before the experiments, the water in the SS was removed by freeze drying, and then the dry SS was ground into a powder to prevent an un even SS composition from affecting the experimental results. The basic properties and organic matter composition of the SS are shown in Table 1, gross chemical fractionation of organic matter in the SS was performed using Waksman's method (Hattori and Mukai, 1986). Besides, five model compounds were selected to represent the five organic substances in SS and also be tested. Humic acid, glucose, glutamic acid, guaiacol, and glycerol were model compounds of humus, sugars, proteins, lignin, and lipids, respectively.

The model compounds and different additives used in the study were purchased from Sigma Aldrich, and all the reagents were American Chemical Society grade. HPLC grade dichloromethane (DCM) purchased from Sigma Aldrich was used for recovery of the tar from the reaction vessel.

2.2. Experimental procedure and product separation

All the experiments were conducted in a stainless steel micro autoclave with a volume of 24.5 mL. The experimental procedures are shown in Fig. 1. First, the feedstocks (real SS or model com pounds) were mixed with distilled water to an moisture content of 80 wt% and added to the micro autoclave. The pressure was set to a predetermined value by adjusting the amount of solution filling the autoclave. The amount of water in the feedstock was 5 mL in this experiment. According to the IAPWS IF97 thermodynamic param eters of water and steam (Wagner et al., 2000), the pressure was 26.5 MPa at 400 °C, which was beyond the critical point (22.1 MPa; 374 °C). Nitrogen gas was then used to remove undesired air from the reactor. Heating was performed in an oven with thermal control at a heating rate of 40 °C/min, and the final temperature was maintained at 400 °C for 30 min. After the reaction, the reactor was removed from the oven and cooled by fan.

The micro autoclave was placed in an airtight gas collecting device and opened to release the gas. The collecting device was described in a previous study (Barreiro et al., 2015). A syringe was used to obtain part of gas from the valve of the collection device, this part of the gas is used for gas component analysis, and the rest amount of gas produced was measured by the displacement of water. Subsequently, solid phase and liquid phase products were separated by filtration. DCM was used to rinse the residue and tar remaining on the walls of the autoclave, and the DCM mixture was also filtered and separated. After filtration, wet solid residue and a mixture of water and DCM were obtained. The solid residue was dried in the oven overnight at 105 °C. The resultant product was char when the feedstock was model compounds. When the feed stock was real SS, the dried solid residue was extracted by tetra hydrofuran (THF) and the insoluble organic matter in the THF was defined as char (determined by loss on ignition at 550 °C for 4 h) (Xu et al., 2012). The aqueous phase was removed by syringe after static stratification of the mixture of water and DCM. Tar was ob tained after the DCM was removed by blowing nitrogen over it.

2.3. Analyses of products and data interpretation

After product separation, the gas composition was determined by manually injecting 100 μL of the gas sample into a gas chro matograph (7890A, Agilent, USA) equipped with a 2 m MolSieve 5 Å and 2 m Porapak Q column, and the gas yield was calculated using Equation (1).

$$Gas\ yield\ (mol\ /\ kg\ organic\ matter)\quad \frac{Mole\ of\ gas}{Mass\ of\ organic\ matter\ in\ feedstock} \tag{1}$$

The GE, carbon gasification efficiency (CE), and hydrogen

Table 1
Properties of the tested sewage sludge.

Organic matter (wt.%)[a]	Ash (wt.%)[a]	Ultimate analysis (wt.%)[a]					Drying method
		C	H	N	S	O[b]	
60.63	39.37	28.37	4.73	4.37	0.53	22.63	Freeze-drying
Proteins (wt.%)[a]	Lipids (wt.%)[a]		Humus (wt.%)[a]		Lignin (wt.%)[a]		Sugars (wt.%)[a]
16.83	3.80		19.73		11.60		1.28

[a] On a dried basis.
[b] Calculated by difference: O (wt.%) 100 wt% - Ash (wt.%) - C (wt.%) - H (wt.%) - N (wt.%) - S (wt.%).

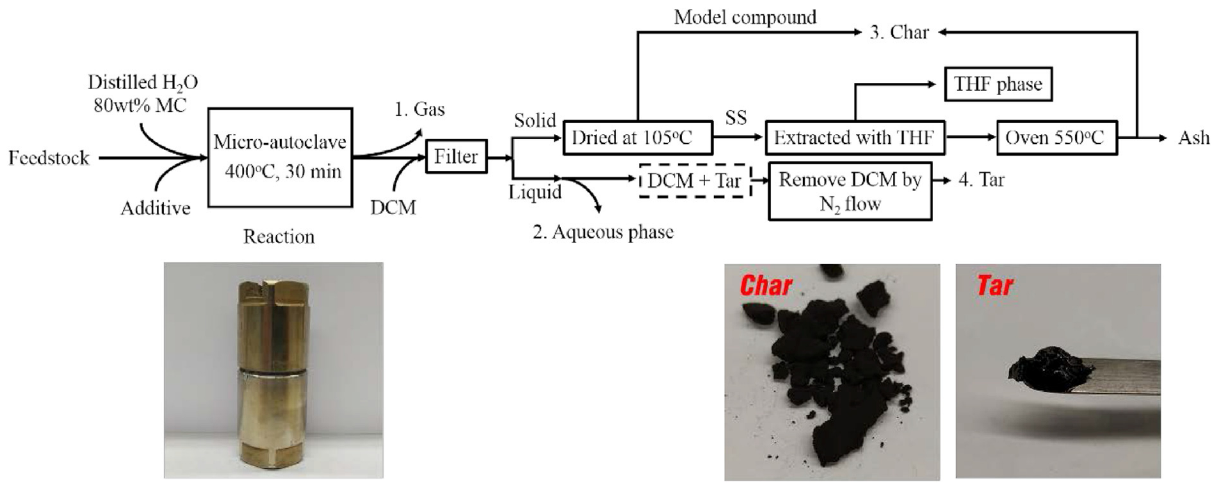

Fig. 1. Schematic diagram of the experimental procedure.

gasification efficiency (HE) were defined according to Equations (2)–(4) to indicate the extent of the gasification reaction.

$$GE\ (\%)\ \frac{Total\ mass\ in\ the\ product\ gas}{Total\ mass\ of\ organic\ matter\ in\ the\ feedstock\ (dry\ basis)} \times 100\% \tag{2}$$

$$CE\ (\%)\ \frac{Total\ carbon\ in\ the\ product\ gas}{Total\ carbon\ in\ the\ feedstock\ (dry\ basis)} \times 100\% \tag{3}$$

$$HE\ (\%)\ \frac{Total\ hydrogen\ in\ the\ product\ gas}{Total\ hydrogen\ in\ the\ feedstock\ (dry\ basis)} \times 100\% \tag{4}$$

The carbon content in the aqueous phase was measured by TOC. An elemental analyzer (Vario EL cube, Elementar, Germany) was used to measure the elemental composition (C, H, N, and S) of the raw SS and carbon content in the solid residue. A Fourier transform infrared spectroscopy (FTIR) spectrometer (Varian 660, Agilent, USA) was used to determine the functional groups present in the char and tar. In addition, the char yield and tar yield were calculated using Equations (5) and (6).

$$Char\ yield\ (\%)\ \frac{Mass\ of\ char}{Mass\ of\ organic\ matter\ in\ the\ feedstock} \times 100\% \tag{5}$$

$$Tar\ yield\ (\%)\ \frac{Mass\ of\ tar}{Mass\ of\ organic\ matter\ in\ the\ feedstock} \times 100\% \tag{6}$$

3. Results and discussion

3.1. Influence of additives on the tar/char yield from dewatered sewage sludge

The char yields from SCWG of real SS are shown in Fig. 2 (a). All five additives reduced the char yield to some degree, and the inhibition extent of the char yield was in the order of NaOH > K_2CO_3 > H_2O_2 > acetic acid > $NiCl_2$. The highest yield of char was produced from the blank test, for which the char yield was 12.6%. By contrast, adding 5 wt% NaOH could reduce the char yield to 3.4%, and the char yields were in the range of 3.9–11.2% with the other four additives.

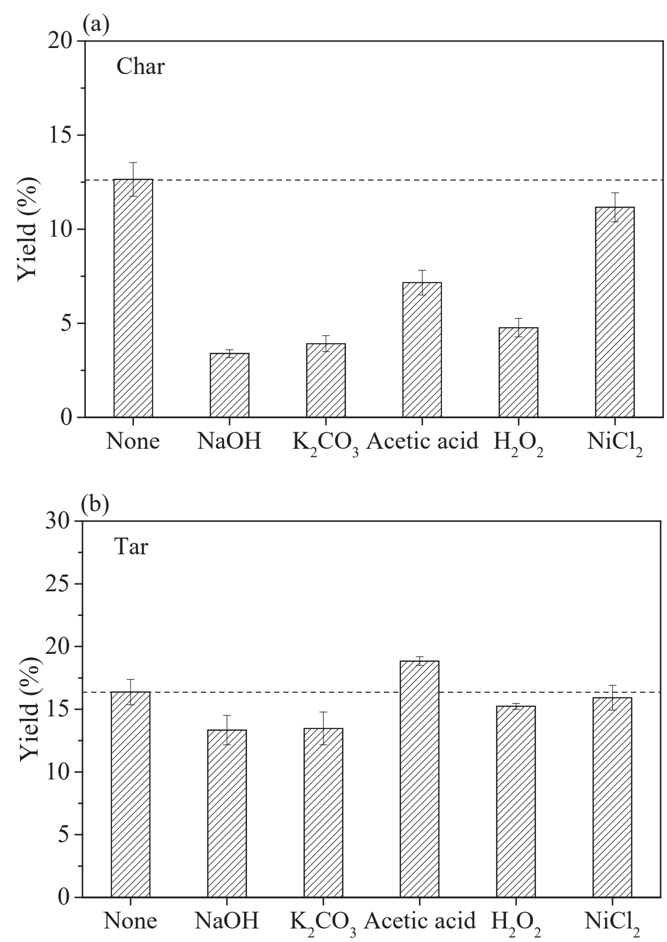

Fig. 2. Influence of different additives on the yield of (a) char and (b) tar in a 24.5 mL autoclave at 400 °C for 30 min.

Compared with the inhibition of char yield, the inhibition effect

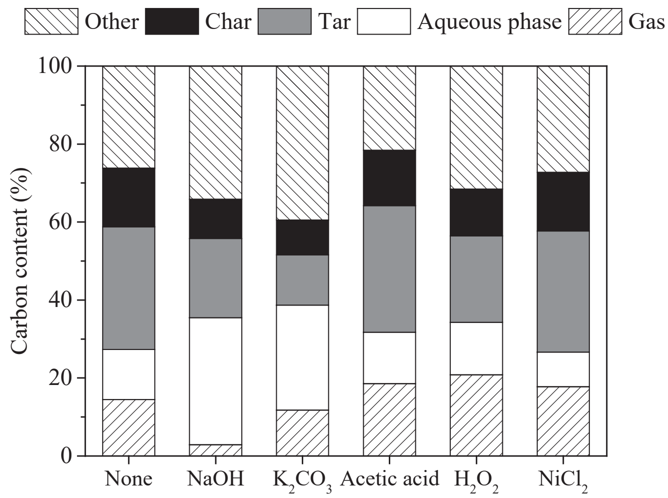

Fig. 3. Influence of different additives on the distribution of carbon in products in a 24.5 mL autoclave at 400 °C for 30 min.

of additives on tar yield were limited; the tar yields with or without additives are displayed in Fig. 2 (b). The effect of each group on the tar yield was in the order of NaOH > K_2CO_3 > H_2O_2 > $NiCl_2$ > blank test > acetic acid. The clearest inhibitory effects were caused by the two alkali additives, but the tar yields still reached 13.3% and 13.5%, while the tar yield was 16.4% in the blank test. The tar yields were 15.2−18.8% when adding the other three types of additives, which were much closer to the tar yield in the blank test (16.4%). When acetic acid was used as an additive, the formation of tar was promoted.

To further understand the mechanism of the additive's effect on the reaction, Fig. 3 shows the distribution of organic carbon in the product after the reaction, and the transformation between the products after adding different additives was determined.

It can be seen that when an alkali additive was used, the proportion of organic carbon in the aqueous phase could be effectively promoted regardless of the basicity. When NaOH and K_2CO_3 were added, the carbon content in the aqueous phase was 32.5% and 27.0%, respectively, while that in the blank test was 12.8%. It can be inferred from the carbon distribution before and after the reaction, the increase in the carbon content in the aqueous phase was maybe caused by two processes. First, CO_2 and CO in the gaseous phase generated HCO_3^- and CO_3^{2-} in an alkaline environment, Gong et al. (2014a) described in detail the capture of CO_2 by alkaline solution in SCWG, CO also further generates CO_2 in alkaline environment and was subsequently captured. That was the reason why the proportion of organic carbon in the gaseous phase product decreased. Second, the hydrolysis reaction of some organic compounds, such as esters, was promoted with alkali additives. That is, more organic carbon in the solid phase was transferred to the aqueous phase, thereby implying that more organic matter in SS was decomposed during SCWG.

Fig. 4 shows the reduction degree in the char/tar yield and carbon content in the char/tar when using different additives. The bar in the graph represent the degree of reduction (when bars are below the ordinate indicated increase). The change in the char/tar yield caused by additives was not consistent with that of the carbon content in the char/tar after using additives. The reduction in the char yield was greater than that of the carbon content in the char. Taking the experimental result of the addition of NaOH as an example, the reduction in char yield was 73.2% with NaOH, while that of carbon content was 33.3%. The char yield and carbon content are both based on the unit weight SS, the difference between the two factor indicated that more oxygen and hydrogen were lost in the process of char formation under the action of NaOH. This may be due to additional dehydration reactions occurred during the suppression of char formation. In addition, the reduction in tar yield was generally less than that of carbon in the tar, which indicated more carbon loss during tar formation with additives, may be owing to occurrence of a decarboxylation reaction and demethanization. Thus, additives not only reduced the yield of tar and char, but also affected the elemental composition and chemical properties of the tar and char.

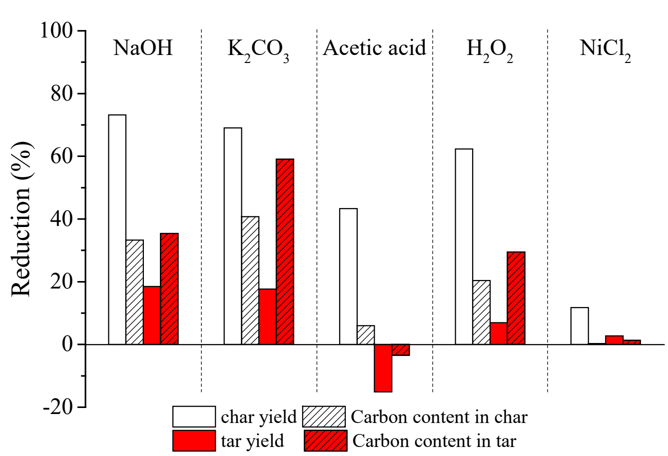

Fig. 4. Reduction in the char/tar yield and carbon content in the char/tar.

3.2. Fourier transform infrared spectroscopy analysis of tar/char from dewatered sewage sludge

FTIR analysis was conducted to investigate the functional groups of char and tar. The FTIR spectra of char with different additives are presented in Fig. 5 (a), and the main identification peaks are marked. The peak at 3410 cm^{-1} was attributed to −OH stretching vibration in hydroxyl or carboxyl groups (He et al., 2013). As shown in Fig. 5 (a), this peak of char with additives became weaker than that of the char without additives. This was due to the dehydration of char. These findings are in agreement with the results in Section 3.1. The peak at 1425 cm^{-1} was assigned to the −C=C stretching in aromatic ring carbons, which indicated that char may pose a potential environmental risk of persistent organic pollution (Kang et al., 2012). The intensity of this peak significantly increases when NaOH was added, and also slightly increase when $NiCl_2$ was used, which suggests the occurrence of aromatization with additives. However, as an alkaline additive, the same results was not found when K_2CO_2 was used. The aqueous solution of $NiCl_2$ was also slightly acidic. Therefore, the promotion of aromatization should be independent of the pH difference caused by the additive. Because of the extra dehydration occurred in the SCWG with additives, the aldol condensation and dehydration of ketones to form aromatic compounds is a possible pathway (Li et al., 2011), which needs to be further explored in the future. The peak at 2923 cm^{-1} was assigned to the asymmetric −C−H stretching of methylene groups (Silva et al., 2012). The peak at 1620 cm^{-1} was due to −C=O stretching vibration in ketone and amide groups (Silva et al., 2012), but this peak was not found when alkaline additives were used. In view of the effect of alkaline additives on hydrolysis during SCWG, it may be that amides were hydrolyzed into carboxylic acid or ammonia under the promotion of alkaline additives. And peak at 1043 cm^{-1} was associated with −C O R in aliphatic ethers and alcohol −C O stretching (ozçimen and Ersoy Meriçboyu, 2010). He

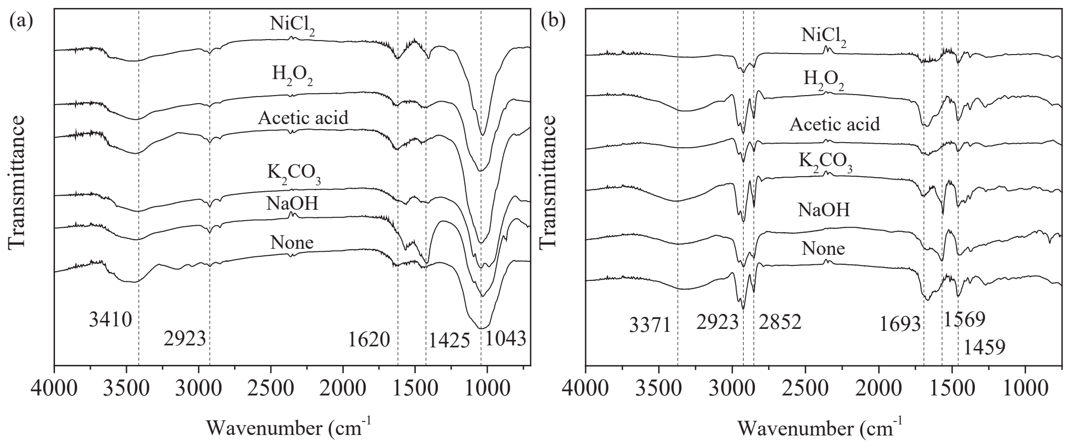

Fig. 5. Fourier-transform infrared spectroscopy spectra of (a) char and (b) tar with different additives.

et al. (2013) examined the hydrothermal carbonization of SS at 200 °C, and hydrochar was obtained. Although the reaction temperature in this study was much higher than that in He et al.'s experiments, the FTIR spectra of char produced in the two experiments were very similar. We also carried out the hydrothermal carbonization experiment of SS at 200 °C and confirm the conclusion, the FTIR spectra of obtained hydrochar is shown in Fig. S1 of the supplementary material. This indicated that the main formation stage of char is in the low temperature stage, while for SCWG, the low temperature stage is the heating stage.

The FTIR spectra of tar with different additives are presented in Fig. 5 (b). The peaks at 3371 cm^{-1} and 2923 cm^{-1} were same as those in the FTIR spectra of char, which were due to −OH stretching vibration and asymmetric −C−H stretching, respectively. The peaks of 3371 cm^{-1} still became slightly weaker with additives, which suggests that dehydration also occurred in tar formation with additive. However, combined with the previous results of Fig. 4, the effect of additives on dehydration was less than that on decarboxylation and demethanization. The peak at 2852 cm^{-1} was attributed to symmetric −C−H stretching of methylene groups (Silva et al., 2012), and the peaks at 1459 cm^{-1}, 1569 cm^{-1}, and 1693 cm^{-1} were all due to the −C=C stretching in aromatic rings (Kang et al., 2012; Foo et al., 2016). These peaks are basically consistent before and after the additives addition, indicating that additives have little effect on the functional group composition of tar, which may be the reason why additives have a little effect on tar yield.

3.3. *Influence of additives on the tar/char yield from each organic compound in dewatered sewage sludge*

As described in the introduction, humus and carbohydrates are potential precursors of char, and lignin, lipids, and proteins are potential precursors of tar. Five simple compounds with typical functional groups were selected as model compounds to represent these five organic substances. Humic acid, glucose, glutamic acid, guaiacol, and glycerol were model compounds of humus, sugars, proteins, lignin, and lipids, respectively. The influence of different additives on char/tar precursors was then studied.

The char yields with and without additives of two potential precursors of char are shown in Fig. 6 (a). It can be seen that without additives, the char yield of humic acid was higher (61.3%), while that of glucose was 19.5%. In addition, the effects of additives on the char yield of two model compounds were also different. The effect of additives on the char formation from humic acid was

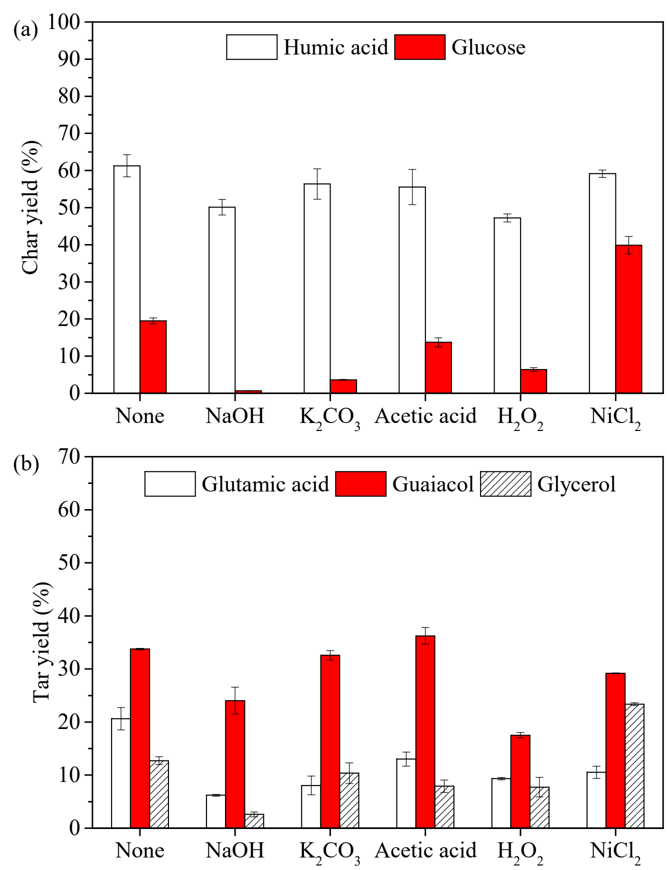

Fig. 6. Influence of different additives on the (a) char yield of humic acid and glucose and (b) tar yield of glutamic acid, guaiacol, and glycerol.

relatively limited. After using additives, the char yields were still 47.2−59.1%. By contrast, the char yield of glucose decreased to 0.63−13.70% under the action of additives, except for $NiCl_2$. This meant that the char produced by the two precursors may be different. Some researchers (Lucian et al., 2019; Volpe and Fiori, 2017) demonstrated that char formation occurs through two reaction pathways, namely (1) solid solid conversion, where char is formed by direct dehydration of biomass and is called primary char, and (2) polymerization reaction of organic matter in the aqueous phase to form secondary char. Karayıldırım et al. (2008) also observed two different structures by SEM in SCWG of real biomass and glucose, and pointed out that the char produced by glucose is secondary char. As indicated in Fig. 6 (a), the two alkaline additives had the clearest inhibition effect on the char yield of glucose, which might have been due to their promotion of hydrolysis and inhibition of the polymerization of intermediate products.

The tar yields of three potential precursors of tar are shown in Fig. 6 (b). The tar yields of glutamic acid, guaiacol, and glycerol without additives were 20.6%, 33.8%, and 12.7%, respectively. The five additives had the least effect on the tar yield of guaiacol, which might have been due to the stable benzene ring structure of guaiacol. The benzene ring structure of guaiacol and lignin may lead to a higher content of polycyclic aromatic hydrocarbons (PAHs) in the produced tar (Wang et al., 2020). The strong oxidation of H_2O_2 is beneficial to the decomposition of the ring structure, which is the most effective way to inhibit the tar yield of guaiacol. The tar yield of guaiacol was only 17.5% when H_2O_2 was added. In our previous studies (Wang et al., 2017), it has also been proved that H_2O_2 can effectively reduce the content of PAHs in products after SCWG of SS. NaOH had a certain inhibition effect on the tar yield of all three model compounds; therefore, NaOH had the most significant inhibition effect on the tar yield from SCWG of real SS.

Furthermore, the char/tar yields obtained from the model compounds were compared with the actual char/tar yields of SS. It is assumed that char and tar were only derived from these precursors in SS, and the tar/char yields obtained from the model compounds represent the tar/char yields of the corresponding organic component in the SS due to their similar chemical structure. That is, char was formed by humus and sugars in SS and that char yields of those were estimated by humic acid and glucose, while tar was formed by protein, lignin and lipid in SS and that tar yields of those were estimated by glutamic acid, guaiacol, glycerol. The theoretical char/tar yields of SS with additives can be calculated by the following equation:

$$\textit{Theoretical char yield}\ (\%) \quad m_{\text{Humus}} \times Y_{\text{Humic Acid}} + m_{\text{Sugar}} \times Y_{Glucose} \tag{7}$$

$$\textit{Theoretical tar yield}\ (\%) \quad m_{\text{Protein}} \times Y_{\text{Glutamic Acid}} + m_{\text{Lipid}} \times Y_{\text{Glycerol}} + m_{\text{Lignin}} \times Y_{\text{Guaiacol}} \tag{8}$$

where m was the proportion of each organic component in the SS (Table 1), and Y is the tar or char yields with additives of the model compounds corresponding to each organic component.

The comparison results are shown in Fig. 7, It can be seen that there was a significant difference between the experimental data of SS and the calculated value based on the model compound experiments (Fig. 7 (a), (b)). The reasons for this difference may be in the following three aspects: First, the model compounds are only the monomer substance, while the organic components contained in SS are much more complicated, so it is difficult to simulate the real reaction process completely. However, it can be seen from Fig. 7 (c) that there was a certain linear correlation between the calculated value and the experimental data of SS. This indicates that although the yield value is different, due to the structural similarity between the model compounds and the real components, the experimental results of model compounds can still reflect the same trend of char/tar yield under the action of additives. Secondly, SS contains a variety of organic components, and these components may interact during SCWG, and this interaction was not considered in the calculation method here. Finally, the influence of the first two points may be further amplified under action of additives. As shown in Fig. 7 (c), the calculated value has a poor correlation with the experiment data of SS when alkaline additives (NaOH, K_2CO_3) or oxidants (H_2O_2) was added, this may be due to the greater impact of these two kinds of additives on the simple model compounds. For example, guaiacol was used as the model compound of lignin, is more likely to undergo ring opening reaction under the action of oxidants than components with more complex aromatic structure.

3.4. *Influence of additives on gas yield*

The char and tar formation during SCWG of wet biomass will lead to a decline in the gas yield. However, the additives may also have an effect on the gas yield while inhibiting char and tar formation. The influences of the five additives on gas formation were studied, as discussed in this section.

The gas yield and gas composition from the SCWG of real SS with and without additives are shown in Fig. 8 (a), and the CE, HE, and GE are shown in Fig. 8 (b). In the absence of additives, the main gas was CO_2 and the proportion of H_2 was relatively low. This conclusion was confirmed in our previous non catalytic gasification experiments (Gong et al., 2014a, 2014b). The alkaline additives are usually regarded as catalysts of hydrogen production, and the hydrogen yields were increased by 5 times and 13 times under the action of NaOH and K_2CO_3, respectively. However, CO and CO_2 transfer into the aqueous phase in an alkaline environment; hence, the yields of CO and CO_2 were very low, and the CE and GE also significantly decreased. The CO_2 yield was increased slightly by adding acetic acid, but almost no H_2 was detected. Matsumura et al. (2018) used acetic acid as a free radical scavenger to inhibit the char formation by free radical reaction during SCWG of shochu residue, and found that acetic acid also inhibits hydrogen formation when the amount of acetic acid addition is too large. The radical that generates hydrogen was also eliminated, thereby resulting in a decrease in hydrogen yield. The amount of acetic acid in this experiment was 5 wt%, so subsequent experiments with lower addition are still needed. The hydrogen formation was also inhibited by H_2O_2, which was due to the reaction of H_2 with H_2O_2 to form water, but was also related to the amount of H_2O_2 addition. After adding H_2O_2, the CE and GE increased significantly. This might have been due to the decomposition of macromolecular organic compounds into smaller molecular compounds that are more easily gasified under the action of H_2O_2. Gong et al. (2017) added various Lewis acids, including $NiCl_2$, in the SCWG of humic acid, and found that the hydrogen yield and HE can be effectively improved. We have also determined the H_2 yield in SCWG of humic acid, the hydrogen yield in the SCWG of humic acid was 2.11 mol/kg feed with 5 wt% $NiCl_2$ dosage, compare to no $NiCl_2$ SCWG of humic acid was 0.45 mol/kg feed, the result was consistent with that of Gong et al. But in this experiment of SS, the promotion of hydrogen production by $NiCl_2$ was limited. This might have been because the composition of the real sludge was more complex than that of the model compound.

The relationship between the total char/tar yield and gas yield is shown in Fig. 9, the data in the figure include both of the experimental results of real SS and model compounds. On the on hand, the linear relationship between the gas yield and the yield of tar and char was not strict. The gas yield may be quite different, even if the char/tar yield was close. For example, the maximum gas yield (14.69 mol/kg organic matter) was approximately 14 times greater than the minimum (1.02 mol/kg organic matter) when the yield of tar and char was 5–10%. This was because the formation of tar and char may have a negative effect on the gas yield, but the type of reactants and additives are also related to gas formation. But on the

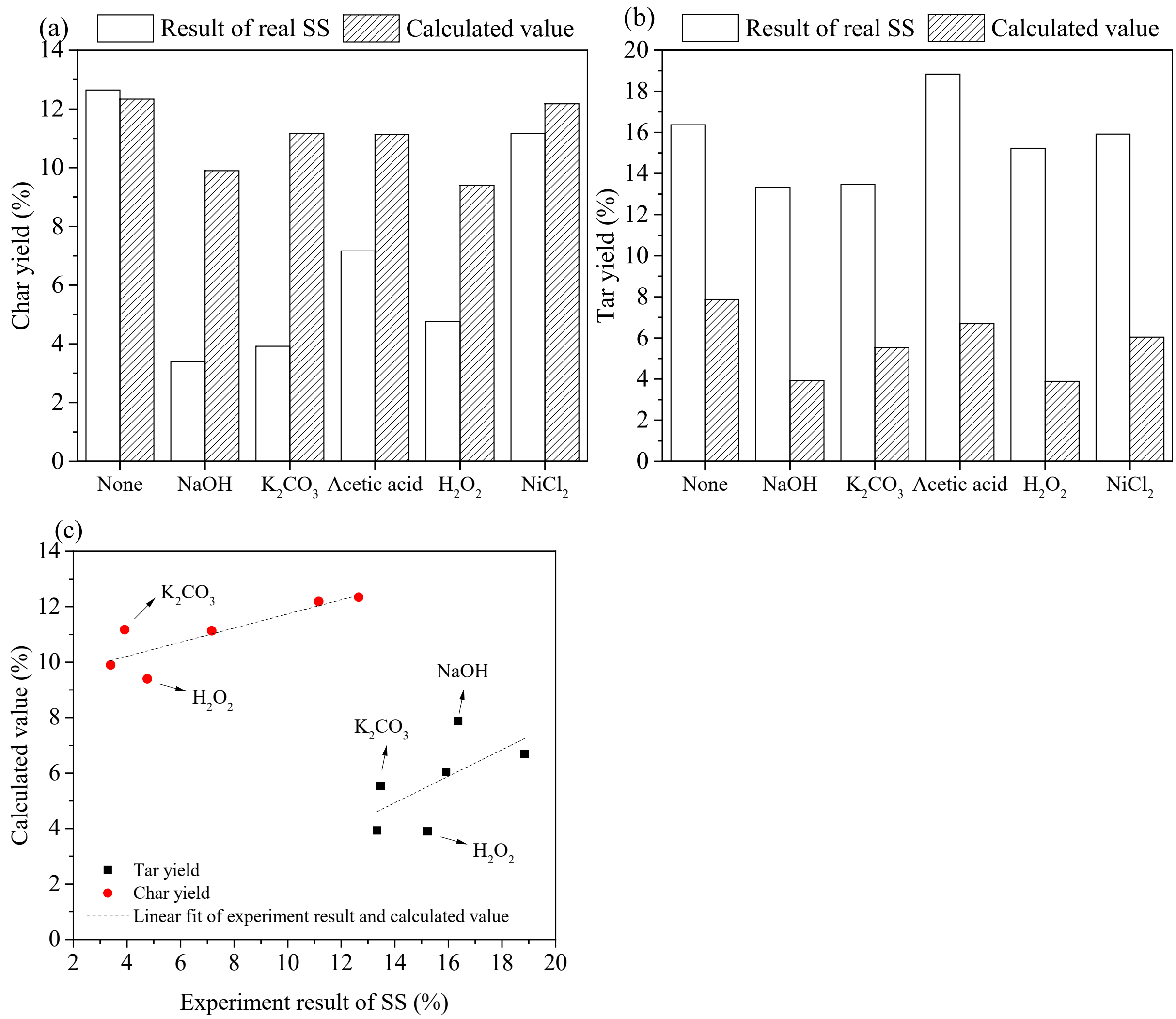

Fig. 7. Comparison of (a) char yield and (b) tar yield obtained from experiment of SS and calculation value, and (c) linear relationship between experiment result and calculation value.

other hand, as the sum of tar and char yield increased, the gas yield tended to decrease. Fig. 9 is divided into four regions according to the yields of tar and char. Regions (1)–(4) correspond to the yields of 0–20%, 20–40%, 40–60%, and 60–80%, respectively. The average gas yields of each region were calculated. The value decreased from 6.97 mol/kg organic matter (region 1) to 2.53 mol/kg organic matter (region 4). In addition, the gas yield decreased with the increase in the tar and char yield under the same additive. This result indicated that the gas yield was affected by different factors. This confirms the inhibition of gas formation by tar and char formation and also suggests that suitable additives can be added to specific biomass to promote gas yield by inhibiting the formation of tar and char.

4. Conclusion

The effects of five additives on char and tar formation during SCWG of real SS and model compounds were investigated in this study. The char formation was significantly inhibited by additives; the char yields were reduced from 12.6% to 3.4–11.2% with different additives, and the inhibition of char formation by examined additives was in the order of NaOH > K_2CO_3 > H_2O_2 > acetic acid > $NiCl_2$. The effect of additives on tar formation was limited; the tar yields were still 13.3–18.8% with additives, while the tar yield was 16.4% without additives. Additives affected the distribution of organic carbon among the products and the elemental composition of the char/tar. The functional groups of the char/tar were analyzed by FTIR, and it was found that the char spectra were very similar to those of hydrochar obtained in the low temperature experiment, which suggested that char may be formed at the heating stage.

The effects of additives on the char/tar yield from SCWG of various precursors were different. The effect of additives on yield of char derived from humus was small, but they were effective in the yield reduction of char derived from glucose, which was related to the different mechanisms of char formation between the two precursors. In addition, the effects of additives on tar formation from lignin were also limited. This was owing to the stable benzene ring structure of lignin. The oxidation property of H_2O_2 was effective in the destruction of the ring structure, and thus would reduce the tar yield of lignin. The additives also influenced the gasification reaction. Alkaline additives significantly reduced CO and CO_2 but promoted H_2 production. Acetic acid and H_2O_2 reduced the H_2 yield.

Credit author statement

Chenyu Wang: Conceptualization, Investigation, Writing

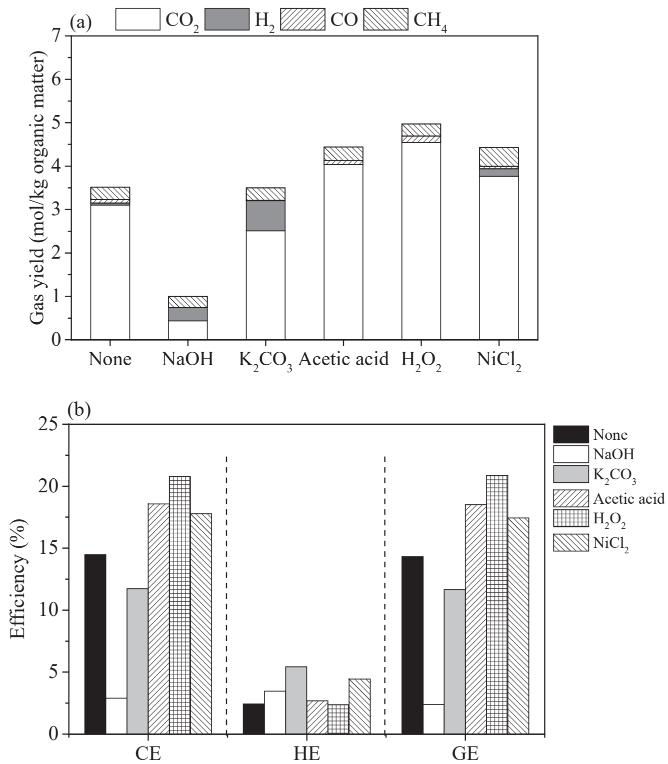

Fig. 8. (a) Gas yield and composition and (b) gasification efficiency (GE) from supercritical water gasification of sewage sludge with different additives.

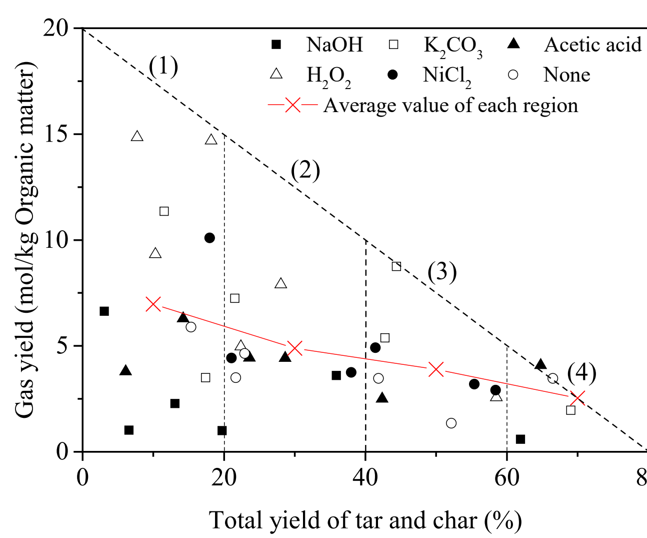

Fig. 9. Relationship between char/tar formation and gas yield from supercritical water gasification of real sewage sludge and model compounds.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.128412.

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