

## Article

# Understanding Hydrothermal Dechlorination of PVC by Focusing on the Operating Conditions and Hydrochar Characteristics

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**Abstract:** To remove chlorine from chlorinated wastes efficiently, the hydrothermal treatment (HT) of PVC was investigated with a lower alkaline dosage in this work. Some typical operating conditions were investigated to find out the most important factor affecting the dechlorination efficiency (DE). The FTIR technique was employed to detect the functional groups in PVC and hydrochars generated to reveal the possible pathways for chlorine removal. The results show that the HT temperature was a key parameter to control the dechlorination reaction rate. At a HT temperature of 240 °C, about 94.3% of chlorine could be removed from the PVC with 1% NaOH. The usage of NaOH was helpful for chlorine removal, while a higher dosage might also hinder this process because of the surface poisoning and coverage of free sites. To some extent, the DE was increased with the residence time. At a residence time of 30 min, the DE reached a maximum of 76.74%. A longer residence time could promote the generation of pores in hydrochar which is responsible for the reduction in DE because of the re-absorption of water-soluble chlorine. According to the FTIR results, the peak intensities of both C=CH and C=C stretching vibrations in hydrochar were increased, while the peak at around 3300 cm<sup>-1</sup> representing the -OH group was not obvious, indicating that the dehydrochlorination (elimination reaction) was a main route for chlorine removal under these conditions studied in this work.

**Keywords:** chlorinated wastes; PVC; hydrothermal dechlorination; dechlorination efficiency; FTIR

## 1. Introduction

Poly (vinyl chloride) is one of the most widely applied chlorinated plastics, and it has been utilized in many areas such as packaging, wrappings, bottles and containers because of its low price and good performance [1]. Accordingly, large amounts of PVC-containing wastes are being generated and needed to be disposed of. Basically, the recycling of polymeric solid wastes can be carried out by re-extrusion, mechanical, chemical and energetic recovery [2]. For PVC-containing wastes, several methods have been proposed for recycling. Among them, thermal recycling (pyrolysis, gasification, hydrogenation, etc.) and incineration have been the main technologies widely applied. However, PVC is rather resistant to incineration because of its high chlorine content (56.8%). As for the thermal degradation, it suffers from toxic emissions and generate a lot of hydrochloric acid (HCl), which can cause corrosion in the furnace and lead to the release of trace amounts of further harmful gases such as

organohalogen compounds and substantial amounts of chlorinated dioxins and furans, resulting in severe environmental and health problems. For landfilling, phthalate and heavy metals (derived from plasticizer and stabilizer) such as lead, cadmium, and tin can leach out, which might contaminate the soil and ground water. In particular, phthalate can be an endocrine disruptor. Recently, it has been suggested that phthalate leakage from PVC products, such as blood bags, baby pacifiers, and toys, can cause health problems [3]. Therefore, dechlorination is an optimal option for the safe disposal of chlorinated organic wastes.

Many studies have investigated PVC degradation by means of both thermal and wet treatments. Yu et al. reviewed the thermal degradation of PVC with emphasis on the recent progress in PVC pyrolysis [4]. The dehydrochlorination of PVC mainly happened at a temperature range of 250–320 °C, depending on the material, the stabilizers and also the additives [5]. According to the thermogravimetry-mass spectrometry (TG-MS) analysis, the degradation could be divided into three stages [6], proceeding from an apparent zero-order reaction to an apparent first-order reaction [7]. To improve the chlorine removal efficiency, many other methods based on pyrolysis have been developed recently. Yuan et al. [8] utilized a gas-liquid fluidized bed reactor to investigate the chlorine behavior and reported that the dechlorination efficiency (DE) was dependent on the reaction temperature and 99.5% of Cl could be removed at a reaction temperature of 300 °C in 1 min. Wu et al. [9] studied the co-pyrolysis behavior of PE (poly ethylene), PVC and PS (poly styrene) and stated that the dechlorination of PVC occurred simultaneously with the rearrangement and cyclization of conjugated polyene, leading to the formation of dioxins. Parts of methyl (–CH<sub>3</sub>) and methylene (–CH<sub>2</sub>–) groups disappeared during the co-pyrolysis of PVC with PS/PE. Pyrolysis is efficient for removing chlorine from PVC, whereas a high temperature was required and the problems of secondary pollution such as emission of HCl, dioxins and corrosion of facilities still existed.

Hydrothermal treatment (HT) is another efficient technology which has the advantage of presenting simple and fast reaction rates, and of being a homogeneous reaction without the limitations of mass transfer [4]. It has been widely applied in the field of wastes to energy (WtE) [1,3,10–16]. In this system, supercritical or subcritical water works as a solvent and reagent for reactions of organic compounds [17]. Endo and Emori [18] reported that 100% of chlorine could be removed at 19.3 MPa and 300 °C. To dechlorinate PVC under mild conditions and also to improve the DE, some additives were utilized. Among them, NaOH was one of the most popular additives. Shin and Yoshinaga stated the NaOH affected the DE and could decrease the hydrothermal temperature from 300 °C [19] to 150–250 °C [19,20]. Some organic solvents such as dimethylsulfoxide [20] and ethylene glycol [21] were introduced to further improve the DE with NaOH. All such experiments indicated these additives and solvents improve the hydrothermal dechlorination efficiency. However, the recycling of solvents was still a problem. Besides that, a high dosage of alkaline chemical reagent increased the experimental cost, eroded facilities, and could harm operators, thus hindering its commercial application.

In this work, we intend to investigate the hydrothermal dechlorination of PVC at a low NaOH dosage, aiming at efficiently removing chlorine from chlorinated wastes. Compared with the high NaOH dosage in other works (0–7 M) [21–23], the NaOH dosage was quite low, thus enlarging the understanding of the hydrothermal treatment of PVC-containing wastes. Additionally, the functional groups were observed by means of FTIR in order to reveal the possible pathways.

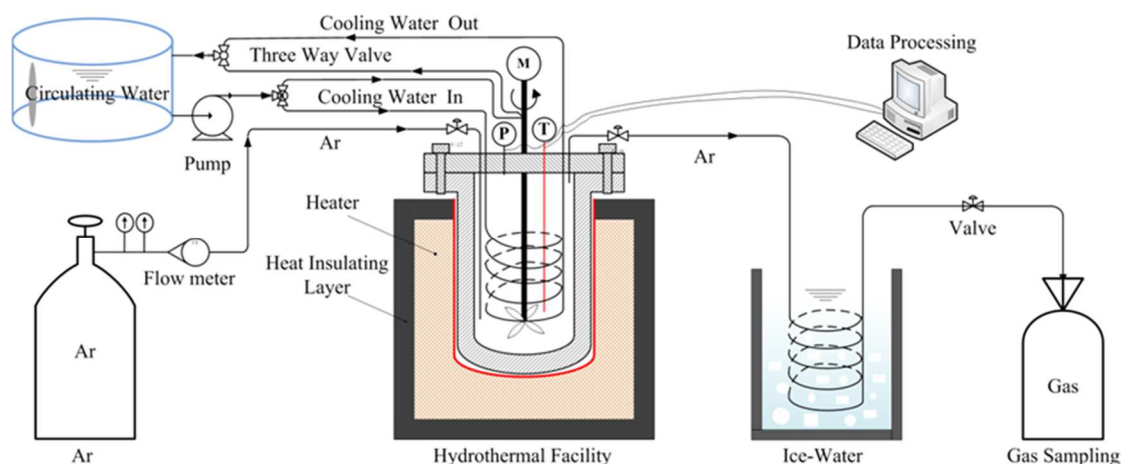
## 2. Materials and Methods

### 2.1. Chemicals

The equipment was provided by Yantai Songling Chemical Equipment Co., Ltd., Yantai, China. Virgin PVC (analytical grade chemical, purity 99.99%) with an average molecular weight ~90,000 Da and a chlorine content of 61.5% was purchased from Youngling Electromechanical Technology Co., Ltd., Shanghai, China. Its particle size was around 110–120 mesh. The other analytical grade chemicals, such as AgNO<sub>3</sub>, NaOH, et al. were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

## 2.2. Hydrothermal Dechlorination

Figure 1 shows a schematic diagram of the batch-type hydrothermal dechlorination facility utilized in this work. The experimental system consists of an autoclave reactor, a cylindrical electronic heat jacket, a circulation cooling water system, a carrier gas supply cylinder and a gas-sampling system with a water-cooling bath. The PVC was hydrothermally dechlorinated in a batch-type autoclave reactor whose volume is around 500 mL with a vertical size of 190 mm and a diameter of 58 mm.



**Figure 1.** Schematic diagram of the equipment for hydrothermal dechlorination of PVC.

Before the HT dechlorination, the PVC pre-mixed with deionized water as the mass ratio (dry basis) of 1:15 (7 g PVC and 105 g deionized water) was loaded into a glass tube with a volume of 450 mL. A certain amount of sodium hydroxide (0%, 1%, 3% and 5% of PVC amount) was also added and then well mixed. After that, the tube was moved into the reactor which was subsequently sealed. Then the reactor was placed in the cylindrical electronic heat jacket and the argon with a purity of 99.999% supplied from a cylinder was used to replace the atmosphere in the reactor for about 5 min. Finally, the reactor was heated up to the target temperature and the mixer was kept stirring at a speed of 50 rpm to ensure the uniformity of reaction temperature within the samples. During the reaction, the temperature was measured by a thermocouple installed inside the reactor to get a feedback signal for controlling the furnace and maintained within  $\pm 5$  °C of the target temperature for the desired time (residence time). After a certain time, the electric heater was turned off and the reactor was cooled down by a circulation cooling water system. When the temperature was lower than 90 °C, the outlet valve was slightly opened to collect the gas as shown in Figure 1. After the pressure and temperature were fell down to the atmospheric and room temperature, the glass tube was taken out to collect the products, which were separated into two parts by filtration. The solid parts noted as hydrochar was well dried in an electric oven at 103–105 °C for 24 h and stored in a desiccator for further analysis. The amount of Cl in the liquid sample was determined by potentiometric titration and the chlorine content in hydrochar was determined according to GB/T 7139-2002 (eqv ISO 1158: 1998), in which the flask combustion-ion titration method was adopted.

In the current research, four reaction temperatures 180 °C, 200 °C, 220 °C and 240 °C were used for the HT dechlorination experiments, respectively. Five residence times 0, 15, 30, 45, and 60 min were utilized for 220 °C to investigate the effect of the residence time on the HT chlorination of PVC. The residence time for the other temperatures was fixed as 60 min and the NaOH dosage ranged from 0% to 5% of the mass of PVC. Each HT dechlorination experiment and test was repeated three times respectively to reduce the experimental errors.

After obtaining the chlorine content in the liquid, the HT dechlorination efficiency (DE) could be derived by the following equation:

$$\text{HT dechlorination efficiency (DE, \%)} = \frac{\text{Cl content in liquid}}{\text{Cl content in PVC}} \times 100\% \quad (1)$$

### 2.3. Fourier Transform Infrared (FTIR) Spectroscopy Analysis

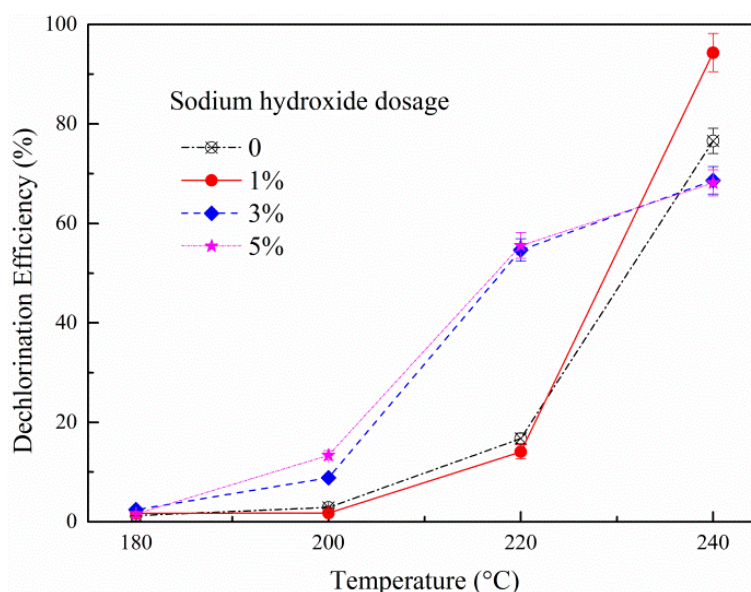
The Fourier Transform Infrared (FTIR) was employed to characterize the functional group changes before and after the HT dechlorination of PVC. The hydrochar were crushed into 200 meshes (around 74  $\mu\text{m}$ ). Two milligram of the sample were mixed with 200 mg KBr (FT-IR grade) and pressed into a pellet. The pellet was immediately measured after preparation under ambient conditions in the mid-infrared area (wave number range 4000–400  $\text{cm}^{-1}$ ) using the transmission mode. The spectra were obtained using Raman Spectroscopy Senterra VERTEX80V (Bruker, Germany). Thirty-two scans were performed with a resolution of 4  $\text{cm}^{-1}$ .

## 3. Results

### 3.1. Effect of Operation Conditions on HT Dechlorination Behavior

#### 3.1.1. Effect of Temperature on HT Dechlorination of PVC

Comparatively, the color of PVC changed from white to light brown for all these hydrochars and got darker and darker with the HT temperature, residence time and also the NaOH dosage. Significant degradation of PVC took place because of the hydrolysis and difunctionalization such as dehydration, recondensation and aromatization [13]. Figure 2 indicates that the HT temperature played a dominant role in the HT dechlorination among all these experimental conditions investigated. Whether adding NaOH or not, the DE kept increasing with the HT temperature. After the HT temperature was higher than 200  $^{\circ}\text{C}$ , the DE was dramatically increased. The highest DE of 94.3% was obtained at a HT temperature of 240  $^{\circ}\text{C}$  in the presence of 1% NaOH. This result indicates that the PVC dechlorination rate was controlled by the HT temperature, which was in accordance with that reported by Yoshioka et al. [21]. It is reasonable because the chemical reaction rate was usually determined by the temperature because of the activation energy.



**Figure 2.** Effect of temperature on HT dechlorination of PVC.



Although a growth trend with the HT temperature was presented in the DE for all conditions, a small difference could be still observed. At a lower NaOH dosage of 0% and 1%, the DE was nearly the same when the HT temperature was below 220 °C. It was slightly increased from 1.6% to around 10%, and then dramatically improved to 55% as the temperature was increased from 180 °C to 220 °C. After the HT temperature was increased to 240 °C, the DE for 1% NaOH was sharply increased from 14% to 94.3%, higher than that without NaOH (the DE was about 76.6%). The DE increase rate kept increasing with the HT temperature. At a dosage of 3% and 5%, the trend of the DE variation with the temperature was almost the same. After the temperature was higher than 220 °C, the DE increase rate reduced a little, which was in contrast to those of 0% and 1%. This is because the chlorine transformation behavior was also affected by some other parameters, such as the alkalis dosage, rotating speed, holding time, etc.

The slope of the curve representing the DE increase rate could be expressed as the dechlorination rate constant,  $k$ , as a function of the HT temperature. In the HT dechlorination of PVC at 3% and 5% NaOH dosages, the DE could be described as an S-type curve. The dechlorination rate was increased with the HT temperature when the HT temperature was lower than 220 °C. However, it decreased a little after the HT temperature was increased from 220 °C to 240 °C. For the sample hydrothermally treated at 0% and 1% NaOH dosages, it kept increasing with the HT temperature. This difference might be ascribed to the variation in the NaOH dosage, which changed the viscosity of the reaction medium. The reaction between the PVC particle and dissolved NaOH happened in a multi-phase hybrid system. After the surface reaction between the PVC particle and NaOH, the OH<sup>-</sup> then penetrates into the PVC particles [21]. A high NaOH concentration may change the surface morphology of the PVC particle, preventing the penetration of OH<sup>-</sup> and slowing down the dechlorination rate.

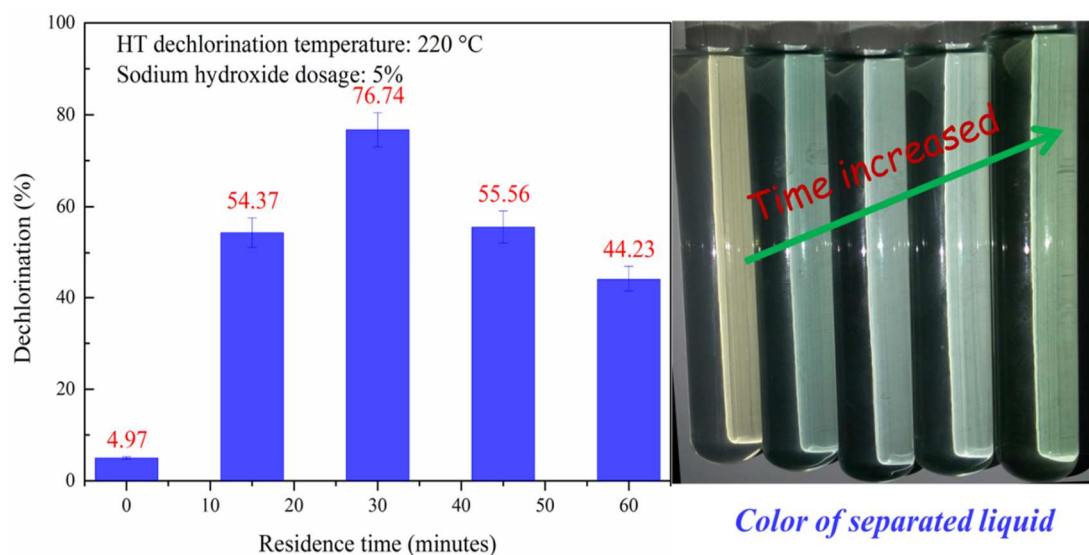
### 3.1.2. Effect of NaOH Dosage on HT Dechlorination of PVC

Figure 2 also presents the effect of the NaOH dosage on the DE. As indicated, the alkalinity was also an important factor affecting the DE of HT dechlorination. To remove the most chlorine from PVC, the optimum NaOH dosage varied with the HT temperature. With the increase of the NaOH dosage, three different trends in the DE were observed in this figure. For PVC dechlorinated at lower temperatures of 180 °C and 200 °C, only slight changes were observed with changes in the NaOH dosage, reaching a maximum dechlorination of 13.38% at 200 °C for 60 min with 5% NaOH. As the temperature rose from 200 °C to 220 °C, the DE was significantly increased. The DE of the sample hydrothermally dechlorinated at 220 °C in the absence of NaOH reached a DE of 16.73% for PVC, which was higher than the maximum DE for the PVC treated at lower temperatures. In addition, the DE increased with the increase of the NaOH dosage, approaching a maximum of 54.62%. When the NaOH dosage reached up to 3%, a slight and negligible increase was observed, indicating that the optimum NaOH dosage was 3% for HT dechlorination of PVC at the condition of 220 °C and 60 min.

At a HT temperature of 240 °C, the DE was first increased and then decreased sharply when the NaOH dosage was increased from 0 to 5%. The maximum DE of 94.33% happened at 1% NaOH at this temperature. When the NaOH dosage was improved from 1% to 3%, the DE sharply decreased from 94.33% to 68.65%. This could be ascribed to the higher viscosity of the reaction system, which resulted in a loss of active sites in the chain [12]. Moreover, the surface poisoning through the formation of metal chloride species obtained from the reaction between the hydrogen chloride and sodium hydroxide might be another reason for the reduction in DE [24]. It is interesting to note that the DEs of PVC hydrothermally dechlorinated at lower NaOH dosages (0% and 1%) were higher than those treated at higher sodium hydroxide dosages (3% and 5%) at a HT temperature of 240 °C. It clearly indicates that the PVC decomposition in subcritical water was a temperature-dependent process. At a HT temperature of 220 °C, the NaOH could play as a catalyst and scavenger [24], which promoted the decomposition of PVC. However, as the decomposition rate also depended on the HT temperature, the maximum DE was around 55.5%. At higher temperatures (e.g., 240 °C), the increase of the sodium hydroxide would hinder the HT dechlorinating of PVC.

### 3.1.3. Effect of Residence Time on HT Dechlorination of PVC

In a certain temperature range, the increase of the residence time could enhance the density, dielectric constant and polarity of the solvent [25]; as a result, the solvent improved the solubility of the carbonization products and increased the reaction rate. Figure 3 shows the effect of the residence time on the DE of PVC hydrothermally treated at a temperature of 220 °C with 5% NaOH. The higher the DE, the darker the separated liquid is. The nickel would be responsible for the light-green color of the separated liquid, which might imply the corrosion of the stainless steel reactor. With increasing the residence time, the DE increased first, and then declined dramatically. At a residence time of 30 min, the DE reached a maximum of 76.74%. This could be ascribed to the excessive residence time promoting the carbonization of the hydrochar and generating many pores enhancing the adsorption capacity. As a result, some water-soluble chlorine was re-absorbed by the hydrochar, causing a reduction in the DE. These results indicate that the operating conditions should be optimized by fully taking the HT temperature, the residence time, the additive dosage, the ratio of water to PVC, the rotating speed, etc., into account. In that case, an orthogonal experiment considering all these factors should be conducted.



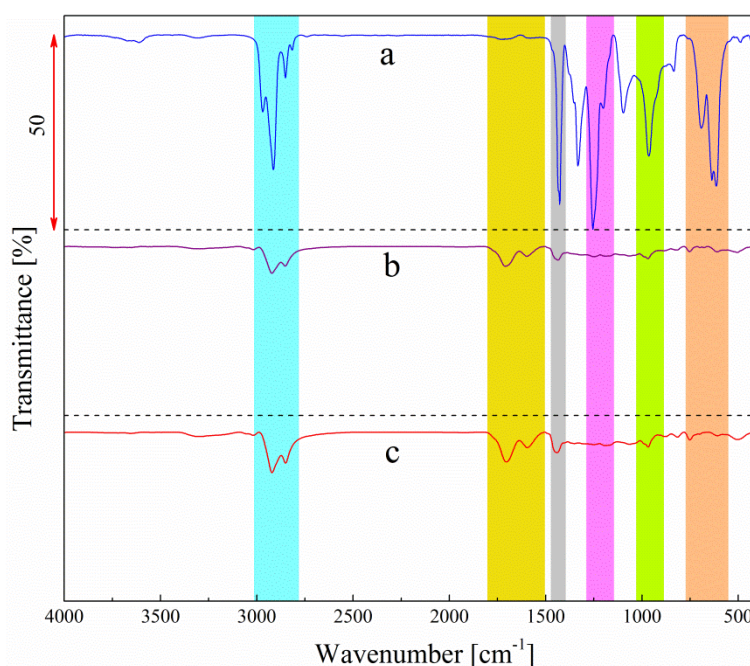
**Figure 3.** Effect of residence time on HT dechlorination of PVC.

### 3.2. Effect of HT Dechlorination on Functional Group Existing in PVC

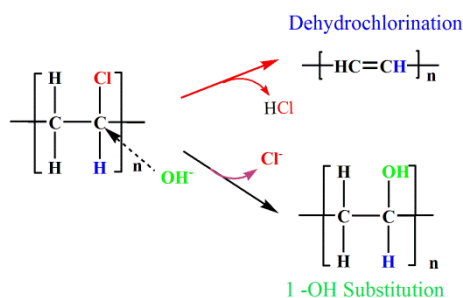
The functional groups of the PVC and the hydrochar were analyzed by FTIR spectrometry and the spectra are shown in Figure 4. The spectra were interpreted according to previously published data [9,21,23,26,27]. Figure 4a shows the spectrum of the original PVC. The strong absorption bands at around 2914  $\text{cm}^{-1}$  and 2851  $\text{cm}^{-1}$  were attributed to  $-\text{CH}_2$  asymmetric and symmetric stretching [27], certifying the existence of the methylene ( $-\text{CH}_2-$ ) group. The absorption band at 2817  $\text{cm}^{-1}$  existing in PVC, which was assigned to C–H stretching in the phase, diminished in the hydrothermally dechlorinated products. The C–H stretching band on neighboring  $\text{CHCl}$  groups at 2969  $\text{cm}^{-1}$  disappeared after the hydrothermal process [27]. The absorption bands at around 1427  $\text{cm}^{-1}$  and 1332  $\text{cm}^{-1}$  were ascribed to the C–H wagging and bending vibration [12]. The bands at 1255  $\text{cm}^{-1}$  corresponded to the skeletal vibration ( $\text{Cl}-\text{C}-\text{H}$ ). The bands at 1097  $\text{cm}^{-1}$  and 964  $\text{cm}^{-1}$  were ascribed to the C–C stretching and  $-\text{CH}_2$  wagging, respectively. Besides, the bands between 600  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$ , 834  $\text{cm}^{-1}$  could be attributed to C–Cl stretching vibrations. The existence of plasticizer could be verified by the absorption bands of PVC at 487  $\text{cm}^{-1}$  and 428  $\text{cm}^{-1}$ .

After the HT dechlorination, the bands at about 2920  $\text{cm}^{-1}$ , 2850  $\text{cm}^{-1}$ , 1427  $\text{cm}^{-1}$  and 960  $\text{cm}^{-1}$  were obviously weakened. The peak at 2914  $\text{cm}^{-1}$  of pure PVC assigned to  $-\text{CH}_2$  stretching was shifted to 2922  $\text{cm}^{-1}$  (as shown in Figure 4b) and 2921  $\text{cm}^{-1}$  (as indicated in Figure 4c) in the hydrochar,

while the skeletal vibration at  $1255\text{ cm}^{-1}$  for pure PVC shifted to  $1249\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$ , and the trans  $-\text{CH}_2$  wagging of PVC presenting at  $964\text{ cm}^{-1}$  shifted to  $969\text{ cm}^{-1}$  and  $968\text{ cm}^{-1}$ . The peaks at around  $1330\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  (corresponding to the C–H bending vibration and the skeletal vibration Cl–C–H) almost disappeared, implying that the skeletal chain was destroyed and part of the chlorine was removed by the hydrothermal reaction. The nucleophilic substitution, cyclization, hydrolysis, oxidation, and thermal degradation intricately proceeded and overlapped to generate aromatic compounds and O-functionalized low-molecular-weight compounds [1,3]. The possible pathway could be summarized as shown in Figure 5, in which the dechlorination proceeded in two ways as dehydrochlorination and substitution (depicted in the dashed box). As for the substitution, one possible and direct way is to replace the  $-\text{Cl}$  with  $-\text{OH}$ , a given two-carbon segment. The other way is to replace both the  $-\text{H}$  and  $-\text{Cl}$  with two  $-\text{OH}$ , a given two-carbon segment. After that, the intramolecular and intermolecular dehydration would happen to generate  $\text{H}_2\text{O}$  and  $\text{HCl}$ . In that case, the functional groups including  $-\text{OH}$  and  $\text{C}=\text{C}-\text{OH}$  would be detected in the hydrochar. In addition, if the dehydrochlorination played a main role, the  $\text{C}=\text{CH}$  would appear. As shown in Figure 4, the bands at about  $3017\text{ cm}^{-1}$  assigned to  $\text{C}=\text{CH}$  appeared and the intensity of  $\text{C}=\text{C}$  (corresponding to  $1600\text{ cm}^{-1}$ ) was increased, indicating the elimination of  $\text{HCl}$  during the HT dechlorination of PVC. The peak at  $750\text{ cm}^{-1}$  ascribed to  $\text{C}-\text{Cl}$  disappeared, indicating the deformation of the functional group and also the skeletal chain. The HT dechlorination of PVC was evidenced by the decreasing intensity of the  $\text{C}-\text{Cl}$  stretching vibration or even the disappearance of chlorine-containing functional groups. The increasing intensity of the  $\text{C}=\text{CH}$  and  $\text{C}=\text{C}$  stretching vibrations in the hydrochar indicated that the dehydrochlorination (elimination reaction) was a main route for chlorine removal during HT dechlorination. The peak at around  $3300\text{ cm}^{-1}$  representing the  $-\text{OH}$  group was not shown, indicating that the replacement of  $-\text{Cl}$  with the  $-\text{OH}$  group was not a main route of dechlorination in this study, whereas the substitution of the  $-\text{OH}$  group was a main reaction route in previous work [16]. One possible reason is that the  $\text{NaOH}$  dosage was quite high, in which the concentration of  $\text{NaOH}$  solutions was 2%~10% (wt.) (equivalent to 80%~400% in our study). As a result, the redundant hydroxide radical would attack the free radicals in PVC and replace them. The other possible reason is that the longer reaction time (4 h) promoted the substitution of  $-\text{OH}$ .



**Figure 4.** FT-IR spectra of (a) PVC; residues obtained by the HT dechlorination of PVC at  $240\text{ }^{\circ}\text{C}$  after 60 min in (b) 0%, and (c) 1% sodium hydroxide.



**Figure 5.** The proposed pathway for chlorine transformation under subcritical water.

#### 4. Conclusions

The HT dechlorination of PVC (poly (vinyl chloride)) was investigated in NaOH solution as a function of temperature, residence time and NaOH dosage. HT is an effective way to clean chlorinated wastes for biofuel production. The HT temperature was a key parameter to control the dechlorination reaction rate. At a HT temperature of 240 °C, about 94.3% of chlorine could be removed from PVC with 1% NaOH. The usage of NaOH was helpful for chlorine removal from PVC, while a higher dosage might also hinder this process because of the surface poisoning and coverage of free sites. To some extent, the DE was increased with the residence time. At a residence time of 30 min, the DE reached a maximum of 76.74%. Lengthening the residence time further would result in a reduction in the DE. According to the FTIR results, the pathways for chlorine transformation were discussed and proposed. The dehydrochlorination (elimination reaction) was thought to be a main route for chlorine removal from PVC under the conditions studied in this work. In order to investigate the treatment of liquid slurry and the fate of potential heavy metals, future works should be performed using commercial PVC containing additives of plasticizers and stabilizers.

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**Author Contributions:** Tian Li and Peitao Zhao conceived and designed the experiments; Tian Li, Peitao Zhao and Zhaozhi Li performed the experiments; Tian Li and Peitao Zhao analyzed the data; Meng Lei and Zhaozhi Li contributed reagents/materials/analysis tools; Tian Li and Peitao Zhao wrote the paper. All authors read and approved the final manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

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