

Cohydrothermal carbonization of waste polyvinyl chloride and wood chip for dechlorination

K Kusakabe^{1,*}, T Steven², JY Ong³, Y Uemura³ and K Ikenaga¹

¹Department of Nanoscience, Sojo University, 4-22-1 Ikeda, Nishi-ku, Kumamoto 860-0082, Japan

²Department of Applied Science, Universiti Teknologi of PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia

³Department of Chemical Engineering, Universiti Teknologi of PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia

Abstract The co-hydrothermal carbonization (Co-HTC) of polyvinyl chloride (PVC) film and wood chip (WC) was conducted at 200-260°C in an autoclave filled in air or nitrogen for the chemical recycling of wastes with dechlorination of PVC. Effects of the Co-HTC temperature and the oxidation reaction during the Co-HTC on the decomposition behaviors were investigated. The percentage decomposition in nitrogen atmosphere increased with increasing the reaction temperature and reached 76.1% at 260°C. The percentage decompositions in nitrogen were several percent higher than those in air. The synergistic effect of PVC and WC for the decomposition was observed at 220°C in N₂. When the Co-HTC was performed in air, decomposition was suppressed, indicating the increase in hydrochar yield. The dechlorination yield was determined from the Cl content in the recovered PVC after the Co-HTC reaction. Under nitrogen atmosphere conditions, the dechlorination yield increased slightly with increasing the temperature. At a carbonization temperature of 260°C, the dechlorination yield of PVC was about 40%.

1. Introduction

The treatment method of waste polyvinyl chloride (PVC) resins discarded from industrial, agricultural, and architectural fields has been established through material recycling in Japan. However, general waste plastics mixed with PVC products have been subjected to the thermal decomposition [1-3] and the landfill treatment. The thermal recycling of PVC is particularly difficult to process because it produces harmful HCl gas and organic halides during pyrolysis. Dechlorination ratio reaches 90% in the advanced PVC pyrolysis method above 600K. [4] However, the yield of solid residue is 10-20% and the loss of hydrocarbon is large. Therefore, the research on efficient dechlorination methods is required.

Hydrothermal carbonization (HTC) technology has been considered as one of the most promising ways of recycling solid waste to produce hydrochar. [5] In HTC treatment, solid waste such as waste plastics and biomass are heat-treated in subcritical water. The advantage of HTC is its relatively low process temperature, no need to dry the feedstock, the homogenized composition of the product, and a high relative carbon content in the product. Previous studies have shown that 50-90% of carbon contained in the feedstock remains in the hydrochar which was produced by HTC. Alkaline compounds are added to the HTC of PVC to enhance the reaction, but environmental problems remain in term of waste treatment. Poerschmann et al., [6] carried out the HTC of PVC at 180-260°C. Dechlorination increased with

increasing reaction temperature and the removal chlorine was almost quantitative above 235°C.

Co-hydrothermal carbonization (Co-HTC) can promote the synergistic interaction between the two feedstocks by the simultaneous HTC treatment. Shen et al. [7] reported that the Co-HTC of PVC-containing medical waste and three lignocellulosic components (lignin, cellulose and hemicellulose). The dechlorination performance of lignocellulosic components is given as the following order: lignin > cellulose > hemicellulose. During the Co-HTC, a large amount of free OH group in biomass converted from organic chlorine in PVC to the inorganic chlorine. Yao and Ma [8] treated PVC and bamboo by Co-HTC at 200, 230 and 260°C. The inorganic-chlorine was removed from the hydrochar in the term of HCl. The bamboo could accelerate the HTC dichlorination of PVC at 200°C because it strengthened the substitution of Cl with OH. While at 230°C and 260°C, the existence of bamboo hindered the dichlorination of PVC in HTC. Huang et al. [9] evaluated the dechlorination efficiency and the inorganics removal efficiency for clean biocoke production through the Co-HTC of PVC and pine sawdust. The most important factor for the dichlorination efficiency was the hydrothermal temperature, followed by residence time and particle size of the sawdust. The dichlorination efficiency could reach 64% by the Co-HTC at a temperature of 260°C for 120 min. The addition of PVC and the temperature increase are not conducive to the formation of porous hydrochar. However, these research works have been conducted on pure PVC or powder. To realize the waste PVC treatment process, Co-HTC of biomass and the

* Corresponding author: kusakabe@nano.sojo-u.ac.jp

commercial PVC resin containing the plasticizers or other additives have to be investigated. In addition, it is necessary to investigate the effect of the oxidation reaction during the Co-HTC.

In this work, Co-HTC of WC and commercial PVC resin film was performed in an autoclave at 200, 220, 240 and 260°C for 120 minutes. Effects of reaction temperature and oxygen atmosphere on the behaviours of the decomposition and the dechlorination were investigated.

2. Materials and methods

2.1 Materials

Wood chip (WC) of *Juglans mandshurica* var. *sachalinensis* for smoked uses was purchased from Shin-fuji Burner Co. Ltd., Japan and used as representative of lignocellulosic biomass. The WC was milled into small pieces and dried at 105°C in an oven for 2 hours. A commercially available PVC resin film with the thickness of 0.1 mm was cut into small pieces of several millimetres in size for use.

2.2 Co-hydrothermal carbonization process (Co-HTC)

The Co-HTC process was conducted using a 25ml autoclave reactor (San-ai Kagaku Co. Ltd., Japan). Figure 1 shows the schematic diagram of Co-HTC of WC and PVC. In each experiment, WC (0.2 g), PVC (0.2 g) and distilled water (15 ml) were loaded into a decomposition container of the reactor. To investigate the effect of oxygen on Co-HTC process, the autoclave was shielded in a glove box filled with nitrogen or air. After heating the electric furnace to the desired temperature (200, 220, 240 and 260°C), the autoclave was placed in the furnace and heated for designed reaction time (120 min.). Separation of the hydrochar and the liquid filtrate was conducted by vacuum filtration. The hydrochar samples were dried in a vacuum oven at 105°C for 1 day to remove moisture.

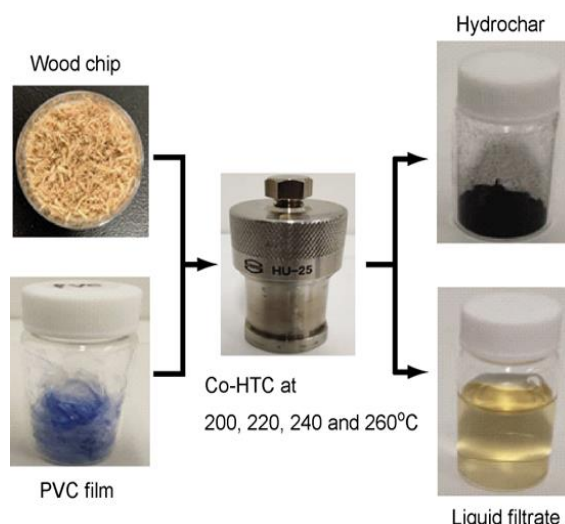


Figure 1. The schematic diagram of Co-HTC of WC and PVC.

2.3 Characterization

The surface morphologies of the raw wood chip and the hydrochar samples were observed with a scanning electron microscope (SEM VE-9800, Keyence Japan). The thermal decomposition behavior of the biochar was evaluated via the thermogravimetric analysis with a TG/DTA (Hitachi A7220, Japan). The hydrochar samples (20 mg) were heated from 30°C to 600°C at a linear heating rate of 10°C/min under an argon flow of 100ml/min.

Percentage decomposition was calculated from the following equation.

$$\text{Percentage decomposition} = \left(1 - \frac{\text{mass of hydrochar}}{\text{mass of feedstock}}\right) \times 100\% \quad (1)$$

When the hydrochar yield is defined as the ratio of mass of hydrochar to mass of feedstock, hydrochar yield is equivalent to the value of $(1 - \text{percent decomposition}/100)$.

The solid carbonized PVC residue was easily separated from the hydrochar. Therefore, Cl content in the PVC residue was measured by the combustion method. 50 mg of the PVC residue which was wrapped with a filter paper, was completely oxidized in a closed flask with a sodium carbonate solution under a pure oxygen atmosphere. The Cl concentration in the sodium carbonate solution was determined via an ion chromatography (Dionex Integrion HPIC system, Thermo Fisher Scientific, USA). The dechlorination yield of PVC was calculated via the following equation.

$$\text{Dechlorination yield of PVC} = \left(1 - \frac{\text{Cl content in carbonized PVC}}{\text{Cl content in initial PVC}}\right) \times 100\% \quad (2)$$

* Corresponding author: kusakabe@nano.sojo-u.ac.jp

3. Results and Discussion

Figure 2 shows the surface morphologies of raw WC and hydrochar. Figure 2a reveals the elongated fibrous shapes of the unreacted WC with the intact surface before Co-HTC process. The smooth surface becomes rough after Co-HTC process. As shown in Figure 2b, the fibrous shape remained at 220°C and the disruption of the cell wall was small. As the temperature was raised to 240 and 260°C (Figure 2c and 2d), the development of pore structure become remarkable due to the evolution of CO₂ and H₂O during the carbonization. At 260°C, the surface morphology of hydrochar obtained in air was almost the same as that in nitrogen.

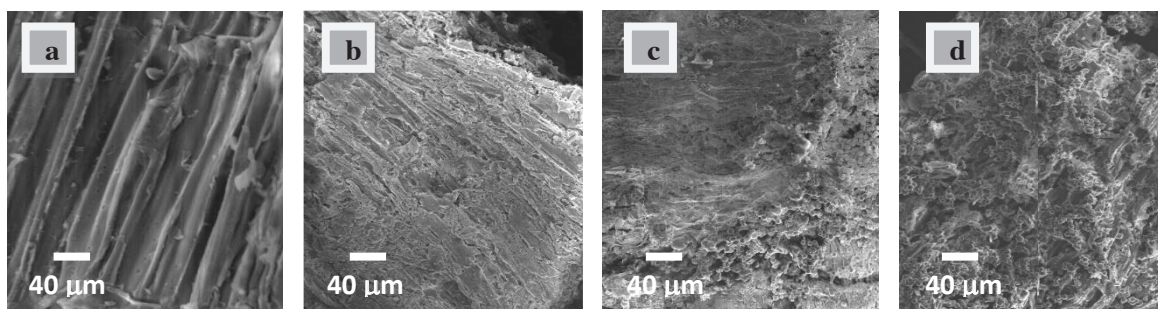


Figure 2. SEM images of (a) woodchip, (b) PVC/WC hydrochar at 220°C, (c) PVC/WC at 240°C, (d) PVC/WC at 260°C : Co-HTC in N₂.

HTC of WC or PVC was performed under the same conditions as Co-HTC of WC and PVC in this study. Figure 3 shows the effect of the temperature on the percentage decomposition in N₂ atmosphere. HTC of WC indicated the highest percentage decomposition. The percentage decomposition of PVC hardly proceeds at 200°C, and it was only 31.4 % at 220°C. However, by performing Co-HTC of PVC and WC, the percentage decomposition of PVC/WC mixture was close to that of WC. A synergistic effect on the decomposition was observed with the combination of PVC and WC at 200-220°C. Yao and Ma [8] reported that the Co-HTC of PVC and bamboo promoted decomposition at 200°C, as in the present study, but conversely suppressed the decomposition at 230°C and 260°C. As shown in Fig. 2, Co-HTC of PVC and WC show no suppression effect at 240°C and 260 °C. These behaviours are thought to be due to the difference in the content of hemicellulose, cellulose and lignin between bamboo and WC.

The percentage decompositions in air and N₂ were compared to clear the effect of oxidation on Co-HTC of PVC and WC. As shown in Figure 4, oxidation by oxygen in air accelerated the decomposition during the HTC of PVC. However, for HTC of WC and Co-HTC of PVC and WC, high percentage decomposition was obtained in N₂ atmosphere. Table 1 summarizes the results of the percent decomposition. In the Co-HTC of PVC and WC, the percentage decompositions in N₂ were several percent higher than those in air. This means that oxygen remains as oxygen-containing functional groups due to WC surface oxidation during

the Co-HTC in air. Assuming that oxygen remains as an oxygen-containing functional group in the solid residue after carbonization, it is considered that the weight of the solid residue increases in air and the percentage decomposition apparently decreases. The total amount of gaseous oxygen in the autoclave was calculated to be 2.56 mg, which is sufficient enough to reduce the percent decomposition by several percent.

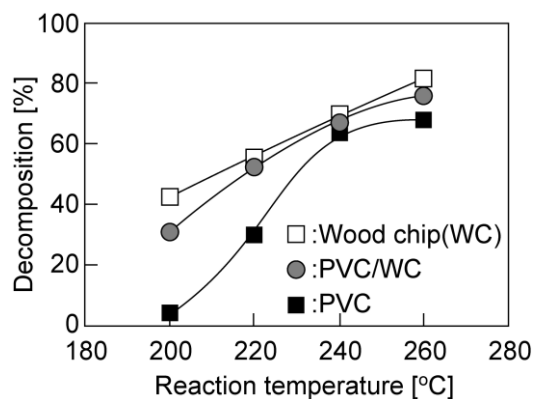


Figure 3. Effect of hydrothermal temperature on the percent decomposition.

In Table 1, the percent decomposition for HTC of WC and PVC are expressed as P_{WC} and P_{PV}, respectively, and the percentage decomposition rates of the Co-HTC are expressed as P_{PVC/WC}. When the synergistic effect due to Co-HTC is evaluated by calculating the value of P_{PVC/WC} / [(1/2) (P_{WC} + P_{PV})], the synergistic effect on decomposition is observed only at 220°C under nitrogen atmosphere. On the other hand, in air, the value of the synergistic effect became less than one at any temperature due to the increase in oxygen-containing functional groups. Conversely, hydrochar yield became high in air.

* Corresponding author: kusakabe@nano.sojo-u.ac.jp

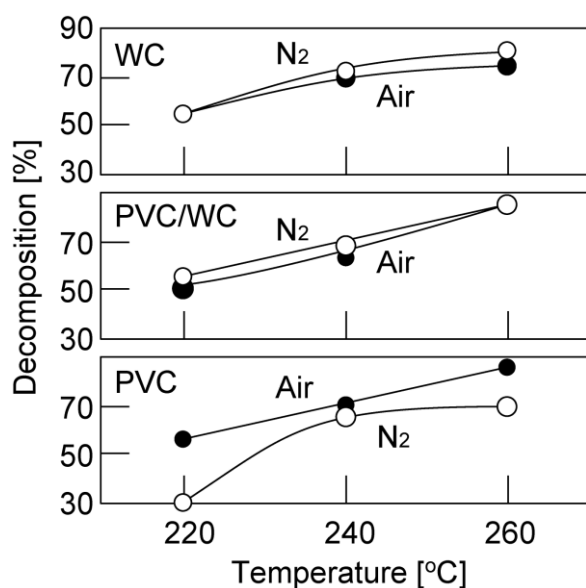


Figure 4. Effect of oxidation during HTC on the percent decomposition.

Table 1. Synergy effect of Co-HTC.

Temp. [°C]	Gas	Percentage decomposition [%]		
		PD _{PVC/WC}	PD _{WC}	PD _{PV}
		Synergy effect		
		$\frac{1}{2}(PD_{WC}+PD_{PV})$	$\frac{PD_{PVC/WC}}{1/2(PD_{WC}+PD_{PV})}$	
220	N ₂	43.43	1.27	31.36
240	N ₂	67.72	1.01	64.93
260	N ₂	75.33	1.01	68.66
220	Air	55.59	0.875	55.45
240	Air	71.68	0.877	71.07
260	Air	80.88	0.912	86.25

Figure 5 reveals that the dechlorination yields for the recovered PVC sample in N₂ are higher than those in air. Under nitrogen atmosphere conditions, the dechlorination yield increased slightly with temperature. Even at a carbonization temperature of 260°C, the dechlorination yield was about 40%. Dechlorination proceeded in two ways: elimination and substitution reaction. For the elimination reaction, chlorine in the polymer chain was converted to hydrogen chloride,

generating a double bond in PVC [10]. As the elimination proceeds, some compounds with polyene structure are formed, and thereafter, aromatic compounds are formed by a cyclization reaction. For the substitution reaction, C-OH functional groups are formed in PVC by a substitution reaction between chlorine in the polymer chain and a hydroxyl group in biomass. The HTC of PVC usually promotes the dechlorination under basic conditions [11], which suggests that oxygen-containing functional groups in biomass would significantly affect the dechlorination reaction.

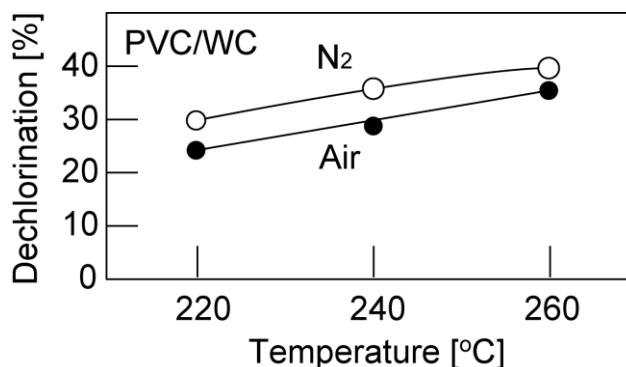


Figure 5. Dechlorination yield for the Co-HTC of PVC and WC.

Figure 6 shows differential thermo-gravimetry (DTG) of feedstock WC and carbon residues after HTC of WC at 220-260°C. The shoulder peak observed in the TG temperature range of 200°C to 220°C indicates the thermal decomposition of hemicelluloses containing in WC [11]. The TG peak at 340°C corresponds to the thermal decomposition of cellulose. The broad peak observed above 380°C is generally considered to be the thermal decomposition of lignin and can be hardly observed in this study, indicating that lignin content in the feedstock WC is low. When the feedstock WC was hydrothermally carbonized at 220°C, the hemicellulose component was preferentially completely decomposed. Increasing the HTC temperature up to 260°C, cellulose component was gradually decomposed. In addition, the broad peak above 380°C became large, indicating the formation of the products by cleavage of the cellulose main chain. The similar results were obtained from the research on the TG measurements of the torrefied wood chip [12].

The DTG of the solid residue after Co-HTC of PVC and WC together with PVC are shown in Figure 7. PVC has a large peak at around 280°C due to the removal of hydrogen chloride and volatilization of lower hydrocarbon aromatic compounds, formed by the dechlorination reaction. A second peak at 450°C was caused by the volatilization of heavier aromatic compounds [13].

* Corresponding author: kusakabe@nano.sojo-u.ac.jp

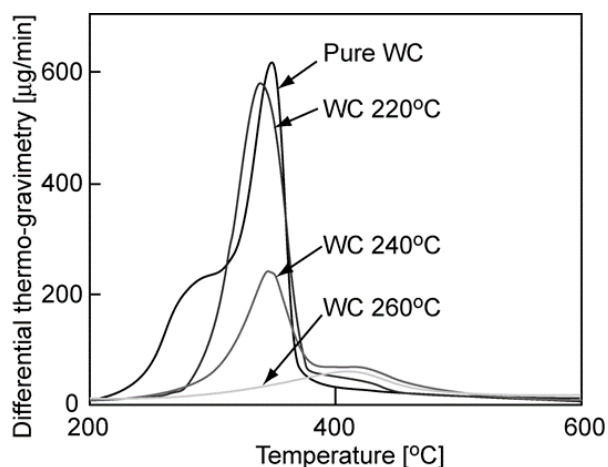


Figure 6. DTG curves obtained from the feedstock WC and the hydrochar after HTC of WC

The DTG of the solid residue after the Co-HTC reaction at 220 °C showed the behaviour similar to that of untreated PVC. For the Co-HTC of PVC and WC, the peak at 340°C in Figure 6 due to the decomposition of cellulose in WC did not appear. It is considered that the cellulose component in WC was decomposed together with PVC at a lower temperature. After the Co-HTC of PVC and WC at 240°C, the peak at 340°C was observed due to the progress of PVC dechlorination.

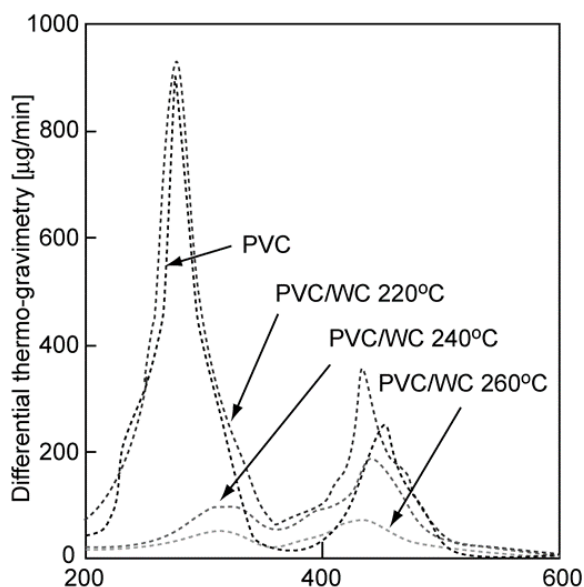


Figure 7. DTG curves obtained from the feedstock PVC and the hydrochar after Co-HTC of PVC and WC

4. Conclusion

Co-hydrothermal carbonization (Co-HTC) process was used to treat the WC and PVC wastes in order to produce hydrochar with dechlorination of PVC. Although the decomposition and the dechlorination of the feedstock were promoted at high temperature, the

hydrochar yield became low in any conditions. Percentage decomposition in air slightly lower than in N₂. This means that the oxygen-containing groups are formed on the surface of WC under the air atmosphere. The dechlorination yield for the recovered PVC after the Co-HTC was increased slightly with increasing temperature from 30% at 220°C to 40% at 260°C in N₂. Judging from this result and the DTG of hydrochar, it indicates that dechlorination is progressing at a low temperature stage. Further research for the improvement of the synergic effect on dechlorination during Co-HTC at low temperatures is needed.

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* Corresponding author: kusakabe@nano.sojo-u.ac.jp