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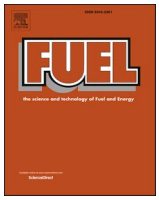
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Full Length Article



Catalytic pyrolysis of paper mill sludge over self-sourced CaO/biochar catalyst under different temperatures☆

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ABSTRACT

In order to realize the harmless treatment and resource utilization of paper mill sludge, the catalytic pyrolysis of paper mill sludge over a self-sourced CaO/biochar catalyst was studied in a two-stage fixed-bed pyrolysis reactor under different temperatures (500, 600, 700 °C) and catalyst/sludge mass ratios (0, 0.5, 1, 2). The experimental results showed that the catalyst addition and higher temperature could promote the decomposition of bio-oil vapors into small molecular gases such as H_2, CH_4, and CO, thus improving non-condensable gas yield and decreasing bio-oil yield. The optimal condition for gas production was when the proportion of catalyst to sludge was 1 at 700 °C. Under the condition, the gas yield was 176.80 ml/g sludge, and the H_2 concentration and yield were 31.97 % and 56.52 ml/g sludge, respectively. CaO/biochar catalyst could reduce the contents of oxygen-containing compounds in bio-oil including acids, esters, and ketones and improve the yield of hydrocarbons, indicating the improved quality of bio-oil. The N-heterocyclic compounds were the main nitrogen-containing species in bio-oil, mainly coming from the decomposition of protein at high temperature. CaO and biochar both played important roles during the catalytic pyrolysis process. In addition, the physical and chemical structures of the catalyst were greatly changed after the reaction. Carbonation of CaO with the CO_2 in the pyrolysis volatiles and the coke formation on the active sites of the catalyst would possibly happen during the catalytic pyrolysis process, resulting in reducing the specific surface area and pore volume of the catalyst. These research results prove that the self-sourced CaO/biochar catalyst plays an important role in the catalytic reaction and promotes the quality improvement of the pyrolysis bio-oil and gas.

1. Introduction

The pulping and papermaking industry is one of the largest industries in the world, as a consequence, the paper mill sludge generated in the wastewater treatment process becomes a major industrial waste [1]. The amount of the domestic paper mill sludge production accounts for about 40 % of the total industrial sludge in China annually [2]. Paper mill sludge normally contains difficult-to-degrade organic substances, trace amounts of heavy metals, pathogens, and other contaminants. Meanwhile, it contains a high amount of organic matter (40–50 %), which has a great potential for thermal utilization [3]. Unfortunately, most of the paper mill sludge currently is not disposed of properly.

Pyrolysis has shown distinct advantages in the treatment of paper mill sludge [4,5]. It can convert waste sludge into gas, liquid, and solid products under an inert atmosphere, where solid biochar can be used as a soil amendment and catalyst [6–8], and non-condensable gas and liquid bio-oil can be treated as fuel. Bio-oil, as the liquid product from paper mill sludge pyrolysis, often has a mass yield of exceeding 40 %, it can be potentially used as a biocrude for the production of green and sustainable fuels and chemicals [9]. However, the direct utilization of paper mill sludge bio-oil is rather difficult due to its high oxygen content, high viscosity, and corrosiveness [10]. Upgrading of bio-oil is thus necessary.

Catalytic pyrolysis is such a process for bio-oil upgrading, which can

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further break down the bio-oil molecules into smaller molecules with the help of catalysts. Among different catalysts, calcium-based materials, such as CaO, are recently developed and known to effectively promote the cracking of high-molecular-weight oxygenated compounds in bio-oil into smaller molecules [11]. Chong et al. [12] reported that CaO could effectively reduce the content of oxygen-rich organic compounds such as acetic acid in bio-oil and enhance its stability. He et al. [13] found that CaO significantly increased the content of aromatic hydrocarbons in bio-oil, while reduced its oxygen content, thus improved the saturates content and the quality of bio-oil. In the meantime, the porous biochar with a high specific surface area is also regarded as an excellent catalyst for bio-oil upgrading. The presence of various oxygen-containing functional groups on the biochar surface as well as its aromatic carbon skeleton are both found to be active during the cracking and deoxygenation of bio-oil, which can be also potentially used for the upgrading of bio-oil from paper mill sludge [14]. Jin et al. [15]demonstrated that biochar could catalyze the cracking of heavy compounds in bio-oil into lighter compounds and permanent gas. Yu et al. [16] found that biochar could effectively reduce the oxygen content and increase the hydrocarbon content in bio-oil. In addition, the CaO and biochar composite also starts to be used as catalyst recently during the catalytic pyrolysis process for bio-oil upgrading. Several novel materials containing calcium and carbon have been developed and have shown excellent properties[17,18]. By combining different types of polymer with oxides and carbon-based materials the new composites with increased and attractive electronic properties could be also fabricated. The addition of a second phase can significantly improve the electronic properties of the resulting composite material[19,20], which is conducive to the catalytic reforming of the sludge. For instance, Xu et al. [21] prepared CaO/biochar catalyst from the pyrolysis and calcination of phenol–formaldehyde resin and Ca $(OH)_2$, it was then used for the pyrolysis of soybean oil. They found that the addition of CaO/biochar significantly promoted the deoxygenation of bio-oil, resulting in the decrease of oxygen content from 14.4 % to 2.4 % and increase of aromatic hydrocarbons from 41.5 % to 81.6 %.

In fact, paper mill sludge has its own unique characteristics compared with other biomass wastes. Due to the papermaking process, the paper mill sludge normally contains a considerable amount of $CaCO_3$, the Ca content is usually over 6 wt% [22,23]. The pyrolysis behavior and bio-oil composition might be largely different with the other biomasses. Also, as a Ca-enriched material, the paper mill sludge has the potential to directly produce CaO/biochar composite catalyst using its own char from pyrolysis. Through a simple calcination process, the $CaCO_3$ in the char would be decomposed to form CaO/biochar. However, the use of CaO/biochar catalyst during the pyrolysis of paper mill sludge, especially the self-sourced CaO/biochar, is still rarely reported so far as we know. The influencing mechanism of CaO/biochar on the formation and distribution of pyrolysis products from paper mill sludge pyrolysis is still remained unclear.

Therefore, in this study, the self-sourced CaO/biochar composite catalyst was firstly prepared by pyrolysis and subsequent calcination of paper mill sludge, and then it was used during the pyrolysis of paper mill sludge process as a catalyst, the volatiles generated from pyrolysis of paper mill sludge immediately went through the downstream catalyst bed for catalytic cracking and reforming in a two-stage fixed-bed reactor. The influence of different temperatures and catalyst ratios on the pyrolysis products were analyzed. The catalytic performance of the CaO/biochar catalysts in the upgrading bio-oil and non-condensable gas was evaluated. The results shown in this study is expected to gain a more in-depth understanding on the mechanism of self-sourced CaO/biochar catalyst on the upgrading of pyrolysis product of paper mill sludge.

2. Experimental

2.1. Paper mill sludge

The raw paper mill sludge was obtained from a local paper-making company. It was dried, crushed, and screened to a particle size of $<$ 150 μm for use. Ultimate analysis of the dried paper mill sludge was conducted using an organic element analyzer (Elemantar, Vario EL cube model), the results showed that it contained 34.95 wt% carbon (C), 5.33 wt% hydrogen (H), 26.20 wt% oxygen (O), 5.51 wt% nitrogen (N), 0.55 wt% sulfur (S), and 27.46 wt% ash, on a dry basis. Proximate analysis of the paper mill sludge was carried out using a muffle furnace according to a China National Standard of "Compilation of General Standards for Coal" (GB/T 212–2008). The results showed that it had 27.46 wt% of ash, 60.47 wt% of volatile matter, and 12.07 wt% of fixed carbon. The content of Ca element in paper mill sludge was analyzed using ICP-OES equipment (Thermo Fisher iCAP PRO), the results showed that it contained 8.30 wt% of Ca.

2.2. Preparation of CaO/biochar catalyst

The CaO/biochar catalyst was prepared following a pyrolysis and subsequent calcination method as mentioned before. A horizontal tube furnace was employed during the process. Accurately weighed 0.5 g of dried paper mill sludge was loaded into the reactor. It was rapidly pyrolyzed at 600 °C for 30 min under a N_2 flow of 50 mL/min to obtain the catalyst precursor of $CaCO_3$/biochar. And then, the $CaCO_3$/biochar was further heated to 800 °C and kept for 2 h with a N_2 flow of 100 mL/min to produce the desired CaO/biochar catalyst. To obtain enough amount of CaO/biochar catalyst, multiple catalyst preparation experiments were conducted, and the resulted catalysts were thoroughly mixed and ground to ensure the consistency.

2.3. Catalytic pyrolysis of paper mill sludge

The catalytic pyrolysis of paper mill sludge over CaO/biochar catalyst was conducted in a two-stage fixed-bed reaction system, as shown in Fig. 1. It consisted of a carrier gas N_2 supply system, a quartz tube reactor (The length is 760 mm, with left and right outer diameters of 8 mm and 22 mm respectively) heated by an electric furnace, a condensation system composed of two acetone washing bottles immersed in an ice-bath, and a gas bag for collecting non-condensable gas.

For each trial, accurate weighed paper mill sludge (0.5 g) and CaO/biochar catalyst (according to the mass ratios of catalyst/sludge of 0, 0.5, 1, and 2) were loaded into the quartz tube reactor in advance as per Fig. 1, N2 flew through the reactor to remove the air inside with a flow rate of 50 mL/min. Firstly, the tube furnace was heated to the desired temperature (500, 600, and 700 °C) and the temperature of the two heating areas is consistent, and then the quartz tube reactor was promptly inserted into the furnace, the reactor outlet was immediately connected with the condensation system. The paper mill sludge inside the reactor was quickly heated and pyrolyzed to generate volatiles, which directly went through and interacted with the CaO/biochar bed, and the resulting vapor products were condensed in the acetone solution, and the non-condensable gas was collected with a gas bag. Each trial lasted for 30 min, and immediately after the experiment, the quartz tube reactor was disconnected from the condensation system and quickly removed from the furnace for rapid quenching. After cooling to room temperature, the solid biochar produced from pyrolysis of paper mill sludge and the CaO/biochar after catalytic pyrolysis were collected for further analysis. The bio-oil captured inside acetone bottles was mixed and collected in a sealed bottle. All the other condensates in the reactor outlet pipe and connecting pipes were also washed with acetone, collected together, and stored in the same bottle in a freezer at −19 °C. Each trial was repeated two or three times to ensure the reliability of the experimental results, an average value with the standard deviation was

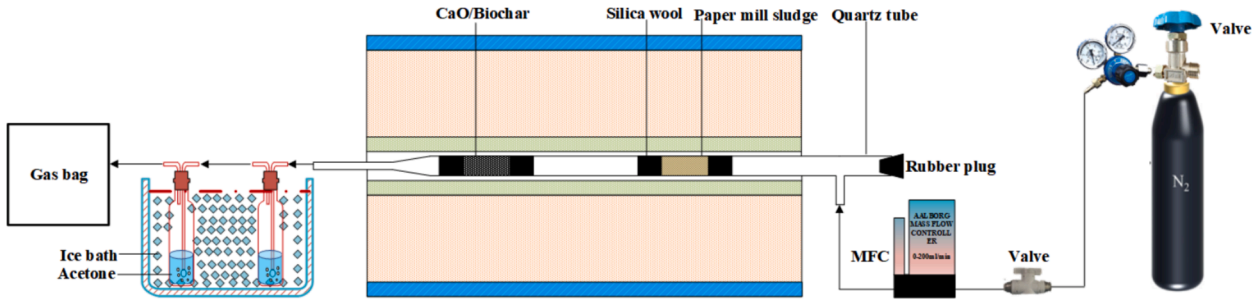


Fig. 1. The diagram of a two-stage fixed bed pyrolysis reaction system.

finally reported in the study.

2.4. Characterization of pyrolysis products and CaO/biochar catalyst

2.4.1. Non-condensable gas

The composition of the non-condensable gas was analyzed by a gas chromatography with a thermal conductivity detector (TCD) and a flame ionization detector (FID) (GC-9790II, Zhejiang Fuli Analytical Instrument Co., Ltd.). The major gas components detected by GC are H_2, CH_4, CO_2, CO, C_2H_4, C_2H_6, C_3H_6, and C_3H_8. For simplicity, C_2-C_3 will be used to represent C_2H_4, C_2H_6, C_3H_6, and C_3H_8. The yield of the non-condensable gas was calculated using the N_2 balance as described elsewhere, as the N_2 volume in the product gas (50 mL/min × 30 min = 1500 mL) and the N_2 concentration (from GC results) were known [24,25].

2.4.2. Newly generated biochar and CaO/biochar catalyst

The newly generated biochar is the solid residue after pyrolysis of paper mill sludge. When there was no catalyst addition, the weight difference of the reactor tube before and after the pyrolysis experiment can be obtained by direct weighing. The yield of newly generated biochar can be thus calculated by subtracting the initial weight of the paper mill sludge and the above weight difference. For the catalytic pyrolysis process, since only the volatiles from the pyrolysis of paper mill sludge interacted with the CaO/biochar catalyst, while the newly generated biochar surely did not contact and react with the catalyst bed, the yield of biochar was thus assumed to be the same as that during the non-catalytic pyrolysis process at the same temperature. The newly biochar yield were calculated using following equations:

$$Y_{char} = \left(m_{char}/m_{sludge}\right) \times 100\% \quad (1)$$

$$m_{char} = m_{sludge} - (m_1 - m_2) \quad (2)$$

Among them, m_{char} represents the mass of biochar collected after the reaction, m_{sludge} represents the original mass of sludge before the reaction, m_1 represents the sum of the mass of the reactor and the original sludge before the reaction, and m_2 represents the sum of the mass of the reactor and the residual biochar after the reaction.

The CaO/biochar catalysts before and after experiment were subjected to X-ray Diffraction (XRD) and N_2 adsorption–desorption tests to identify the possible structure changes during the experiment.

2.4.3. Bio-oil

The yield of bio-oil was calculated by difference, as the yields of other two products (biochar and non-condensable gas) were determined as mentioned above. It should be mentioned that, as bio-oil was captured by acetone, the evaporation of acetone would be difficult to quantify, and the direct weighing method was thus inappropriate for acquiring bio-oil yield.

The composition of bio-oil from the non-catalytic/catalytic pyrolysis of paper mill sludge was analyzed with a Gas Chromatography-Mass Spectrometry (GC–MS, Agilent 6890 GC and 5975 MS) with a HP-5MS column (30 m × 0.25 mm × 0.25 μm). The temperature of the GC injection port was set as 275 °C, and the split ratio was 10:1. The heating program of the GC oven was as follows: the initial temperature was 40 °C and held for 3 min, then ramped at a rate of 5 °C/min to 200 °C, and finally increased at a rate of 10 °C/min to 280 °C, holding for 3 min. The MS was operated at 70 eV in an electron ionization mode, and the mass scan range was 30–300 amu, with NIST11.L as the spectral library. The peak area was used to represent the quantity of a specific substance. Considering the weight difference in the paper mill sludge used in each experiment and the bio-oil dissolved in varied amounts of acetone, the peak areas of all identified substances were converted using the following equation:

$$Q = S_{peak}/m_{sludge} \times m_{liquid} \quad (3)$$

Among them, Q represents the peak area after the equation conversion, S_{peak} represents the peak area of the detected bio-oil by GC–MS, m_{sludge} represents the mass of the sludge used in the experiment, and m_{liquid} represents the sum of the mass of bio-oil and acetone collected after the reaction.

The resulted peak areas would thus semi-quantitatively represent the yields of the bio-oil substances[26,27]. However, it should be noted that the compounds detected by GC–MS are only part of the bio-oil components, many heavy compounds cannot be separated by the GC column and will not be detected by the MS. Additionally, different compounds have different response factors (peak area to mass concentration) for quantification, leading to significant variations in content values. Therefore, it can only serve as a rough indication for bio-oil yield.

3. Results and discussion

3.1. Yields of pyrolysis products

The effects of temperature and addition of CaO/biochar catalyst on the yields of pyrolysis products from paper mill sludge pyrolysis are shown in Fig. 2. From Fig. 2 (a), it can be seen that without catalyst, when pyrolysis temperature was increased from 500 to 700 °C, the biochar yield decreased from 46.22 wt% to 40.2 wt%, and the non-condensable gas yield increased from 11.8 wt% to 17.5 wt%. Higher temperature led to more thorough decomposition of paper mill sludge. The bio-oil yield firstly increased and then decreased, reaching its maximum yield of 44.25 wt% at 600 °C. On the one hand, the increase of temperature (500–600 °C) resulted in more condensable volatiles releasing. On the other hand, too high temperature (600–700 °C) would intensify the secondary reactions of volatiles vapors, leading to the decrease of bio-oil yield [28]. Similar results were also reported in previous research [29].

As shown in Fig. 2 (b), with the addition of CaO/biochar catalyst (mass ratio of catalyst/sludge of 1), the biochar yield was considered the same as that without catalyst at the same temperature, as the newly generated paper mill sludge biochar did not contact and react with the adjacent catalyst bed. While the non-condensable gas yield increased and the bio-oil yield decreased, possibly due to the catalytic cracking of

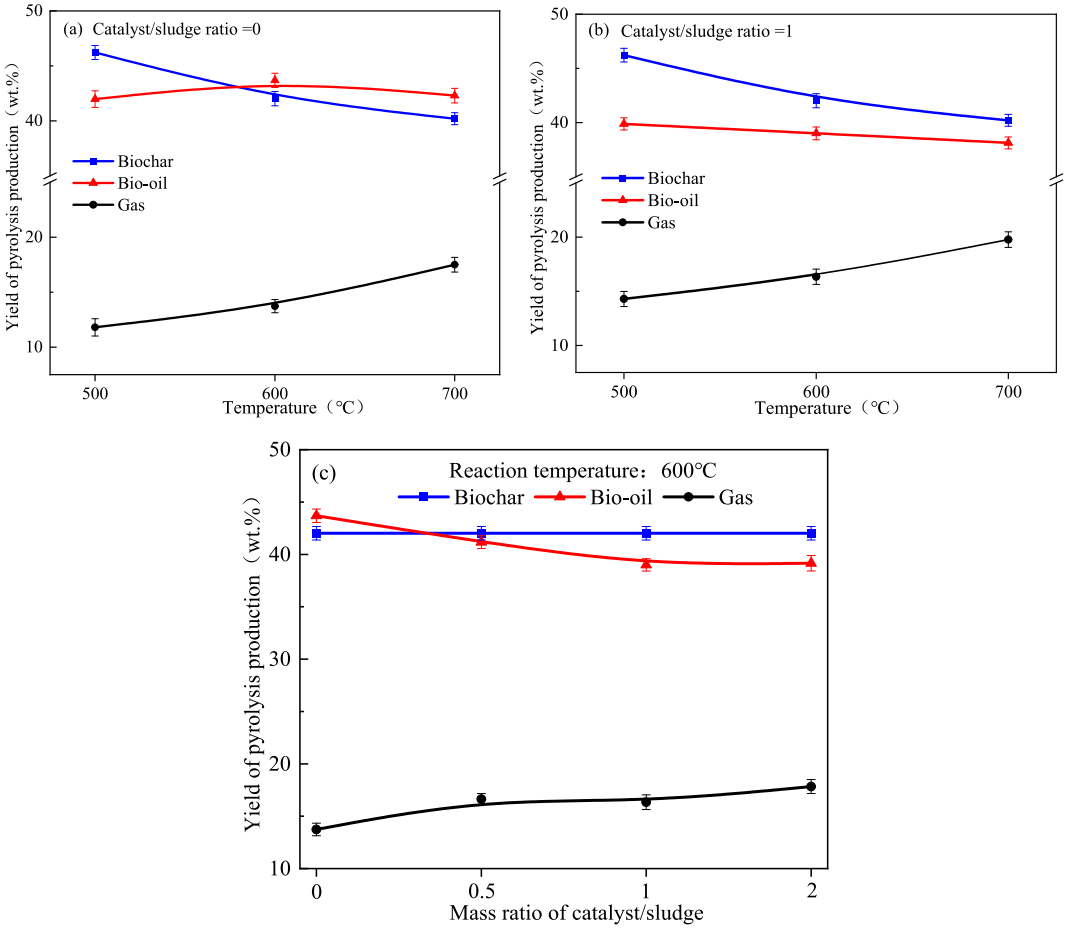


Fig. 2. Yield of pyrolysis products from paper mill sludge without/with catalyst under different temperatures and catalyst/sludge ratios: (a), (b) temperature, (c) mass ratio of catalyst/sludge.

large molecular compounds in the sludge volatiles into small molecular compounds over CaO/biochar catalyst [30]. Also, with the help of CaO/biochar catalyst, the H_2O and CO_2 in the volatiles might undergo a series of reactions to reform the volatile compounds, such as steam/dry reforming of organic compounds or CO in volatiles. They might also directly react with biochar in the catalyst through water–gas reaction ($C + H_2O \rightarrow CO + H_2$) and Boudouard reaction ($C + CO_2 \rightarrow 2CO$) to produce more gas [31]. It should be noted that the decrease of bio-oil yield exceeded the increase of non-condensable gas yield, which means that the total yields of pyrolysis products decreased after catalytic pyrolysis (i.e. less than 100 wt%). It indicated that the CaO/biochar catalyst gained weight increase after reaction. CaO capturing the CO_2 in the volatiles to form $CaCO_3$ might be one possible reason, as later proved by XRD results in Fig. 6. Also, coke formation on the catalyst surface due to volatiles cracking might be another reason [32,33]. With the increased temperature, the bio-oil yield decreased monotonically, which showed different trend with that without catalyst. Higher temperature could enhance the cracking/reforming of volatile/bio-oil vapors to further

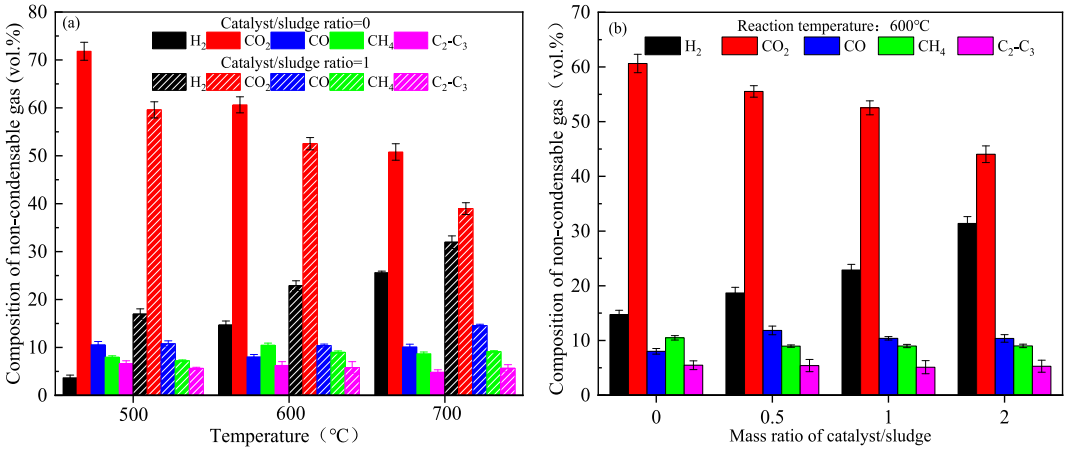


Fig. 3. Composition of non-condensable gas from paper mill sludge pyrolysis without/with catalyst under different temperature and catalyst ratio: (a) temperature, (b) mass ratio of catalyst/sludge.

decrease its yield. As shown in Fig. 2 (c), it can be observed that with the increase of catalyst/sludge ratio from 0 to 2 at 600 °C, the non-condensable gas yield increased from 13.73 wt% to 17.83 wt%, and the bio-oil yield decreased from 44.25 wt% to 39.68 wt%. More catalyst addition indeed enhanced its catalytic effect on volatiles cracking. However, when the mass ratio of catalyst to sludge was more than 1, the enhancing effect on the catalytic effect was relatively insignificant.

3.2. Composition and volumetric yield of non-condensable gas

Fig. 3 shows the effects of temperature and addition of CaO/biochar catalyst on the composition of non-condensable gas. From Fig. 3 (a), it can be seen that the non-condensable gas mainly contained H_2, CO_2, CO, CH_4 and a certain amount of C_2-C_3 gases with CO_2 accounting for the largest volume share (e.g., over 70 vol% without catalyst addition at 500 °C). Without and with CaO/biochar catalyst addition, the increase of temperature showed very similar effect on the changes of gas composition, resulting in the increase of H_2 content, the decrease of CO_2 content, and insignificant change of CO, CH_4 and C_2-C_3 gases. Higher temperature and catalyst addition facilitated the secondary cracking of volatiles to generate a H_2-rich gases. Moreover, the addition of catalyst led to a larger increase in H_2 content at lower temperature (e.g. 500 °C). From Fig. 3 (b), it can be found that the addition amount of CaO/biochar catalyst also exhibited significant effect on the composition of non-condensable gas. With the increase of catalyst addition, similar trend was found as that of temperature increasing, the H_2 content increased significantly, while the CO_2 content decreased, indicating the enhanced secondary reactions (e.g., dehydrogenation) over more catalysts. Nevertheless, the gas composition could only reflect the relative volumetric percentage changes in the non-condensable gas, while it did not represent the absolute changes in the yields of each gas components.

Fig. 4 shows the effects of temperature and addition of CaO/biochar catalyst on the volumetric yields of non-condensable gas. From the figure, it can be observed that the increase of temperature and catalyst/sludge ratio both enhanced the production of non-condensable gas due to the enhanced cracking of volatiles, the total gas yields all increased without/with catalyst addition[34,35]. For instance, when temperature increasing from 500 to 700 °C, without catalyst addition, the total gas yield increased from 69.56 to 136.45 mL/g sludge; while with mass ratio of catalyst/sludge of 1, the total gas yield increased from 98.15 to 176.80 mL/g sludge. The addition of CaO/biochar catalyst further enhanced the decomposition of volatiles. And such enhancing effect was strengthened with the increase of mass ratio of catalyst/sludge, as the total gas yield increased from 93.14 to 153.04 mL/g sludge when the mass ratio of catalyst/sludge increasing from 0 to 2 at 600 °C.

It can be also observed from the Fig. 4 that the yields of each gas type have increased to varying degrees, which might be attributed to the following aspects: For H_2, as the dominant component of the combustible gas, its yield increase might be attributed to the cracking of saturated hydrocarbons at lower temperature and the dehydrogenation condensation of aromatic compounds at higher temperature [28]. At the same time, the presence of catalyst promoted a series of reactions such as tar reforming (tar + H_2O → CO, CH_4, and H_2), water–gas reaction (CO + H_2O → CO_2 + H_2) and water–gas shift reaction (C + H_2O → CO + H_2), resulting in formation of more H_2 [36]. For CO_2, its yield increase was partly due to water–gas shift reaction (CO + H_2O → CO_2 + H_2) possibly enhanced by CaO [37]. Also, the CaO/biochar catalyst would promote the decarboxylation reaction of volatiles during the process, especially at higher temperature, facilitating the formation of CO_2 [27]. It should be also noted that part of the CO_2 was captured by the CaO in the catalyst during the process, but its yield still showed an overall increasing trend even when the mass ratio of catalyst/sludge increased. Combined with the results of gas composition in Fig. 3, it can be clearly seen that the composition and quality of the non-condensable gases have been greatly improved. For CO, its yield increase was mainly due to the enhanced decomposition of oxygen containing functional groups (e.g., carbonyl groups) and the promotion of catalytic reforming reactions such as water–gas reaction (C + H_2O → CO + H_2) as well as Boudouard reaction (C + CO_2 → 2CO), at higher temperature and with catalyst addition. The yield changes of CH_4, C_2 and C_3 gases were relatively insignificant, mainly due to the release of volatile small molecule gases under high temperature and catalyst action. They were formed through the cracking of relatively stable aromatic hydrocarbons and alkanes in the volatiles and were closely related to functional groups such as methyl, methoxy, and methylene [38].

3.3. Composition and yields of bio-oil

The bio-oil was analyzed using GC–MS, and the results are shown in Fig. 5. Considering the complex composition of bio-oil from paper mill sludge pyrolysis, the detected major compounds were classified into nine categories: aliphatics, aromatics, 4 organic oxygen species (OOSs): acids, ketones, esters and phenols, as well as 3 organic nitrogen species (ONSs): nitriles, amines and N-heterocyclics.

For aliphatics and aromatics in bio-oil, as shown in Fig. 5 (a) and (c), it can be seen that with pyrolysis temperature increasing from 500 to 700 °C, the yields of aliphatics decreased and the yields of aromatics increased for both without and with catalyst addition. The cracking of aliphatics to small molecular gases and the dehydrogenation condensation of volatile compounds to form aromatics at higher temperatures might be the possible reason [39]. Furthermore, with catalyst addition (mass ratio of catalyst/sludge of 1), more aliphatics with less aromatics were obtained, indicating the enhanced cracking of volatile compounds over CaO/biochar catalyst during the process. In addition, with the increase of catalyst/sludge ratio at 600 °C, the yields of aliphatics increased, while the yields of aromatics decreased, further implying that

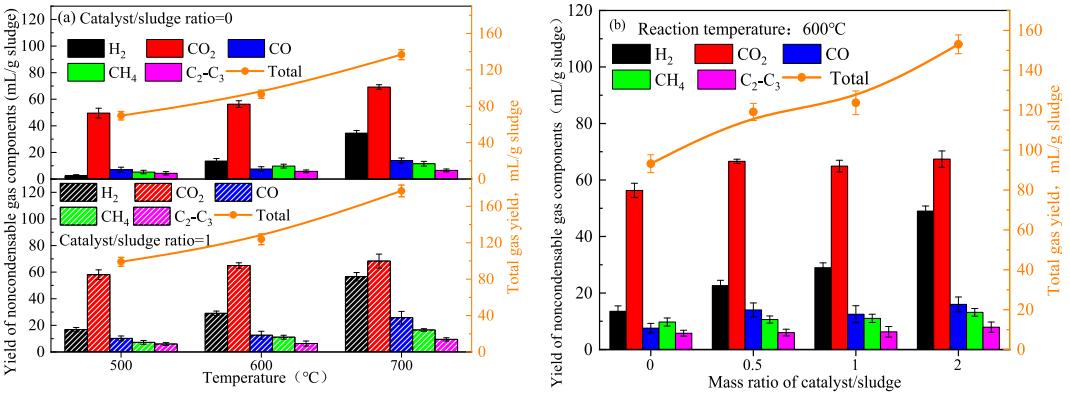


Fig. 4. Yield of non-condensable gas from paper mill sludge pyrolysis without/with catalyst under different temperature and catalyst ratio: (a) temperature, (b) mass ratio of catalyst/sludge.

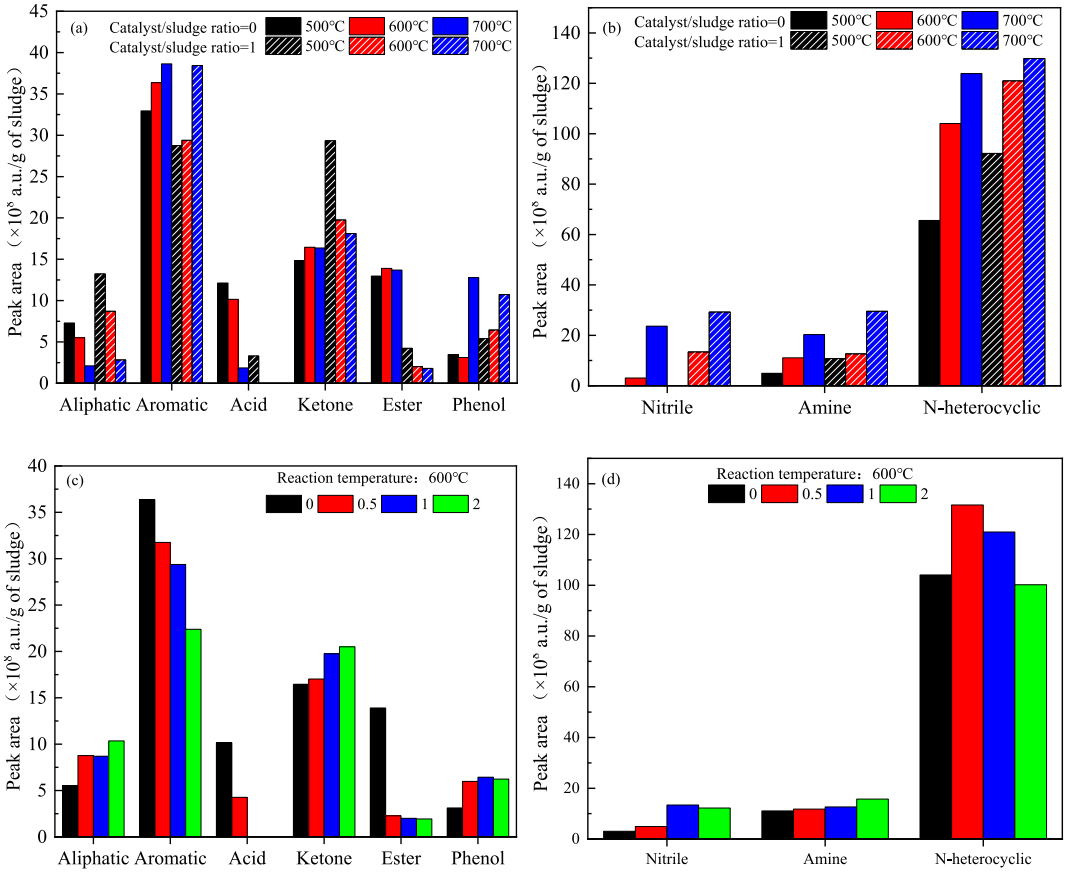


Fig. 5. Yield of bio-oil detected by GC–MS from paper mill sludge pyrolysis with/without catalyst under different temperature and catalyst ratio: (a) and (b) temperature, (c) and (d) mass ratio of catalyst/sludge ratio.

the CaO/biochar catalyst might promote the cracking/reforming of aromatic compounds into aliphatics. Similar phenomenon was also found in previous studies [28,38].

For OOSs, as also shown in Fig. 5 (a) and (c), the yields of acids decreased significantly with the increase of temperature and the addition of CaO/biochar catalyst. The thermal instability of carboxylic acid was an important reason, which may be degraded to CO_2 at higher temperature. In addition, with the increased mass ratio of catalyst/sludge, the content of acids gradually decreased until it disappeared. According to the previous studie [40], CaO preferentially reacted with acids in bio-oil, reducing the relative content of acids. In the meantime, biochar could promote the decarboxylation of carboxylic acids in bio-oil, resulting in the producing more CO_2. It is consistent with the increase of CO_2 production as presented in Fig. 4 (a) and (b). The yield of esters did not change significantly with the increase of temperature, but with the addition of catalyst, the ester contents decreased significantly, and gradually decreased with the increase of catalyst/sludge ratios. This could be attributed to the decomposition of esters into CO_2 over CaO in the catalyst [41,42]. Meanwhile, the yield of ketones changed obviously after the addition of CaO/biochar catalyst, and there were two main phenomena: the yield of ketones gradually decreased with the increase of temperature in the presence of CaO/biochar catalyst and the yield of ketones increased with the increase of the catalyst/sludge ratio at 600 °C. It has been observed that the alkaline sites such as Ca on biochar in the catalyst are conducive to the formation of ketones in previous studies [43]. At the same time, the increase of temperature further promoted the decarbonylation of ketone to CO, resulting in the yield of ketone decreased. Moreover, the content of phenols in bio-oil increased with raising pyrolysis temperature and addition of catalysts especially at high temperature. Literature has shown that phenols were mainly derived from the pyrolysis of polysaccharides and proteins [44]. The decrease of OOSs content in bio-oil reflected that the quality of bio-oil was improved by the action of high temperature and catalyst. In this process, some organic macromolecular oxygen-containing compounds were converted into small molecular non-condensable gases, which was consistent with the results in section 3.2.

For ONSs, as shown in Fig. 5 (b) and (d), they were the major compounds in the bio-oil from paper mill sludge pyrolysis. Various N-containing compounds including nitriles, amines and N-heterocyclics were detected from the bio-oil due to the high N content in the paper mill sludge feedstock. The N in paper mill sludge was mainly from the proteins, which then went into the bio-oil through pyrolysis. According to the N content of paper mill sludge (5.51 %) determined by the elemental analysis, the protein content of the sludge could be estimated as around 34.44 %, which was higher than that of typical municipal sludge (20–30 %) [45]. From Fig. 5 (b) and (d), it can be seen that N-heterocyclic compounds were the most ONSs in bio-oil. The N-heterocyclic compounds included pyrrole, pyridine, pyrimidine, and indole etc. it has been found that some amino functional groups in proteins nucleic acids could form N-heterocyclic compounds through dehydrogenation [46]. Furthermore, the Maillard and ring closure reactions at high temperature were also beneficial to the formation of N-heterocyclic compounds [47]. Although the content of N-heterocyclic compounds increased after catalyst cracking/reforming, the content of N-heterocyclic compounds decreased with the increase of catalyst addition ratio when the ratio > 1 as shown in Fig. 5 (d). Catalytic cracking/reforming could promote the reduction of N-heterocyclic compounds content to some extent. Specifically, CaO in the catalyst promoted the cracking reaction of nitrogen heterocyclic compounds in bio-oil. For example, C9H17NO has an inherent C=O structure, which can further undergo cracking and denitrification reactions to produce ketones and small molecular gases after ring-opening [48,49]. In addition, the oxygen-containing functional

groups on biochar can further promote the cracking reaction of nitrogen heterocyclic compounds, which promotes the nitrogen removal performance of bio-oil. Moreover, some nitrile and amine compounds also presented in bio-oil, but the catalyst exhibited very limited effect on them.

To sum up, although the addition of CaO/biochar catalyst could somehow deoxygenate the bio-oil, especially at higher temperature, the bio-oil still contained a lot of N-containing organic compounds. The clean utilization of such bio-oil as fuel might be not applicable as the removal of high content of N would be rather difficult and economically unfeasible. Considering the high contents and diverse types of of N-containing organic compounds in bio-oil, it might be more advantageous to extract high-value compounds other than to remove the ONSs, or to selectively produce value-added N-containing chemicals, thereby achieving its high-value utilization.

3.4. Characterization of CaO/biochar catalyst

Fig. 6 shows the XRD patterns of the paper mill sludge biochar obtained at 600 °C (precursor of the CaO/biochar catalyst, without calcination at 800 °C) and the CaO/biochar catalyst. From the figure, it can be found that $CaCO_3$ peaks were identified in the catalyst precursor (biochar), which was later decomposed to form CaO at 800 °C as the active component for the catalyst, as illustrated by the XRD pattern of CaO/biochar catalyst. $CaCO_3$ was a filler used in the papar industry, part of them eventually went into the paper mill sludge. The presence of CaO components in the catalyst ensured the success of the CaO/biochar catalyst preparation, and the exposure of Ca also provided additional active sites for the upgrading of bio-oil besides biochar.

The changes in the pore structures of CaO/biochar catalyst before and after the reaction were also analyzed, and the resutls are shown in Fig. 7 and Table 1. From Fig. 7 (a), it can be observed that the adsorption and desorption isotherms of CaO/biochar catalysts before and after reaction both belonged to type IV, the adsorption amount increased slightly at low relative pressure ($P/P_0 < 0.1$), it increased fast at a high relative pressure of > 0.7, and a significant hysteresis loop was observed for both samples, indicating the catalysts were a kind of mesoporous material. From Fig. 7 (b), it can be found that the peak value of pore volume distribution was mainly concentrated in the range of 3–4 nm, indicating that the pore contribution in this range was the largest and the most probability of occurrence. According to the classification of pores (micropores: < 2 nm; mesopores: 2–50 nm; macropores: > 50 nm),

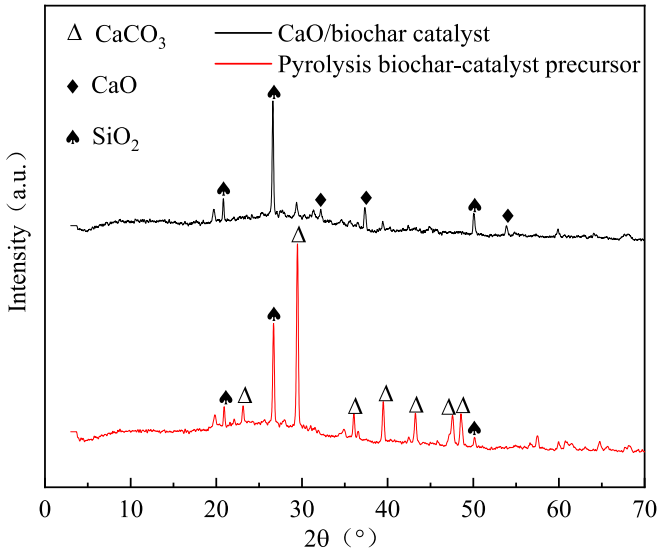


Fig. 6. XRD patterns of pyrolysis biochar-catalyst precursor and CaO/biochar catalyst.

it can be also concluded that the mesopore was the main pore structure of the biochar. It was worth noted that the adsorption amount and pore volume of the catalyst in the same region decreased significantly after the catalytic reaction as shown in Fig. 7 (a) and (b). Furthermore, Table 1 also shows that the specific surface area and pore volume of the catalyst decreased after the reaction, and the average pore size increased. These results implied that the catalytic cracking of paper mill sludge volatiles might cause the formation of coke over the CaO/biochar catalyst surface, which deposited in or blocked the catalyst pores[50]. Small hydrocarbon or aromatic molecules generated from bio-oil cracking at high temperatures could polymerize on the catalyst surface, forming carbon deposits that cover active sites and reduce catalytic activity. Meanwhile, high temperature, the microporous structure on the surface of biochar catalyst may collapse, resulting in a decrease in specific surface area, a decrease in reactivity, and a deterioration in structural stability [51,52]. Also, the CaO carbonation with CO2 in the volatiles to form CaCO3 might also block the pores of the catalyst. CaO in the catalyst reacts with CO_2 to form $CaCO_3$, which may cause the pore structure of the catalyst to be blocked. This reduces the specific surface area and porosity of the catalyst and prevents the reactants from effectively contacting the active site. In addition, the formation of $CaCO_3$ may mask changes in the surface active site and crystal structure of the catalyst, resulting in a decrease in the reactivity of the catalyst and instability of the overall structure [53,54]. These issues require further investigation in the future.

4. Conclusion

The catalytic upgrading of bio-oil from paper mill sludge pyrolysis over self-sourced CaO/biochar catalyst was studied in a two-stage pyrolysis reactor. The main conclusions can be summarized as follows:

(1) Higher pyrolysis temperature and the presence of catalyst were conducive to H_2 generation. The utilization of CaO/biochar catalyst for the catalytic pyrolysis has significantly changed the properties of the volatiles released during pyrolysis, improving the yield of the gas and reducing the yield of the bio-oil. The optimal condition for gas production was when the proportion of catalyst to sludge was 1 at 700 °C. Under the condition, the gas yield was 176.80 ml/g sludge, and the H_2 concentration and yield were 31.97 % and 56.52 ml/g sludge, respectively.
(2) The active sites and oxygen-containing functional groups on the catalyst played an important role in the catalytic reforming of sludge volatiles. And the presence of CaO in the catalyst further promoted the decomposition of acids and esters in the bio-oil and reduced the content of oxygen-containing compounds and improved the quality of the bio-oil.
(3) The microporosity analysis results before and after the catalyst reaction showed that the specific surface area and pore volume of the catalyst decreased after the catalytic reaction possibly due to the coke formation and CaO carbonation, which should be further addressed.

The above research results have fully verified the important role of the self-sourced CaO/biochar catalyst in the catalytic reaction and have improved the quality of paper sludge pyrolysis bio-oil and gas.

Aiming at the challenges of catalyst deactivation and bio-oil quality improvement in the catalytic pyrolysis process of paper mill sludge in the future, we propose a systematic technical route: Through the design of carbon resistant and highly stable CaO/biochar catalyst (such as carrier modification and active component regulation), combined with two-stage pyrolysis (low temperature pretreatment – high temperature catalytic cracking), the deep transformation of macromolecular organic compounds of pyrolysis volatiles of sludge is realized. The collected bio-oil is post-processed to improve the quality of the bio-oil. The roadmap provides theoretical and technical support for high-value paper mill

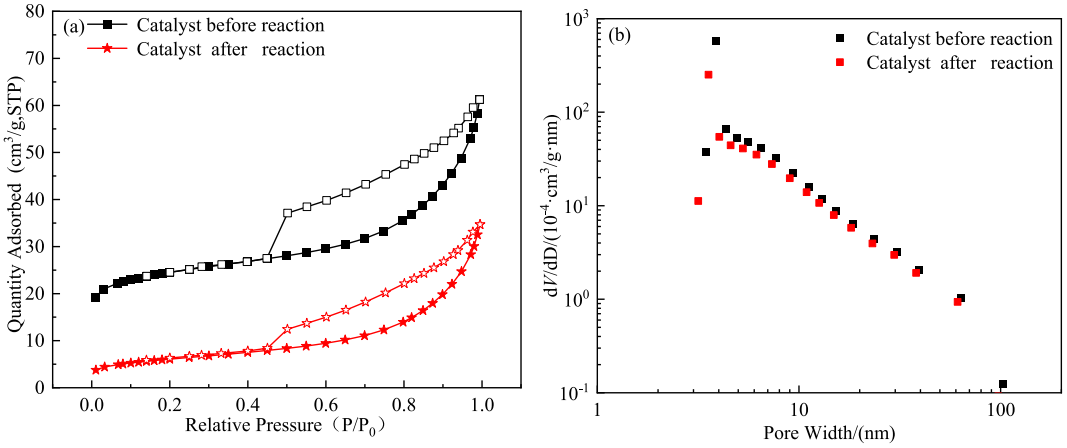


Fig. 7. N_2 adsorption and desorption analysis of catalyst before and after reaction: (a) N_2 adsorption and desorption isotherms (b) Pore volume distribution.

Table 1
Microporosity of CaO/biochar catalyst before and after reaction.

	Catalyst before reaction	Catalyst after reaction
BET surface area (m^2/g)	81.30	21.48
Pore volume (cm^3/g)	0.10	0.06
Average pore size (nm)	6.32	7.07

sludge and sustainable energy conversion through the collaborative optimization of "catalyst – process – product".

CRediT authorship contribution statement

Wantong Kai: Writing – original draft, Investigation, Formal analysis, Data curation. **Xing Xie:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Dan Lin:** Writing – review & editing, Methodology, Formal analysis. **Yusuf Makarfi Isa:** Validation, Investigation, Formal analysis. **Alexander Kozlov:** Validation, Methodology. **Maxim Penzik:** Validation, Investigation. **Bin Li:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition.

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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Data availability

Data will be made available on request.

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