Hydrothermal Carbonization of Medical Wastes and Lignocellulosic Biomass for Solid Fuel Production from Lab-scale to Pilot-scale

Yafei Shen ^{1,2}*, Shili Yu ¹, Shun Ge ², Xingming Chen ¹, Xinlei Ge ^{1*}, Mindong Chen ¹

¹ Jiangsu Engineering Technology Research Center of Environmental Cleaning Materials (ECM), Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (AEET), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

² Nanjing Tianbo Environmental Technology Co., Ltd, Nanjing 210047, China

Corresponding Author

*E-mail: shen1225@nuist.edu.cn (Y. Shen); caxinra@163.com (X. Ge)

ABSTRACT

An alternative way has been proposed for the PVC-containing medical wastes valorization by co-hydrothermal carbonization (HTC) with lignocellulosic biomass. The organic-Cl in PVC can be converted to the inorganic-Cl via hydrolysis, defunctionalization, recondensation, and aromatization in the HTC process. Followed by the washing process with the condensed water, the inorganic-Cl with high water-solubility could be removed from the solid products (i.e. hydrochar). Lignin as a biomass component can significantly improve the dechlorination efficiency of PVC in the HTC process. Here, the dechlorination performance of lignocellulosic components is given as the following order: lignin > cellulose > hemicellulose. In addition, lignin can adjust the particle sizes of solid products by inhibiting the agglomeration in the order of lignin > hemicellulose > cellulose. In the pilot-scale HTC process, the addition of woodchips improves the dechlorination efficiency of hospital wastes (HW). The hydrochar particles with low-chlorine content and higher heating value could be used as a clean coal-alternative fuel.

Keywords: *dechlorination; hydrothermal carbonization (HTC); PVC; lignocellulosic biomass; solid fuels*

1. INTRODUCTION

Plastic waste has become a major component of both industrial and municipal wastes due to the worldwide use of plastic products. Therefore, the disposal of plastic wastes is increasingly considered a major environmental issue. Recycling is by far the most sustainable method of plastic waste disposal. However, the variety of additives used in the manufacture of plastic goods results in separation and decontamination difficulties, which greatly limits the recycling of waste plastics. In addition, landfilling has become limited due to high population densities, high costs, and environmental concerns such as soil contamination and harmful influences on ecosystems [1]. However, although waste disposal by means of incineration possesses many advantages, including a high degree of destruction, reduction of land usage and the potential for energy recovery, thermal decomposition of the halogenated plastics can cause serious environmental problems such as toxic dioxin emission [2-4].

Polyvinyl chloride (PVC) is a major source of chlorine for chlorinated dioxin formation during the incineration of municipal wastes. When PVC waste is burnt, a lot of hydrochloric acid (HCl) can be generated; this can corrode the boiler tube and lead to the release of trace amounts of further harmful gases such as organohalogen compounds, possibly causing pollution issues [5, 6]. Recently, hydrothermal carbonization (HTC) as a novel thermal conversion process that can be used to convert waste streams into sterilized, value-added hydrochars, especially for the polymer-derived wastes including bio-wastes [7-13], and plastic wastes [14, 15]. HTC as a kind of hydrothermal processing has been mostly used on bio-wastes recycling, but it is rarely reported on exploring the carbonization of plastic wastes or of utilizing HTC as a sustainable waste-to-energy technique [16]. Based on the processing

conditions and the target products, hydrothermal processing can be classified into different fields of applications (Fig. 1). Main regions are HTC, liquefaction, and hydrothermal gasification. For instance, low-temperature hydrothermal processing (e.g., HTC) is often used as a sterilization step within fermentation processes to inhibit that bacterial cultures reach the environment. Starting from temperatures of about 100 °C and more likely from above 180 °C HTC is applied to produce the solid products for different purposes [17]. The HTC process has proven to reach energy yields of more than 80% for woody biomass in the pilot scale [18]. The energy yield of a HTC conversion process represents how much of the energy-content of the starting material is converted to the solid product. Therefore, the HTC-process is expected to be a future energy-efficient way to convert wet biomass to solid fuels [7, 19, 20].

Typically, HTC of biomass is achieved in water at elevated temperatures (180-250 °C) under saturated pressures (e.g., 2-10 MPa). It has been reported that the chemical transformations of lignocellulosic model compounds under pressure in the HTC process, particularly cellulose, pentoses/hexoses (glucose and xylose), starch, and phenolic compounds (as illustrated in Fig.2) [21]. The initial reaction occurring as biomass heated up in water is the hydrolysis of cellulose to glucose, which is the decisive difference to thermochemical conversion [8]. The hydrolysis provides way to homogeneous reactions in an aqueous solution, which are not limited by heat and mass transfer. Same holds true for the destruction of lignin to its main product phenol. In the HTC of organic matrices (e.g., PVC), significant decomposition processes include hydrolysis as the initial step, followed by defunctionalization such as

dehydration and decarboxylation, and finally recondensation and aromatization [15]. It was proven that organic chlorine in PVC could be effectively converted to inorganic chlorine via the HTC process at high temperatures (>250 °C) and high pressures, e.g., subcritical or supercritical process [14, 15].

In the previous work, municipal solid wastes (MSW) including PVC were pretreated by the HTC process at relatively lower temperatures (around 210 °C) [22-25]. The solid products could be used as coal alternative fuels with low chlorine content. The purpose of this work is to treat the PVC wastes by the HTC at a lower temperature (210 °C). The lignocellulosic components (e.g., cellulose, xylan, and lignin) will be applied and studied, in terms of the dechlorination performance and the solid particle size distribution. Noteworthy, it is the first time to study the washing process by recycling the condensed water. As a case study, the co-HTC process of PVC wastes, e.g., hospital wastes (HW) with woodchips will be preliminary studied for the solid hydrochar fuel production in a pilot-scale plant.

2. MATERIALS AND METHODS

2.1. Feedstocks

In the lab-scale process, the feedstock of PVC (Cl content: 57%) was purchased from *Wako Pure Chemical Industries, Ltd.* PVC was ground in a planetary ball mill to pass a 0.25-mm screen. The lignocellulosic model compounds such as lignin, cellulose, hemicellulose (e.g., xylan) were blended with PVC in the HTC process. In the pilot-scale process, the complex feedstocks of the PVC wastes (i.e., hazardous HW) were collected by the specific containers,

which cannot be directly touched by researchers. The HW mainly contained the PVC medical products along with waste clothes, paper, tissue and organs. Therefore, the total-Cl content cannot be accurately given. The total-Cl content in the HW was assumed as 57% to identify the effect of woodchips on the PVC dechlorination. In addition, cellulose, hemicellulose, and lignin were the three main components in woody biomasses, so the bio-waste of woodchip (<1 mm) is employed. The hemicellulose, cellulose and lignin were determined following the procedure reported by Allen et al. [26]. The carbohydrate composition of the woodchip is mainly composed of cellulose (48.2%), lignin (25.8%) and hemicellulose (16.5%).

2.2. The HTC processes of medical wastes

The lab-scale HTC processes were conducted in an autoclave reactor (volume: 500 ml) with an electronic heater, which was coupled with a motor stirrer [27]. PVC (5 g) was blended with lignocellulosic biomass component (5 g) by the ball-milling for 10 min. The solid mixture (10 g) dissolved in the distilled water (20 g) were fed to the HTC reactor. As the temperature increasing, the water steam can be generated automatically. In this study, the holding time was controlled at 30 min as the reactor temperature increase to the target value (210 °C). The primary solid products were further treated by the washing process.

The pilot-scale HTC apparatus was mainly composed of HTC reactor (volume: 1.5 m³), steam boiler, condenser, dehydrator, screening machine (as illustrated in Fig. 3). Initially, HW (250 kg) blended with woodchips (250 kg) was fed into the HTC reactor. After that, the saturated steam generated from the boiler was continuously injected to the HTC reactor.

As the inner pressure of the HTC reactor reached the desired pressure (2.2 MPa, 2.4 MPa), the pressure of the boiler maintained for a certain period. The holding time was controlled at 30 min. To finish the HTC process, pressure was released by discharging the steam to a condenser, and then the condensed water was guided to a large water tank. When the inner pressure of the reactor reached the atmospheric pressure, the solid products were dehydrated by steam in the dehydrator. Dry products were pushed out to a sieving machine by rotating the stirrer acting as a screw conveyor. The solid products were further treated by washing process using the condensed water.

2.3. Washing Process

In common, the condensed liquid from the HTC and dehydration process required to be further treated. It can also be used as an agent to remove the soluble chlorine from the solid products by washing process. As illustrated in Fig. 4, the solid products were initially washed for 15 min by distilled or primary condensed water in a flask with a stirring speed of 600 rpm. The mass ratio of solid and water was controlled at 1:5 each time. After the washing process, the liquid phase was filtrated by a vacuum pump, to wash out the primary HTC-derived solid products. Water was recycled for five times in this route. Therefore, the total mass ratio of solid product and water was 1:1.

2.4. Analytical Methods

Chlorine analysis

The chlorine in the liquid phase was defined as the soluble-Cl. For the soluble-Cl analysis, the solid product in the distilled water was stirred at a speed of 600 rpm for 30 min with a ratio of 1:60, and then water was separated by the vacuum filtration. The total-Cl content

in the liquid phase is measured by a chloride ion selective electrode (Orion 4 star and chloride ISE Orion 9617 BNWP). And the total-Cl content in the solid phase was determined by the Schoniger's method [28]. Therefore, the insoluble-Cl content of solid product was calculated by difference ([insoluble-Cl] = [total-Cl] – [soluble-Cl]). Each measurement was performed for three times to ensure the reproducibility. And the average value was adopted.

Characterization of HTC products

The solid products were separated by using different pore sizes of sieves (0.15-2mm), and then recorded by the mass fraction. The proximate analysis was conducted by a thermogravimetric analyzer (TGA, SHIMADZU D50, TGA/DTA, Japan). The ultimate analysis was performed by an elemental analyzer (Elementar's Vario MICRO Cube, USA). The higher heating value (HHV) was measured by a digital calorimeter DSK-200 and DCS-196. The surface characteristics of solids were analyzed by a scanning electron microscope (SEM, JSM-6610LA, Japan). The functional groups were analyzed a fourier transform infrared spectroscopy (FT-IR, JIR-SPX200). The liquid was analyzed by a gas chromatography - mass spectrometry (GC-MS) equipped with Rtx-5MS, 30 m-long, 0.25 mm-ID, and 0.25 µm-film thickness column (GCMS-QP2010 SE, Shimadzu Inc.). The kinematic viscosity of liquid was measured by Lexible and Convenient Operation Kinematic Viscosity Analysis Equipment.

3. RESULTS AND DISCUSSIONS

3.1. Dechlorination Efficiency of Hydrochar in the Lab-scale Experiment

Lignocellulose including cellulose, lignin, hemicellulose (e.g., xylan) was blended with PVC to study the dechlorination performance in the HTC process. The chlorine in the solid phase

was transformed to the liquid and gas phases (as shown in Fig. 5). In this study, the dechlorination efficiency was defined as equation 1 (E1). Generally, the addition of lignocellulose improved the dechlorination efficiency of solid in the HTC process. In particular, co-HTC of PVC with the lignin showed a highest dechlorination efficiency prior to the washing process. It might be attributed to a synergistic effect of lignin on the enhancement of the PVC dechlorination in the HTC process.

$$\text{Dechlorination Efficiency (DE, wt\%)} = \frac{\text{Total Cl} - \text{Solid Cl}}{\text{Total Cl}} \times 100\% \quad (\text{E1})$$

As shown in Fig. 6, the addition of lignocellulose (i.e. cellulose, lignin, and xylan) can enhance the dechlorination efficiency of PVC in the HTC process. By co-HTC of PVC with lignin, the dechlorination efficiency increases from 6.33% to 15.8%. Besides, the washing process can significantly improve the dechlorination efficiency. In addition of lignin, the dechlorination efficiency increases from 48.2% to 89.5% by the HTC and washing process. In general, the dechlorination performance of lignocellulosic components can be given as the below order: lignin > cellulose > hemicellulose (e.g., xylan).

Mass ratio of lignocellulose and PVC is considered as an important parameter in the HTC and washing process. As shown in Fig. 7, the dechlorination efficiency generally increases with the increase of its mass ratio. As for lignin, it can be found that the dechlorination efficiency increases rapidly as the lignin/PVC is below 1.0. After that, the increase tendency is gradually weakened. From this result, it is suggested that the optimal mass ratio of lignin/PVC is 1.0. The addition of lignocellulose (e.g., lignin) has little effect on the PVC dechlorination in the HTC process as the mass ratio reaches a certain value.

3.2. Characterization of Hydrochars

FTIR Analysis

The functional groups of the solid products (i.e. hydrochars) can be characterized by the FTIR analysis. Fig. 8 shows the FT-IR spectra of PVC, HTC-PVC and HTC-PVC-lignin. It can be found that PVC exists the alkane groups of CH between 2850 to 3000 cm^{-1} and 1350 to 1480 cm^{-1} . The peaks between 2700 and 3000 cm^{-1} represent the aliphatic groups of CH, CH_2 , and CH_3 . The absorption peaks of alkyl halide groups of C-Cl are presented from 600 to 800 cm^{-1} . These absorption peaks appear in the spectra of HTC-PVC and HTC-PVC-lignin as well. Compared with the FT-IR spectra of PVC and HTC-PVC, the obvious differences take place between 1670 and 1820 cm^{-1} , which indicates the carbonyl group of C=O. Compared with the spectra of HTC-PVC-lignin and HTC-PVC, new absorption peaks appear (e.g., 1000-1100 cm^{-1} : the alcohol groups of C-OH, 1500-1600 cm^{-1} : the aromatic groups of C=C, 3010-3100 cm^{-1} : the alkene groups of =CH, and 3500-3700 cm^{-1} : the alcohol groups of free OH). Besides, the absorption peak from 600 to 800 cm^{-1} is weakened, indicating the decrease of C-Cl group, while the absorption peak from 1670 to 1820 cm^{-1} is enhanced, which indicates the increase of C=O functional group.

Furthermore, thermal dechlorination of PVC mostly follows a free radical mechanism [29]. The reaction can start with the production of free radicals and chloroallylic structures characterized by low thermal stabilities. A subsequent stepwise of HCl elimination results in the polyene formation, which is a non-free radical reaction mechanism [30]. Obviously, conjugated double bonds could be created by a “zipper” mechanism [31]: once a double

bond has formed, the allylic chlorine atom on the C-atom adjacent to the double bond splits off HCl forming two double bonds during the HTC process, which in turn activates adjacent chlorine to propagate the dehydrochlorination process. In aqueous suspensions, PVC degradation could be assumed by ionic chain reactions and cracking. Beyond that, nucleophilic substitution with water as the nucleophile proceeds to generate alcohols, diols, and polyols. Reactive polyenes with the diol/polyol structures, are regarded as the precursors of aromatic compounds and oxygen-functionalized low molecular weight compounds. It is emphasized that temperatures below 450 °C and high water densities are favour of OH-nucleophilic substitution with water acting as a role of nucleophilic agent (as illustrated in [Fig.9](#)) [15].

In the HTC process, the lignin fragments can be decomposed to phenolics via hydrolysis and further form the phenolic hydrochar via polymerization. The phenolic hydrochars derived from the surface fragments of non-dissolved lignin can locate on the surface of non-dissolved lignin or polyaromatic char, and then the formed holes are stuffed or covered. The formation of lignin hydrochar is illustrated in [Fig. 10A](#). [32, 33] However, the cellulose can keep the fiber skeleton with the microsphere produced after the HTC [32]. As a phenolic polymer, both fragmentation and condensation reactions take place in the lignin degradation under HTC [34, 35]. During the molecular transformation of lignin, the macromolecular bulk of lignin is selectively fragmented by ether bounds splitting through hydrolysis reactions ([Fig. 10B](#)). The lignin conversion produce mainly an oligomeric residue by a preferential oxygen-carbon linkages splitting. Meanwhile, the oxygenated hydrocarbons with 2-6 carbon atoms and substituted phenols accumulate in the reaction medium, contributing to the large amounts

of hydroxyl radical generation [32].

These results can also explain the increase of dechlorination efficiency in the presence of lignin. The aromatic group of C=C (1500-1600 cm⁻¹) can indicate that lignin is hydrolyzed into the phenolic substances, such as catechol and phenol, and these substances are reacted with PVC. During PVC hydrolysis and dechlorination reactions, lignin can provide a larger amount of free OH bond (600-800 cm⁻¹). The alcohol group of C-OH (1000-1100 cm⁻¹) can indicate that the substitution of the -OH group takes place. Subsequently, the increase of C=O (1670-1820 cm⁻¹) indicates that more -OH group is converted into the C=O group via the oxidative reaction. Furthermore, the appearance of the =CH (3010-3100 cm⁻¹) group indicates the enhancement of PVC dechlorination. The mechanism can be summarized as the following reactions (R1 - R3).

SEM Analysis

Fig. 11 shows the SEM micrographs of PVC before and after HTC. It can be observed that the uniform hydrochar particles are agglomerated after HTC. Additionally, PVC presents a porous structure, which is caused by swelling reaction during the hydrolysis reaction, and the solid particles are aggregated with each other to form a hard cluster. It can be attributed to the PVC initially melting by thermal processing at a lower temperature. After that, the structure

of the melted PVC is changed under a high pressure, thus forming a hard cluster. By co-HTC with the cellulose, the non-hydrolyzed cellulose is stuck on the surface of hydrochar resulting in the formation of a carinate coarse surface. It is most likely caused by the hydrophilicity of cellulose. Moreover, the outer surface of the cellulose hydrochar particles contain a high concentration of reactive oxygen groups (i.e. hydrophobic shell), whereas the oxygen in the core forms less reactive groups (i.e. hydrophilic core) [36]. The cellulose cannot prohibit the aggregation of hydrochar particles. As above, the cellulose keep the fiber skeleton to form microsphere after the HTC process [32]. The produced hydrochar can easily condense around the fiber skeleton. Compared with the HTC-PVC, the hydrochar of HTC-PVC-cellulose is still a cluster, but easier to grind. It is noted that the solid particles keep uniform without aggregation after co-HTC with hemicellulose and lignin. The presence of lignin significantly inhibits the agglomeration of solid particles. In general, lignin has a high potential for the PVC dechlorination followed by the reduction of solid particle size. Furthermore, the hydrochar with fine particle size is favour of the downstream thermal process. The effect on hydrochar particle adjustment can be given as below: lignin > hemicellulose (e.g., xylan) > cellulose.

3.3. HTC Process of HW in the Pilot-Scale Plant

Effect of HTC process

Compared with the cellulose, lignin, and xylan hydrochars, the surface characteristics of wood hydrochars can indicate that interactions among cellulose, lignin, and hemicellulose occur [32]. Lignocellulosic biomass can be added to improve the dechlorination performance in the HTC of HW. Fig. 12A shows the dechlorination efficiency of HW by co-HTC with woodchips, which is improved from 15% to 38%. The addition of woodchip can offer

cellulose, hemicellulose and lignin. On one hand, the dechlorination efficiency increases due to the PVC-lignin interaction (e.g., solid-solid reaction). On the other hand, there are a large amount of cloth and paper in HW. The main component of cloth is cellulose, whilst paper is mainly composed of cellulose and hemicellulose. Fig. 12B shows the effect of HTC pressure. Obviously, the dechlorination efficiency increases with the increase of the HTC pressure. By co-HTC with the woodchip, the dechlorination efficiency increases by 5%. As the saturated steam used in the HTC process, a higher reaction pressure corresponds to a higher reaction temperature. Consequently, the rate of dechlorinating reaction increases with the increase of reaction temperature.

Effect of washing process

Dechlorination performance by washing process is defined as the soluble-Cl removal efficiency. Therefore, the soluble-Cl removal efficiency by washing process can be estimated by E2.

$$\text{Soluble Cl removal efficiency (wt. \%)} = \frac{\text{Soluble-Cl}}{\text{Total-Cl}} \times 100\% \quad (\text{E2})$$

As shown in Fig. 12C, it can be found that the soluble-Cl removal efficiency is about 83%, which keeps stable before the 3rd washing process, and then decreases from the 4th washing process. It indicates that the condensed water has a considerable performance on the washing process. The decrease of chlorine removal efficiency may be caused by the changes of physicochemical characteristics of water in the recycling process.

As for the whole washing process, the total mass ratio of solid product and water is 1 (defined as H&W 1:1). The total soluble-Cl removal efficiency is very meaningful for the

pilot-scale HTC and washing process. The total soluble-Cl removal efficiency by the condensed and distilled water for washing process are compared. As shown in Fig. 12D, the chlorine removal efficiency is about 80% by the distilled water, while it reaches 83% by the condensed water, which shows a good performance on the washing removal of soluble-Cl.

After the 4th washing process, the dechlorination efficiency by the condensed water obviously decreases. The reason is preliminarily studied by the SEM and the viscosity analyses. It can be seen that many pore structures form in the solid phase after the washing process. Meanwhile, the viscosity of liquid increases with the increase of washing times (Fig. 13), thus resulting in the increase of the surface tension of the liquid. Furthermore, the liquid may not go through the pores to completely wash the soluble-Cl out. Therefore, it is noted that after 4th washing, the high viscosity of the recycled liquid results in the increase of surface tension and inhibits the liquid to stream through the pore structures.

Properties of HW hydrochar

The properties of the hydrochar are characterized by the proximate analysis, ultimate analysis and heating value analysis, etc. As presented in Table 1, the solid products with relatively high heating values can be used as coal alternative fuels. The higher heating value (HHV) increases with the addition of lignocellulose. The HHV increases from 24.18 MJ/kg to 28.30 MJ/kg in the presence of woodchips (210 °C, 2.4MPa). In the HTC process, the solid product yield and H/C–O/C ratio decrease where the energy density increases with the increase of the reaction temperature and the reaction time. It is reported that the HHV of lignin is considerably higher than that of hemicellulose [37]; thus the removal of

hemicellulose derived from biomass can yield a product with increased lignin content and energy density. Due to the presence of subcritical water, the decomposition of hemicellulose is rapid in the HTC process [38]. As expected, the high energy density of the HTC solid product can be achieved. Significantly, lower HTC pressure is much favour of the solid fuels production due to the increase of HHV. However, a lower pressure can result in the increase of moisture content. In addition, the nitrogen content in the hydrochar decreases by HTC with woodchip, which is favor of thermal decomposition process with a lower NO_x emission.

The *Van Krevelen* diagram can provide the general information about the quality and type of fuel. A fuel with a lower O/C-H/C atomic ratio is considered highly favorable because of the decreased smoke, water vapor and energy losses experienced during the combustion [39]. As illustrated in Fig. 14, the solid products from slow-pyrolysis and HTC exhibit low H/C-O/C ratios than raw biomass. However, the H/C-O/C ratios for the hydrochar obtained from HTC (similar to those of coals) are higher than that for the biochar obtained from the slow-pyrolysis [40]. It is suggested that the ratio of reaction rate of decarboxylation to dehydration is much higher in HTC compared to that in the slow-pyrolysis process [8]. Therefore, HTC has a high potential for the production of coal alternative clean solid fuels. In this work, the HW after co-HTC with woodchips at 2.4 MPa can produce the solid fuel with a *Van Krevelen* diagram as lignite, similar as the formation of various coals (i.e. coalification) from the HTC of dead plants under the high temperature and pressure conditions (Fig. 14).

It is significant to obtain a self-sustained solid waste treatment system that can utilize the by-product as the energy source to run the process. For example, the municipal solid waste

(MSW) of HW + woodchip could be converted to the hydrochar and used as a boiler fuel to generate the steam. In this study, the HW is assumed as PVC. [Table 2](#) shows the operating parameters of the HTC process under the optimized condition. And the heating value of the dry solid waste was considered as the datum (100%) for the energy balance calculation. The energy required for the boiler fuel could be calculated by the water and steam enthalpy difference through the boiler, combined with the claimed boiler efficiency and utility. Besides, the energy loss to the condenser and the water content in the product were calculated according to the temperature of product. The heat loss was obtained from the difference in the total energy balance. The total energy balance of the HTC process by using the hydrochar derived from HW + woodchip under 2.4 MPa is shown in [Fig. 15](#). It could be found that the typical amount of energy required to treat the MSW waste (PVC + woodchip) was approximately 1/4th the energy content in the hydrochar, indicating that the HTC process is self-sustaining for the production of solid fuels.

The particle size is another important parameter of the solid fuel property. In general, uniform and fine particles are more preferred for the thermal decomposition, including combustion. By co-HTC with woodchip, the particle distribution of solid fuel can be improved. The average particle size of solid product is around 0.94mm (HW 2.4 MPa), and 0.77mm (HW + woodchip 2.4 MPa). Co-HTC of HW with woodchip presents an ultrafine and uniform solid particle size distribution, especially in terms of 0.5-1 mm (50% of mass fraction). Interestingly, the particle size of solid product decreases with the increase of the HTC pressure. It might be attributed to the higher HTC pressure contributes to destroy large size particles. Solid product has different average particle sizes in terms of 1.35 mm, 1.88 mm, and 1.20 mm,

respectively, suggesting that higher HTC pressure or addition of woodchips can enhance the crushing of the material to produce smaller particle solid. For instance, the mass fraction of the solid particles (>2 mm) decreases from 40.3% to 1.6%, with the reaction pressure increasing from 2.2 MPa to 2.4 MPa. Furthermore, the mass fraction of the solid particles (i.e. 0.5-1 mm) increases from 13.8% to 49.9% (Fig. 16A). Therefore, a higher HTC pressure can significantly reduce the particle size of solid product. Small particles will be favor of pelletizing or burning of solid fuel and centralized particle size distribution is favor of the fluidization in the thermal processing [41-43], it can be concluded that a higher HTC pressure in the presence of lignocellulosic biomass upgrades the HW-derived solid fuel with the maximum fraction as high as 78% of smaller particles below 1 mm (Fig. 16B).

4. CONCLUSIONS

The organic-Cl in the PVC can be transformed into the inorganic-Cl via hydrolysis in the HTC process. The washing process by the condensed water further removed the soluble-Cl from the solid products. In addition of lignocellulose especially for lignin can significantly improve the dechlorination efficiency, which increases from 6.33% to 15.8% by co-HTC of PVC with lignin. Followed by the washing process, the dechlorination efficiency increases from 48.2% to 89.5%. The dechlorination performance of lignocellulosic components can be given as the following order: lignin > cellulose > hemicellulose (e.g., xylan).

On one hand, co-HTC with woodchips can improve the dechlorination efficiency of HW; on the other hand, it optimizes the solid particles of hydrochars. The presence of lignin significantly inhibits the agglomeration of solid particles. The effect on the particle

adjustment can be given as follows: lignin > hemicellulose (e.g., xylan) > cellulose. The total chlorine removal efficiency can reach about 83% by the HTC (210 °C, 2.2MPa) and washing process using the condensed water. Co-HTC of HW with woodchip produces the fine and uniform solid particles, especially in terms of 0.5-1 mm (50% of mass fraction). Therefore, co-HTC with lignocellulosic biomasses will be a considerable way for PVC wastes treatment along with the production of solid fuels with high heating values. Some future works should be conducted, including the analyses of gas and liquid products, the thermal processing of the solid product, as well as the materials and energy balances in the integrated process of HTC followed by washing process using the condensed water.

ACKNOWLEDGEMENTS

This work is financially supported by the *Startup Fund for Introducing Talent* at NUIST (Grant 2243141501046). The authors are gratefully to acknowledge the financial supports by the National Science Foundation of China (Grant 21407079, 91543115 and 91544220), and the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (Grant 16KJB610012).

REFERENCES

- [1] J. M. Saquing, C. D. Saquing, D. R. U. Knappe, M. A. Barlaz, Impact of plastics on fate and transport of organic contaminants in landfills. *Environ. Sci. Technol.* 2010, 44, 6396-6402.
- [2] T. Katami, A. Yasuhara, T. Okuda, T. Shibamoto, Formation of PCDDs, PCDFs, and coplanar PCBs from polyvinyl chlorine during combustion in an incinerator. *Environ. Sci. Technol.* 2002, 36, 1320-1324.
- [3] T. Hatanaka, A. Kitajima, M. Takeuchi, Role of chlorine in combustion field in formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during waste incineration. *Environ. Sci. Technol.* 2005, 39, 9452-9456.

-
- 457 [4] J. Choi, O. Kim, S. Y. Kwak, Suppression of dioxin emission in co-incineration of poly(vinyl
458 chloride) with TiO₂-encapsulating polystyrene. *Environ. Sci. Technol.* 2007, 41, 5833-5838.
- 459 [5] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, Thermal degradation of PVC: A review. *Waste*
460 *Management* 2016, 48, 300-314.
- 461 [6] Y. Shen, R. Zhao, J. Wang, X. Chen, X. Ge, M. Chen, Waste-to-energy: Dehalogenation of
462 plastic-containing wastes. *Waste Management* 2016, 49, 287-303.
- 463 [7] A. Funke, F. Ziegler, Hydrothermal carbonization of biomass: a summary and discussion of
464 chemical mechanisms for process engineering. *Biofuels Bioprod. Bioref.* 2009, 4, 160-177.
- 465 [8] J. A. Libra, K. S. Ro, C. Kammann, A. Funke, N. C. Berge, Y. Neubauer, M. M. Titirici, C.
466 Fühner, O. Bens, J. Kern, K. H. Emmerich, Hydrothermal carbonization of biomass residuals: a
467 comparative review of the chemistry, processes and applications of wet and dry pyrolysis.
468 *Biofuels* 2011, 2, 89-124.
- 469 [9] L. Xiao, Z. Shi, F. Xu, R. Sun, Hydrothermal carbonization of lignocellulosic biomass.
470 *Bioresour. Technol.* 2012, 118, 619-623.
- 471 [10] M. Makela, V. Benavente, A. Fullana, Hydrothermal carbonization of lignocellulosic
472 biomass: effect of process conditions on hydrochar properties. *Appl. Energy* 2015, 155,
473 576-584.
- 474 [11] H. S. Kambo, A. Dutta, Strength, storage, and combustion characteristics of densified
475 lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. *Appl.*
476 *Energy* 2014, 135, 182-191.
- 477 [12] S. M. Heilmann, J. S. Molde, J. G. Timler, B. M. Wood, A. L. Mikula, G. V. Vozhdayev, E. C.
478 Colosky, K. A. Spokas, K. J. Valentas, Phosphorus reclamation through hydrothermal
479 carbonization of animal manures. *Environ. Sci. Technol.* 2014, 48, 10323-10329.
- 480 [13] P. Zhao, Y. Shen, S. Ge, Z. Chen, K. Yoshikawa, Clean solid biofuel production from high
481 moisture content waste biomass employing hydrothermal treatment. *Appl. Energy* 2014, 131,
482 345-367.
- 483 [14] A. Kubatova, A. J. M. Lagadec, S. B. Hawthorne, Dechlorination of lindane, dieldrin,
484 tetrachloroethane, trichloroethene, and PVC in subcritical water. *Environ. Sci. Technol.* 2002,
485 36, 1337-1343.
- 486 [15] J. Poerschmann, B. Weiner, S. Wosidlo, R. Koehler, F. D. Kopinke, Hydrothermal
487 carbonization of poly(vinyl chloride). *Chemosphere* 2015, 119, 682-689.
- 488 [16] N. D. Berge, K. S. Ro, J. Mao, J. R. V. Flora, M. A. Chappell, S. Bae, Hydrothermal
489 Carbonization of Municipal Waste Streams. *Environ. Sci. Technol.* 2011, 45, 5696-5703.
- 490 [17] S. Kieseler, Y. Neubauer, N. Zobel, Ultimate and proximate correlations for estimating the
491 higher heating value of hydrothermal solids. *Energy Fuels* 2013, 27, 908-918.
- 492 [18] A. Tremel, J. Stemann, M. Herrmann, B. Erlach, H. Spliethoff, Entrained flow gasification
493 of biocoal from hydrothermal carbonization. *Fuel* 2012, 102, 396-403.

494 [19] P. Gao, Y. Zhou, F. Meng, Y. Zhang, Z. Liu, W. Zhang, G. Xue, Preparation and
 495 characterization of hydrochar from waste eucalyptus bark by hydrothermal carbonization.
 496 *Energy* 2016, 97, 238-245.

497 [20] A. Álvarez-Murillo, E. Sabio, B. Ledesma, S. Román, C.M. González-García, Generation of
 498 biofuel from hydrothermal carbonization of cellulose. Kinetics modelling. *Energy* 2016, 94,
 499 600-608.

500 [21] A. Kruse, A. Funke, M. M. Titirici, Hydrothermal conversion of biomass to fuels and
 501 energetic materials. *Current Opinion in Chemical Biology* 2013, 17, 515-521.

502 [22] P. Prawisudha, T. Namioka, K. Yoshikawa, Coal alternative fuel production from municipal
 503 solid wastes employing hydrothermal treatment. *Appl. Energy* 2012, 90, 298-304.

504 [23] M. Muthuraman, T. Namioka, K. Yoshikawa, Characteristics of co-combustion and kinetic
 505 study on hydrothermally treated municipal solid waste with different rank coals: a
 506 thermogravimetric analysis. *Appl. Energy* 2010, 87, 141-148.

507 [24] L. Lu, T. Namioka, K. Yoshikawa, Effects of hydrothermal treatment on characteristics and
 508 combustion behaviors of municipal solid wastes. *Appl. Energy* 2011, 88, 3659-3664.

509 [25] Y. Jin, L. Lu, X. Ma, H. Liu, Y. Chi, K. Yoshikawa, Effects of blending hydrothermally treated
 510 municipal solid waste with coal on co-combustion characteristics in a lab-scale fluidized bed
 511 reactor. *Appl. Energy* 2013, 102, 563-570.

512 [26] S.E. Allen (Ed.), *Chemical Analysis of Ecological Materials*, Blackwell Scientific
 513 Publications, Oxford, 1989, pp 46-61.

514 [27] Y. Shen, Dechlorination of poly(vinyl chloride) wastes via hydrothermal carbonization
 515 with lignin for clean solid fuel production. *Ind. Eng. Chem. Res.* 2016, 55, 11638-11644.

516 [28] J. Haslam, J. B. Hamilton, D. C. M. Squirrell, The determination of chlorine by the oxygen
 517 flask combustion method: a single unit for electrical ignition by remote control and
 518 potentiometric titration. *Analyst* 1960, 85, 556-560.

519 [29] W. H. Starnes, How and to what extent are free radicals involved in the nonoxidative
 520 thermal dehydrochlorination of poly(vinyl chloride)? *J. Vinyl Addit. Technol.* 2012, 18, 71-75.

521 [30] W. H. Starnes, X. Ge, Mechanism of autocatalysis in the thermal dehydrochlorination of
 522 poly(vinyl chloride). *Macromolecules* 2005, 37, 352-359.

523 [31] N. Nagai, R. L. Smith, H. Inomata, K. Arai, Direct observation of polyvinylchloride
 524 degradation in water at temperatures up to 500 °C and at pressures up to 700 MPa. *J. Appl.*
 525 *Polym. Sci.* 2007, 106, 1075-1086.

526 [32] S. Kang, X. Li, J. Fan, J. Chang, Characterization of hydrochars produced by hydrothermal
 527 carbonization of lignin, cellulose, D -Xylose, and wood meal. *Ind. Eng. Chem. Res.* 2012, 51,
 528 9023-9031.

529 [33] S. Kang, X. Li, J. Fan, J. Chang, Hydrothermal conversion of lignin: A review. *Renew. Sust.*
 530 *Energy Rev.* 2013, 27, 546-558.

-
- [34] J. Barbier, N. Charon, N. Dupassieux, A. Loppinet-Serani, L. Mahe, J. Ponthus, M. Courtiade, A. Ducrozet, A. A. Quoineaud, F. Cansell, Hydrothermal conversion of lignin compounds. A detailed study of fragmentation and condensation reaction pathways. *Biomass Bioenerg* 2012, 46, 479-491.
- [35] A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, Lignin valorization improving lignin processing in the biorefinery. *Science* 2014, 344, 1246843.
- [36] M. Sevilla, A. B. Fuertes, The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon* 2009, 47, 2281-2289.
- [37] A. Demirbaş, Estimating of structural composition of wood and non-wood biomass samples. *Energy Sources* 2005, 27, 761-767.
- [38] W. Yan, T. C. Acharjee, C. J. Coronella, V. R. Vásquez, Thermal pretreatment of lignocellulosic biomass. *Environ Prog Sustain Energy* 2009, 28, 435-440.
- [39] Z. Liu, A. Quek, S. Kent Hoekman, R. Balasubramanian, Production of solid biochar fuel from waste biomass by hydrothermal carbonization. *Fuel* 2013, 103, 943-949.
- [40] H. S. Kambo, A. Dutta, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sust. Energ. Rev.* 2015, 45, 359-378.
- [41] C. Ryu, Y. B. Yang, A. Khor, N. E. Yates, V. N. Sharifi, J. Swithenhank, Effect of fuel properties on biomass combustion: Part I. Experiments – fuel type, equivalence ratio and particle size. *Fuel* 2006, 85, 1039-1046.
- [42] M. Iggländ, H. Leion, T. Mattisson, A. Lyngfelt, Effect of fuel particle size on reaction rate in chemical looping combustion. *Chem. Eng. Sci.* 2010, 65, 5841-5851.
- [43] M. L. Holtmeyer, B. M. Kumfer, R. L. Axelbaum, Effect of biomass particle size during cofiring under air-fired and oxyfuel conditions. *Appl. Energy* 2012, 93, 606-613.

566

567

568 **Table 1. Properties of Hydrochars Derived from HW by HTC and Washing Process**

HTT-product (as received)	Moisture (wt.%)					
HW 2.4 MPa	11.65					
HW + Woodchip 2.2 MPa	19.45					
HW + Woodchip 2.4 MPa	10.29					
Proximate Analysis (dry-basis)	Ash	Volatile	FC	HHV (MJ/kg)		
	(wt.%)	(wt.%)	(wt.%)			
HW 2.4 MPa	2.25	95.73	2.02	24.18		
HW + Woodchip 2.2 MPa	5.78	84.53	9.69	30.52		
HW + Woodchip 2.4 MPa	5.72	86.73	7.55	28.30		
Ultimate Analysis (dry-basis)	C (wt.%)	H (wt.%)	N (wt.%)	O* (wt.%)	O/C	H/C
HW 2.4 MPa	59.58	6.18	0.65	33.59	0.42	1.50
HW + Woodchip 2.2 MPa	59.72	7.08	0.54	32.66	0.41	1.42
HW + Woodchip 2.4 MPa	66.89	7.03	0.40	25.68	0.29	1.26

*Notes: HW – hospital waste; FC – fixed carbon; HHV – higher heating value; * - by difference.*

569

570 **Table 2. Operating parameters of the HTC process (PVC + woodchip)**

Parameter	Value
Processing time	120 min
Input MSW	500 kg
Raw MSW heating value	22.0 MJ/kg
Moisture content of raw MSW	33.2%
Output product	760 kg
Product heating value	24.2 MJ/kg
Moisture content of hydrochar	55.9%
Fuel consumption	59 L
Average boiler utility	4.9 kW
Average motor ampere	12 A
Water consumption	706 L
Steam temperature	220 °C
Steam pressure	2.4 MPa
Condensed water	320 L
Condensed temperature	100 °C

571

572

573

Figure 1. Application fields of hydrothermal processes [17]

574

575

576

577

578

579

580

581

582

583

584

585

586

587

Figure 2. Principle reaction pathways of HTC [21]

Figure 3. Schematic of the pilot-scale setup for HTC of PVC wastes with woodchip

Figure 4. Flow chart of the washing process for the HTC-derived solid product

Figure 5. Mass balance of chlorine in the lab-scale HTC process of PVC (210 °C, 2.2MPa)

Figure 6. Addition of lignocellulose on dechlorination efficiency of PVC

Figure 7. Dechlorination efficiency of PVC by the HTC and washing process

Figure 8. FT-IR spectra of PVC before and after HTC (PVC, HTC-PVC, and HTC-PVC-lignin)

Figure 9. Possible reaction pathway of PVC decomposition in the HTC process

Figure 10. (A) Formation pathways of lignin hydrochar [31]; (B) HTC conversion of lignin [33]

Figure 11. SEM micrographs of PVC-derived solid fuels before and after HTC (210 °C, 30 min)

Figure 12. (A) Chlorine distribution of the HW hydrochars; (B) Total-Cl in the HW hydrochars after the washing process; (C) Effect of washing times on the soluble-Cl removal efficiency; (D) Chlorine removal efficiency of the condensed and distilled waters used for one time.

Figure 13. The changes of solid surface micrograph (i.e. SEM image) and liquid viscosity

Figure 14. Van-krevelen diagram of the HW-derived solid products

Figure 15. Energy balance of the self-sustained HTC process

Figure 16. (A) Mass fraction of the solid products with different particle sizes; (B) Cumulative particle size distribution