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Effect of Acidic Hydrochar on Plastic Crude Oil Produced from Hydrothermal Liquefaction of Waste PVC

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Abstract: In this study, the effect of hydrothermal liquefaction (HTL) of waste PVC was investigated in the presence of acidic hydrochar. The hydrochar was prepared by hydrothermal carbonization of pineapple waste at 250 °C and at 1 h in the presence of citric acid. Hydrochar was acidic, stable, and porous and contained acidic functional groups. Hydrochar was co-fed with PVC during HTL to enhance HTL conversion and quality of the plastic crude oil. HTL experiments were performed at 300–350 °C, 0.25–4 h of reaction times, and 0–20 wt% hydrochar-to-PVC ratio. The plastic crude oil was separated from the solid residue to evaluate HTL conversion and to analyze elemental compositions, boiling point distribution, alteration of chemical bonds, and chemical compositions. The results showed that acidic hydrochar enhances HTL conversion with a maximum value of 28.75 at 5 wt% hydrochar content at 350 °C and 0.5 h. Furthermore, plastic crude oils contained no chloride but contained significantly high carbon and hydrogen, resulting in a higher heating value of up to 36.43 MJ/kg. The major component of the plastic crude oil was 3, 5 dimethylphenol produced ranging from 61.4 to 86.4% (percentage of total identified area) according to gas chromatography mass spectroscopy (GCMS) data.

Keywords: hydrothermal liquefaction; waste plastics; hydrochar; subcritical water; crude oil

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1. Introduction

Plastic items have become a vital component of our manufacturing and way of life as a result of the ongoing global economic growth, and the waste plastics generated by human activity now constitute a severe risk to the planet [1–4]. Nearly 300 million tonnes of waste plastics are produced annually in the world [5]. One of the main types of waste plastic is polyvinyl chloride (PVC) [6]. PVC has been utilized extensively in the production of machinery, packaging, transportation, and piping because of its durability [7,8]. The disposal of huge volume of waste PVC is currently a major environmental pollution issue [9,10]. Most waste PVC is either burned or landfilled, but only a small portion is recycled [11]. Both the incineration and landfilling contribute to the ecosystem pollution and squanders resources [12].

A viable and sustainable method for the disposal of waste plastic is to convert it to plastic crude oil, thus reducing energy consumption [13]. Plastic crude oil usually has a higher heat value (HHV) in comparison to bio-oil, which is produced from biomass, since waste plastic typically possesses nearly no O_2 atoms and numerous H_2 atoms. Different technologies for converting waste plastic into crude oil, including pyrolysis and hydrothermal liquefaction (HTL), have been developed [13]. Unlike pyrolysis, where high temperature is required for the conversion, HTL is the process of turning waste in to liquid products in water at a temperature range of 280–374 °C and a pressure range of 7–30 MPa [13]. HTL has been found to be an economically feasible technique that produces crude oil with an appropriate HHV, reduced oxygen contents, high conversion rates, and

regulated water content. In subcritical conditions, HTL employs pressurized containers to maintain water in the liquid phase instead of drying the feedstock. Water is an inexpensive and ecologically friendly solvent [14,15]. Subcritical water has a low viscosity as well as a high diffusion capacity, which promotes homogeneity and speeds up the reaction rate [16,17]. PVC is a thermoplastic polymer compound that has a high viscosity and a low heat conductivity when melted [17–20]. Water can significantly compensate for the limited thermal conductivity of plastics and accelerate the hydrolysis reaction during the HTL process; thus, waste PVC might be depolymerized into crude oil [21,22]. In recent years, some researchers studied the possibility of using HTL to depolymerize PVC [23–27]. For example, supercritical water was used by Yoshiyuki et al. to test its potential for degrading PVC [28]. The outcomes show that PVC may be broken down into different chemical compounds in liquid and gas phases. Kubátová et al. investigated PVC depolymerization using subcritical water [29]. According to their research, the PVC starts degrading beyond 250 °C, and at 370 °C, around 44% of the starting material was still present as residue.

While HTL product distribution is influenced by temperature and reaction time, it has been proven that presence of acids could enhance the HTL process [30]. For example, the presence of HCl improved the bio-oil yield and higher heat value (HHV) during HTL of municipal sewage sludge [31]. As a liquefaction catalyst, sulfuric acid was found to be able to break down macromolecules into lower molecular weight compounds [32,33]. Ross et al. found that using formic acid and acetic acid as microalgae liquefaction catalysts might optimize the flow characteristics of biooil [34]. Although the effect of some liquid acid on the HTL process has been studied, to the best of the author's knowledge, no research has been carried out on the influence of a solid acid on the HTL process. Solid acids are preferred to liquid acid catalysts in many industrial chemical processes thanks to their benefits of high acidity, simple separation, low corrosion properties, and good recyclability [35–37]. Developing solid acid catalysts from renewable biomass has significant strategic implications in terms of sustainability [35], and a few studies have been performed to generate solid acid from biomass [30,38,39]. For example, hydrochar-based solid acid catalysts were generated from cornstalk with SO_3H groups by using hydrothermal carbonization (HTC) [35]. We recently generated an HTC hydrochar-based solid acid from pineapple using HTC in presence of citric acid [40]. Hydrochar is a carbon-containing solid product derived from HTC that has rich surface functional groups and has been utilized for a variety of applications [41].

The objective of this work was to study the effect of HTC hydrochar containing acidic functional groups on the HTL of PVC. HTL experiments on waste PVC were carried out to ascertain the impact of hydrochar loading, HTL reaction temperature, and residence time on its depolymerization. Plastic crude oil was analyzed to determine the chemical alterations occurring during HTL reactions, and the HHV, range of boiling point, and functional group of the plastic crude oil. Finally, a reaction mechanism for the HTL of waste PVC is proposed. The novelty of this work relies on the effect of hydrochar on the HTL of waste PVC. The results of this work shade light on the possible development of a sustainable process for upcycling waste PVC.

2. Material and Methods

2.1. Material

Waste PVC water pipe was sourced from a commercial retail shop. A high purity (99.5%) dichloromethane and nitrogen gas (99.9%) were purchased from Fisher Scientific (Waltham, MA, USA) and NexAir (Melbourne, FL, USA), respectively. The acidic hydrochar, which had been produced in our recent work [40], was used in this study. For generating the acidic hydrochar, HTC of pineapple waste (PA) was carried out at 220 °C at 1 h residence time in the presence of citric acid. The total acidic group of the hydrochar was 1587.9 μmol/g. The ultimate analysis of waste PVC and hydrochar used in this study is presented in Table 1. The inorganic elements of waste PVC ash are illustrated in supplementary data (Table S1).

Table 1. Ultimate analysis of waste PVC and HTC acidic hydrochar.

Sample	C (wt%)	H (wt%)	N (wt%)	S (wt%)	Cl (wt%)	Ash (wt%)
PVC	34.69 ± 1.34	4.18 ± 1.65	BD *	BD	52.15	9.05 ± 0.45
acidic hydrochar	59.82 ± 2.15	5.23 ± 0.50	BD	BD	BD	1.01 ± 0.21

* BD: Below detection limit.

2.2. Hydrothermal Liquefaction Process

The HTL trials were carried out using a 100 mL Parr Hast-C (Hastalloy C) batch reactor (model 4560, Moline, IL, USA). Hastelloy C alloy's primary function is to effectively survive high-temperature, high-stress service in environments that are moderately to highly corrosive and/or erosion-prone, where more prevalent and less expensive iron-based alloys would fail. A ceramic electrical heater was used to heat the reactor at 5 °C/min. For each trial, 4.0 ± 0.1 g of powdered waste PVC and required amount of acidic hydrochar were loaded into the reactor with required amount of deionized water to achieve a mass ratio of 1:10 of solid (PVC + hydrochar): water. To eliminate any air from the headspace, the reactor was purged with nitrogen 3 times. The HTL trials were carried out at temperatures ranging between 300 and 350 °C, residence times between 15 min and 4 h, and hydrochar loadings between 0 and 20 wt% (compared to the PVC weight). The reactor was instantly cooled down to room temperature by a water bath right at the end of the residence time of the trial, and the gaseous products were vented in a fume hood. To separate the HTL process liquid from the solid particles, the solution was collected and filtered using a vacuum filtering system. Dichloromethane (DCM) was used to separate the plastic crude oil from the aqueous phase through a liquid–liquid extraction (LLE) process. The solid residues were dried in a drying oven at 105 °C for 24 h, and plastic crude oil was placed in a refrigerator at a temperature of 4 °C for subsequent characterization. The following equation was used to calculate the PVC HTL conversion:

$$PVC\ HTL\ conversion = (1 - \frac{weight\ of\ dried\ solid\ after\ HTL}{weight\ of\ waste\ PVC}) \times 100\% \quad (1)$$

All trials were replicated, and the average results with standard deviation are presented. As this study was focused on the conversion and quality of the plastic crude oil, solid residue, gaseous phase, and aqueous phase were not further characterized.

2.3. Characterization of Plastic Crude Oils

The ultimate analysis was performed using a Thermo Flash 1112 Elemental Analyzer (Waltham, MA, USA). As the plastic crude oils were dissolved in DCM, a specific amount of the solution was dried by natural convection utilizing an aluminum sample pan. About 9.75 ± 0.25 mg of vanadium pentoxide was added with around 2.0 ± 0.5 mg DCM-free plastic crude oil. Elemental carbon, hydrogen, sulfur, and nitrogen were measured from the elemental analyzer, while elemental oxygen was calculated by difference method. The HHV of plastic crude oil was calculated using the Dulong formula [42]:

$$HHV\left(\frac{MJ}{Kg}\right) = 0.3383\,C + 1.422\left(H - \frac{O}{8}\right) \quad (2)$$

The boiling point (BP) distributions of the plastic crude oils were determined using a Perkin Elmer TGA 4000 (Waltham, MA, USA). An inert environment with a constant nitrogen flow rate of 20 mL/min was used for the TGA analysis. The plastic crude oils were heated up to 40 °C from 25 °C and then held isothermal for 10 min to eliminate any trace of residual DCM (Boiling point of DCM at atmospheric pressure is 39.6 °C). The temperature was then raised at a continuous rate of 20 °C/min from 40 to 600 °C. The sample was held isothermal for 5 min at 600 °C, and then, the heating stopped.

A Nicolet 6700 FTIR Spectrophotometer (Waltham, MA, USA) was used to carry out the FTIR analysis. Spectra scanned in the 500–4000 cm^{-1} range allowed for the identification of the functional groups in the HTL crude oils. Since the crude oils and DCM were combined, a droplet of the sample was dropped to an IR card, where the DCM was left naturally evaporated for 5 min. The analysis was then conducted under the following setting: data accumulation: 64, resolution: 4.

Gas chromatography mass spectroscopy analysis were carried out on an Agilent 7890 GC combined with a 5975 Mass Spectrometric Detector. GCMS was equipped with a Supelco Equity 1701 column. The intake was maintained at 250 °C with a split ratio of 1:1 and a helium flow of 5 mL/min. The oven was preheated for 4 min to 45 °C and then heated for 20 min at a rate of 3 °C/min. Without any overlapping chromatogram peaks, all samples were doped (0.1 wt%) with an internal standard (n-decane, 99%).

3. Results and Discussion

3.1. HTL Conversion of Waste Polyvinyl Chloride

The conversion of waste PVC under different HTL treatment conditions is shown in Figure 1. The residual percentage portion of solid waste PVC converted via HTL is termed HTL conversion. The experiments also generated a negligible amount of gases when compared to the solid and liquid HTL products. To study the impact of acidic hydrochar on the HTL process, experiments were carried out by loading hydrochar in the range of 0 to 20% at 0.5 h (residence time) at 325 °C (reaction temperature). Based on the literature [23,43], the starting operating temperature and residence time were taken into consideration. Waste PVC without hydrochar loading was used as feedstock for the first trial as the control run. As shown in Figure 1a, the HTL conversion for the control run is 28.53% at 0.5 h and 325 °C. Figure 1a shows that loading hydrochar has a positive effect on the HTL conversion. The literature reports that HTL conversion increased when using acid as a catalyst through liquefaction [44]. For instance, Ross et al. used organic acid catalyst in HTL of microalgae, and they observed a positive effect on HTL conversion [34]. Since the organic acid is used in the earlier study, it serves more as a reagent than a catalyst. This is crucial because, in contrast to alkali catalysts, they boost the HTL conversion through this process [34]. Figure 1a shows that HTL conversion increases sharply from 28.53% to 50.25% by loading hydrochar from 0% to 5% at 0.5 h and 325 °C. However, by increasing the hydrochar from 5% to 20%, the HTL conversion decreases slightly (about 2%), which indicates the loading hydrochar of more than 5% could not improve the HTL conversion. When H_2SO_4 was utilized as a catalyst in the thermochemical liquefaction of biomass, a similar trend was observed [32]. The HTL conversion raised as acidity increased; however, when acidity increased further, the trend reversed [32]. This was most likely owing to large volume of hydrocarbons decomposing into polar water-soluble organics, and/or because the major component of bio-oil tends to create residue (due to repolymerization) under a very acidic environment [44].

A series of HTL experiments were then conducted at 0.5 h in the presence of 5 wt% hydrochar to further explore the impact of HTL temperature. It is evident from Figure 1b that reaction temperature has a significant effect on the HTL conversion because the HTL conversion increases from 40.22% at 300 °C to 55.83% at 350 °C. The results show that the reaction kinetics is slow at 300 °C, indicating this temperature is not enough to break the PVC into shorter polymer chains. Ross et al. also found that a high acidic HTL conversion is achieved at a high temperature (350 °C) [34].

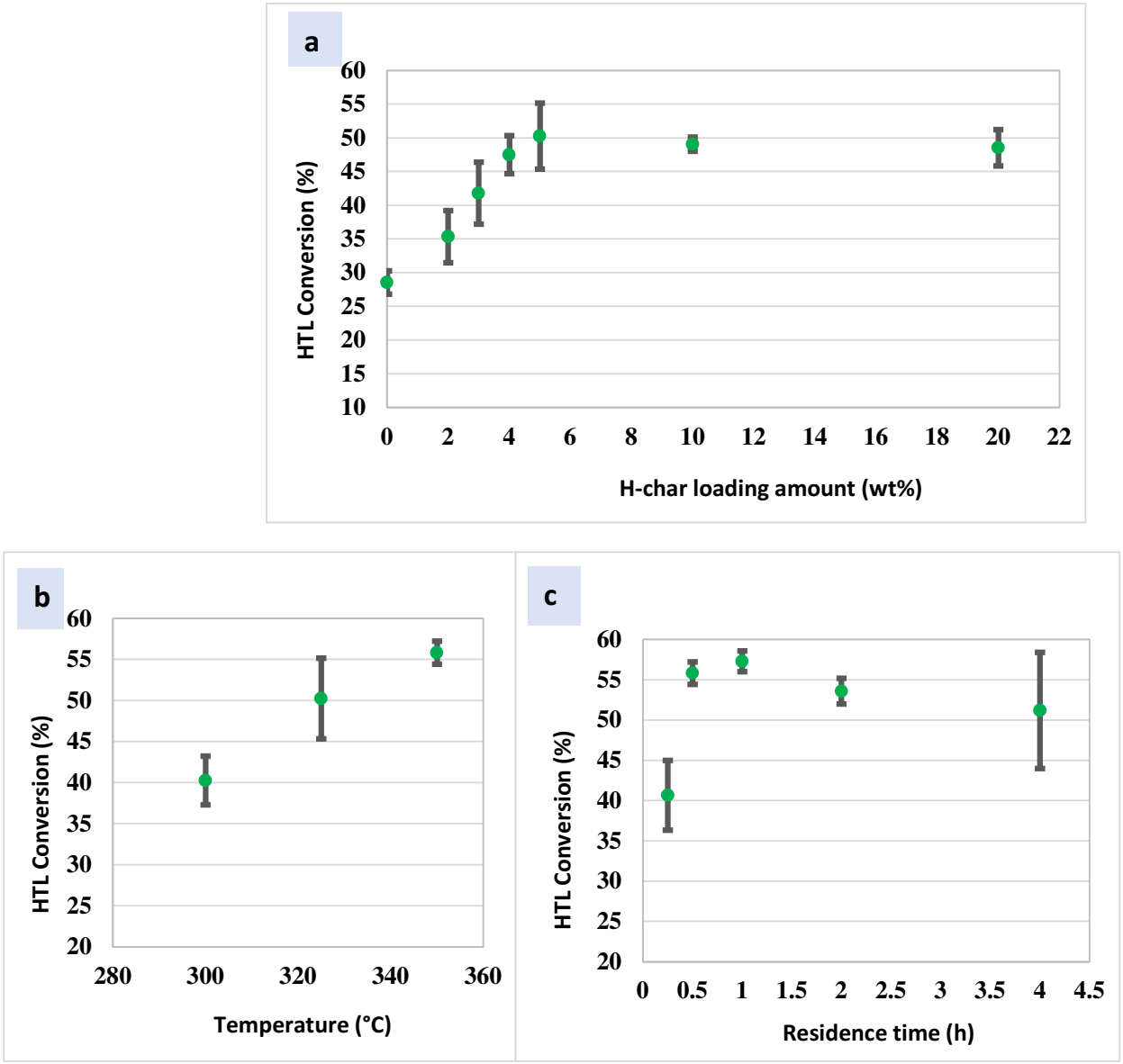

Figure 1. The effect of (**a**) acidic hydrochar loading (at 325 °C and 0.5 h), (**b**) reaction temperature (at 0.5 h and with 5 wt% acidic hydrochar loading), and (**c**) residence time (at 350 °C and with 5 wt% acidic hydrochar loading) on the HTL conversion.

To evaluate the effect of the residence time on HTL conversion of waste PVC, residence time was also varied from 15 min to 4 h with 5 wt% hydrochar loading at 350 °C. Based on the result (Figure 1c), by increasing residence time from 0.25 h to 1 h, HTL conversion increases from 40.65 to 57.28%; nevertheless, the HTL conversion decreases after 1 h. Zou et al. [32] showed a similar result for the changing yield of liquefaction with residence time. This is due to the rivalry of two liquefaction-related reactions, namely hydrolysis, and repolymerization. The feedstock is first broken down and converted into small compounds, and when the reaction period is extended, these compounds may subsequently rearrange to produce solid residues by condensation, cyclization, and polymerization [32].

3.2. Elemental Compositional Analysis of HTL Crude Oils

To ascertain the elemental composition, the plastic crude oils were analyzed by ultimate analysis. Table 2 lists the elements that make up the plastic crude oils produced during HTL. Overall, the elemental contents of the plastic crude oils vary significantly. The

carbon content is between 62.25 and 76.30 wt%, the hydrogen content is in the range of 7.25 to 9.30 wt%, and the oxygen content is between 14.39 and 29.0 wt%. Nitrogen and sulfur contents are below the detecting limits.

Table 2. Variation of elemental composition, and HHV of the HTL crude oils at various process conditions.

Exp No.	Hydrochar Loading (wt%)	Temperature (°C)	Time (h)	Carbon (%)	Hydrogen (%)	Other Elements * (%)	HHV ** (MJ/kg)
1	0	325	0.5	67.62 ± 0.28	7.65 ± 0.34	22.00 ± 0.32	29.84
2	2	325	0.5	69.2 ± 0.58	8.2 ± 0.15	22.6 ± 0.45	31.05
3	3	325	0.5	68.3 ± 1.36	8.1 ± 0.29	23.6 ± 1.65	30.43
4	4	325	0.5	70.2 ± 0.45	8.5 ± 0.15	21.3 ± 0.53	32.05
5	5	325	0.5	71.5 ± 1.05	9.1 ± 0.27	19.4 ± 0.85	33.68
6	10	325	0.5	71.2 ± 0.23	8.8 ± 0.13	20 ± 0.29	33.05
7	20	325	0.5	72.3 ± 0.95	9.15 ± 0.23	18.55 ± 1.14	34.17
8	5	300	0.5	62.25 ± 0.76	7.85 ± 0.31	29.9 ± 0.97	26.91
9	5	350	0.5	74.22 ± 0.74	9.22 ± 0.25	16.56 ± 0.97	35.28
10	5	350	0.25	68.25 ± 0.95	7.25 ± 0.28	24.5 ± 0.91	29.04
11	5	350	1	74.56 ± 0.63	9.36 ± 0.32	16.08 ± 0.62	35.68
12	5	350	2	75.25 ± 1.12	9.23 ± 0.43	15.52 ± 1.02	35.82
13	5	350	4	76.36 ± 0.85	9.25 ± 0.25	14.39 ± 0.78	36.43

* Other elements content, which may include oxygen, chlorine, or other minor additives, was calculated by difference method. ** HHV was calculated from the average ultimate analysis results.

Adding hydrochar to waste PVC causes an increase in carbon and hydrogen contents and a decrease in oxygen content; as a result, generating plastic crude oils with higher HHV. Furthermore, increasing the loading amount of hydrochar causes a further increment in the carbon and hydrogen contents and a reduction in the oxygen content. For example, by loading hydrochar from 0 to 20 wt% at 325 °C and 0.5 h, the carbon content increases from 67.62 to 72.3 wt%, the hydrogen content increases from 7.65 to 9.15 wt%, oxygen content decreases from 24.73 to 18.55 wt%, and HHV increases from 29.36 to 34.17 MJ/kg. According to Liu et al., employing organic acid through HTL results in greater HHVs than that of the feedstock (municipal sewage sludge) because it raises the contents of hydrogen and carbon whereas decreasing the amounts of oxygen [31]. Additionally, Ross et al. reported that the use of organic acids results in a high-quality bio-crude [34].

The reaction temperature causes the most substantial effect on carbon and oxygen contents in crude oils. As seen in Table 2, when the temperature increases from 300 to 350 °C at 0.5 h and 5 wt% hydrochar, the carbon content increases from 62.25 to 74.22 wt%, the oxygen content decreases from 29.9 to 16.56 wt%, and the HHV increases from 26.91 to 35.28 MJ/kg. Moreover, the hydrogen content increases by about 1.37 wt% when the temperature increases by about 50 °C, thus demonstrating that rising temperatures have a favorable impact on the quality of crude oil. Most likely, the water viscosity drop at high processing temperatures improves water diffusivity into waste PVC, leading to a higher extent of conversion [45]. Mahesh et al. [45] observed that the bio-crude oils have a higher carbon content than the raw material and carbon content increase with temperature. Moreover, the increase in reaction temperature causes significant deoxygenation in bio-crude, which leads to the higher HHV and better stability of bio-crude [34,45]. The residence time has also a considerable influence on elemental composition through HTL. It can be seen in Table 2 that when the residence time rises from 0.25 to 4 h at 350 °C in presence of 5 wt% hydrochar, the carbon content increases from 68.25 to 76.36 wt%, the hydrogen content increases from 7.25 to 9.25 wt%, and oxygen content decreases from 24.5 to 14.39 wt%. Mahesh et al. revealed that as residence time increases, the carbon and oxygen content of the bio-crude increase and decrease, respectively, resulting in greater HHVs than the feedstock [45].

All plastic crude oils show a H/C atomic ratio in the range of 1.26 to 1.51, and an O/C atomic ratio in the range of 0.14 to 0.36. Figure 2 shows that, in most cases, loading hydrochar leads to a reduction in the O/C and H/C atomic ratios. Liu et al. [31] observed

the same trend for the O/C atomic ratio when HCl and HNO_3 is added to municipal secondary sludge through HTL; however, the H/C atomic ratio of their bio-oils decreased. Plastic crude oil obtained at 300 °C and 0.5 h, and plastic crude oil sample obtained at 350 °C and 0.25 h show different behavior. Temperature and residence time have a stronger effect on the O/C ratio and H/C ratio variation in comparison to hydrochar loading. It is obvious that low temperature (300 °C) or low residence time (0.25 h) are insufficient for the deoxygenation of crude oils.

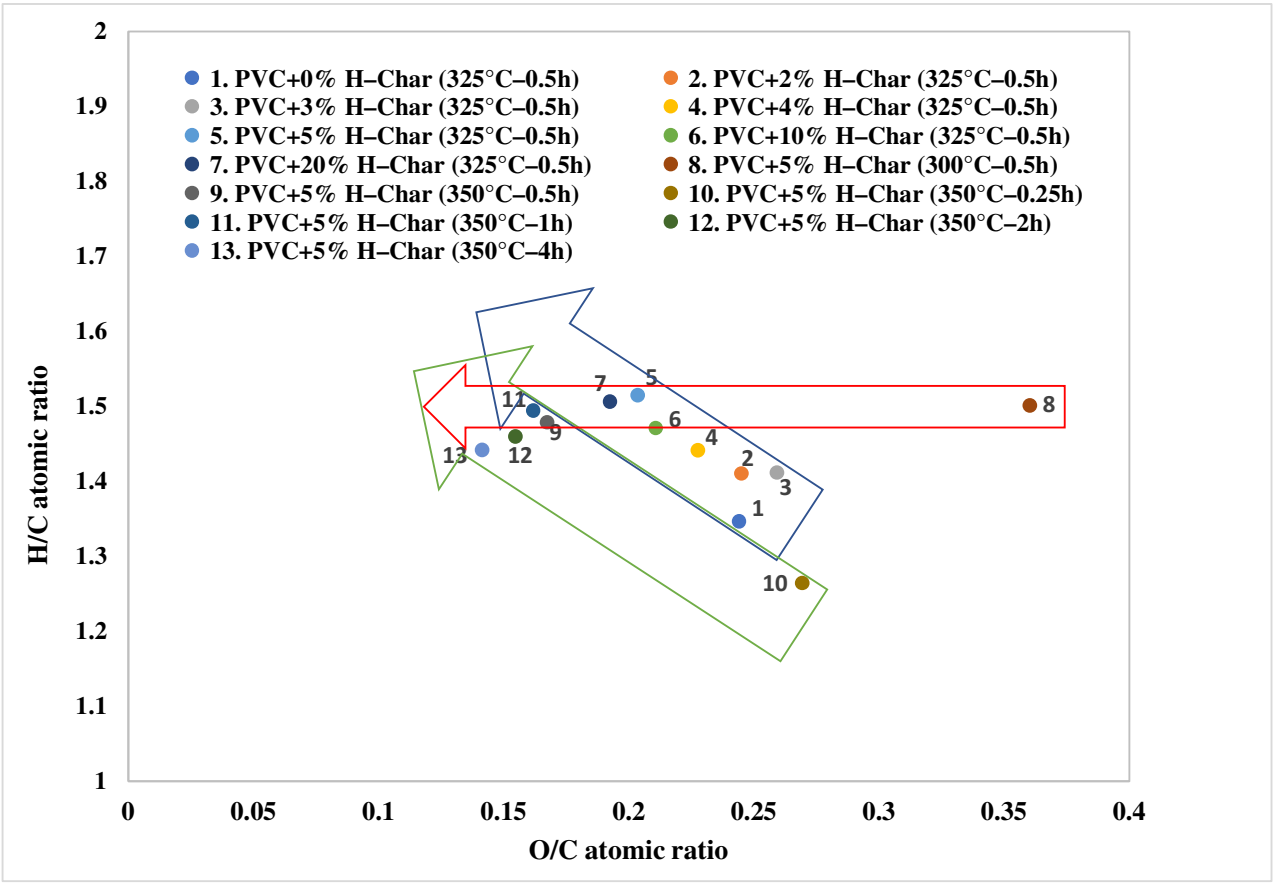

Figure 2. Van Krevelen diagram of crude oils produced at various HTL conditions (blue arrow: effect of increasing acidic hydrochar loading, green arrow: effect of increasing residence time, red arrow: effect of increasing reaction temperature).

3.3. Boiling Point Distribution of HTL Crude Oils

The different compositions of crude oils produced at different HTL operating condition led to a significant difference in their distribution of boiling points. The portion of plastic crude oil that is volatile under 400 °C is the most valuable for manufacturing liquid fuels; hence, this is an indicator of the crude oil's quality and prospective application [42]. TGA analysis was used to assess the devolatilization properties of the oils. The TGA analysis data are illustrated in Figure 3, which displays the weight loss from each crude oil sample at various temperature ranges. Compounds with boiling points below 40 °C are not shown in Figure 3 because they would be lost during DCM evaporation from the plastic crude oil. The main products of HTL of waste PVC are oil molecules that volatilized in the boiling range of gasoline, kerosene, and diesel (63.82–87.27%). Figure 3 shows that loading hydrochar leads to a larger portion of the lighter compounds. When the hydrochar loading increases from 0 to 20 wt%, the portion of gasoline increases from 17.74 to 43.1 wt%; thus, hydrochar loading has a positive effect to reduce the portion of residual fuel oil with high boiling temperature (>570 °C). Higher volatility of crude oils produced with the acidic

hydrochar could be explained by its ability of breaking more C–C bonds thus leading to a reduction in heavier products [42]. Liu et al. [31] found that HCOOH, HCl, H_2SO_4, and HNO_3 pretreatment can produce lighter oil fractions of bio-oil through HTL. The boiling points of main proportion of the bio-oil generated by the HCl pretreatment was below 150 °C (23.18%).

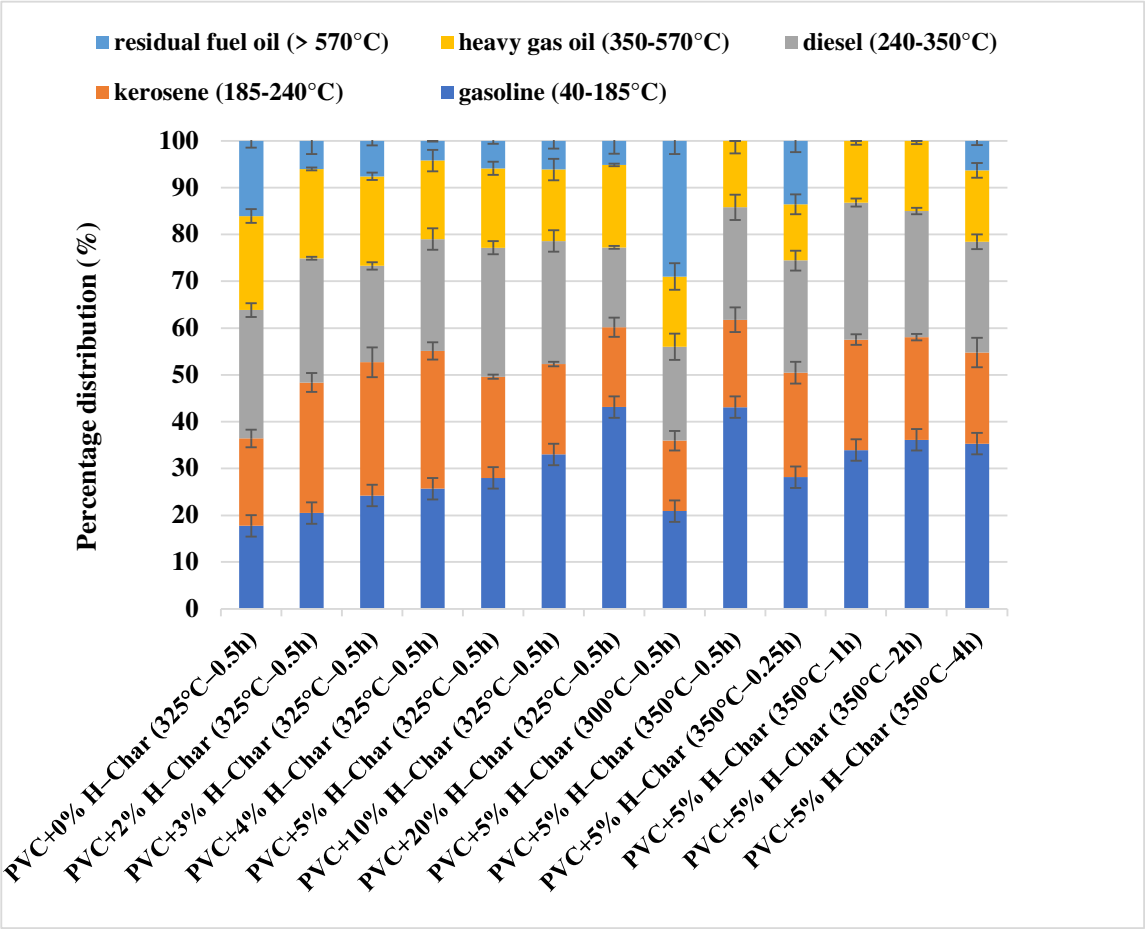

Figure 3. Distribution of boiling points of the crude oils at various HTL reaction conditions.

As seen in Figure 3 the temperature has a significant effect on the fuel oil quality. By raising the temperature from 300 to 350 °C at 0.5 h, the portion of gasoline, kerosene, and diesel increases from 56.72 to 85.81 wt%. When the HTL temperature rises from 300 to 350 °C at 0.5 h, the fraction of residual fuel oil (>570 °C) likewise falls from 29 to 0 wt%. As expected, rising HTL temperature leads to an increase in the proportion of lighter components, due to an increase in the rate of thermal cracking processes [42]. Seshasayee et al. [42] reported that HTL of polypropylene increased significantly the production of lighter oils when the temperature rises from 400 to 450 °C.

The results show that residence time also influences the range of lighter oil fractions in the plastic crude oils. As shown in Figure 3, increasing the residence time reduces the amount of heavier fractions, leading to an increase in the lighter fractions. For example, when residence time increases from 0.25 to 0.5 h, the proportion of gasoline, kerosene, and diesel increases from 74.42 to 85.81 wt% and decreases the proportion of residual fuel oil from 13.57 to merely 0 wt%. The results show that 0.25 h might not be sufficient to break C–C bonds at large extent, and thus, the percentage of lighter products is low [46]. Nevertheless, when the time of the reaction increased from 2 to 4 h, the proportion of residual fuel oil increased from 0 to 6.3 wt% probably due to the formation of aromatic compounds promoted by the reduced content of hydrogen [46].

Overall, our TGA analysis demonstrates that the molecules in the crude oils produced by HTL of PVC volatilize at the same temperature levels as those in refinery feedstocks, suggesting that they may likely be handled using the current infrastructure for petroleum refining. Moreover, the TGA data demonstrate that the weight loss distributions are significantly influenced by the HTL temperature, residence time, and hydrochar loading; therefore, fine tuning of reaction parameters should be carried out to achieve desirable distribution. However, these variables would also impact HTL conversion, necessitating a deeper comprehension of the many tradeoffs to achieve the best HTL conditions.

3.4. FTIR Analysis of HTL Crude Oils

FTIR spectroscopy was used to examine the functional groups of PVC and hydrochar, and the resulting spectra are displayed in Figure 4. The presence of plasticizer is confirmed by the existence of PVC absorption bands at 487 and 428 cm^{-1} [27]. The prominent peak at 750 cm^{-1} proves that primitive samples of C–H bending exist. The PVC chain's skeletal vibration might be attributed to the band at 1097 cm^{-1} [23]. The presence of C–O in plastic crude oils is shown by the strong peak in the region of 1150 to 1225 cm^{-1}, which is most likely caused by the phenol derivatives that were found in GCMS data (discussed later). A small band at 1621 cm^{-1} was detected. The band at 1621 cm^{-1} could be assigned to the stretching vibrations of –C=C– bonds on aromatic rings [25]. Because of the existence of –CH2– groups in PVC, the asymmetric and symmetric stretching of –CH2 was attributed to the absorption bands at 2914 cm^{-1} [23]. The presence of O–H in crude samples is also demonstrated by the absorption bands detected between 3580 and 3700 cm^{-1}.

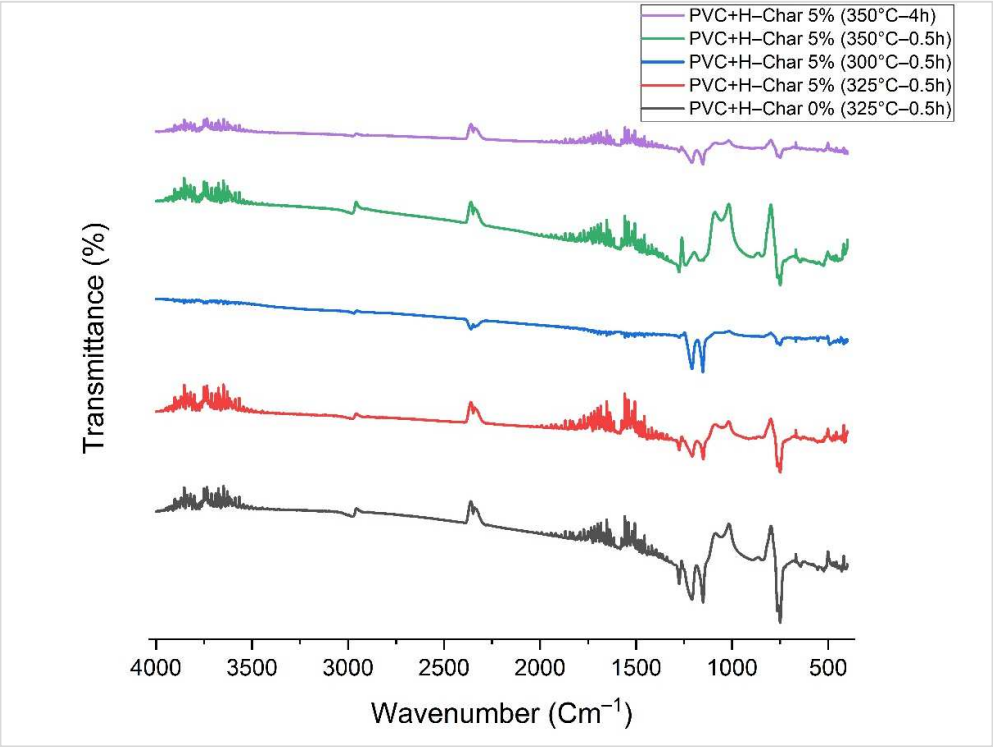

Figure 4. FTIR analysis of the crude oils at various HTL reaction conditions.

Figure 4 shows that the crude sample at 300 °C and 0.5 h has weaker peaks at 750 and 1621 cm^{-1} in comparison to the crude sample at 350 °C and 0.5 h. It means by increasing temperature, the amount of C–H bond and –C=C– increases in crude oil samples. Furthermore, Figure 4 shows that the peaks in the range of 1150 and 1225 cm^{-1} become weaker by loading hydrochar which could be due to the deoxygenation process. These results are in line with the CHNS result. The crude sample at 350 °C and 0.5 h has stronger

peak at 1650 cm^{-1} in comparison to the crude sample at 350 °C and 4 h, which shows the aromatic components decrease by increasing residence time.

3.5. Chemical Composition of HTL Crude Oils

The chemical compositions of plastic crude oils were identified using GCMS. In Figure 5, the effects of hydrochar loading, reaction temperature, and residence time are compared with respect to the proportion of total area occupied by various compounds. The detailed GCMS data are given in Tables S2–S14. The results show that the plastic crude oils derived from HTL have comparable chemical compositions, mostly consisting of phenolic, hydrocarbon, and ketone components.

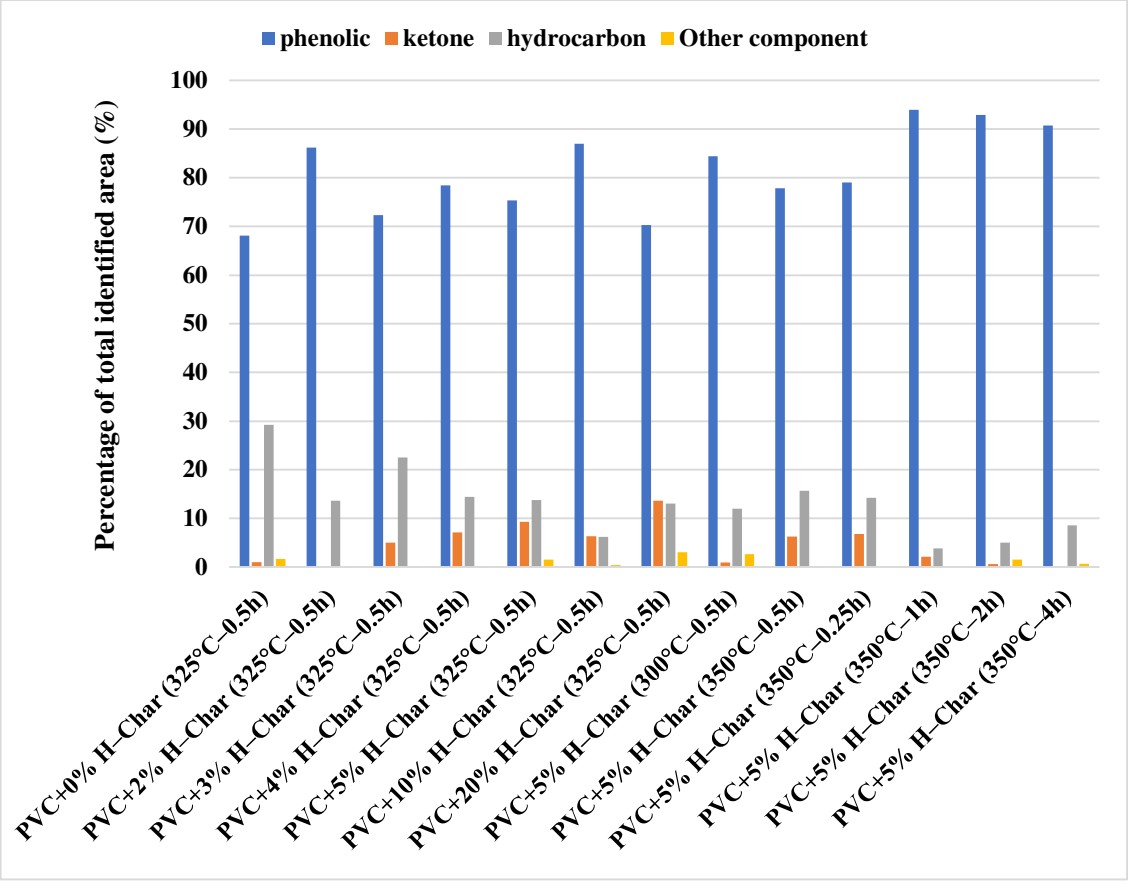

Figure 5. Effect of acidic hydrochar loading, reaction temperature, and residence time on percentage of total area of the phenolics, ketones, hydrocarbons, other components of crude oil.

The results show that acidic hydrochar affected the relative quantities of components but did not change the chemical compositions of crude oil. As it can be seen in Figure 5, loading hydrochar generally increases the amount of phenolic and ketone components and decreases the amount of hydrocarbon components. For example, the amount of phenolic components, as main oxygen components in crude oil, increases from 68.13 to 87.01 wt%, the amount of ketone components increases from 0.9 to 6.39 wt%, and the amount of hydrocarbon components decreases from 29.2 to 6.16 wt% by loading 10 wt% hydrochar. Liu et al. found that acid (HCl) pretreatment increases the quantities of oxygenated substances such as ketones that were found in bio-oil [31,47].

The temperature has a positive effect on hydrocarbon and ketone components and a negative effect on the phenolic components. By raising the temperature from 300 to 350 °C, the amount of hydrocarbon components increases from 11.99 to 15.7 wt%, the amount of ketone components increases from 0.9 to 6.29 wt%, and the amount of oxygenated compo-

nents decreases from 84.43 to 77.82 wt%. This result is compatible with a higher extent of depolymerization, leading to an increase in the production of aromatic compounds [48]. This beneficial effect of HTL temperature on hydrocarbon production has also been reported in the literature [49,50]. An important parameter influencing how quickly polymers depolymerize is reaction temperature. Many cracking reactions occur only after the system has created enough energy to break the chemical bond that holds polymers together [51]. According to López et al. [52], PVC's major mass loss occurred in the range of 250 to 320 °C. The main reaction at this step is polymer dehydrochlorination, which results in de-HCl PVC and the production of volatiles compounds. The volatiles consist primarily of HCl, with trace amounts of benzene, toluene, and other light hydrocarbons [48].

A careful look at the data show that the influence of residence time on the liquefaction process appears to be distinct from the impact of reaction temperature. Increasing the residence time favors the depolymerization of plastics over the conversion between the components [51]. Residence time has indeed a significant impact on the formation of phenolic components. As reported in Figure 4, the phenolic components increase from 79.04 to 93.99 wt% when residence time increases from 0.25 to 1 h, but it drops to 90.73 wt% at the longest residence time investigated (4 h). Furthermore, the amount of hydrocar components decreases from 14.18 to 3.84 wt% when the residence time raises from 0.25 to 1 h, but it increases to 8.46 wt% when the residence time raises to 4 h. The amount of ketone components decreases from 6.78 to 0 wt% when the residence time raises from 0.25 to 4 h.

3.6. Proposed HTL Reaction Mechanism

To understand the degradation mechanism of PVC in Hydrochar, the GCMS results were studied, and a possible reaction mechanism is proposed in Figure 6. The first degradation step for PVC is the dechlorination process, which is expected to be caused by nucleophilic substitution of the chlorine by a hydroxyl group to form a polyol or dehydrochlorination to form polyenes [53]. This step can be further broken down into the heterolytic cleavage of the chlorine atom from the PVC molecule and the subsequent nucleophilic substitution by the hydroxyl group. The heterolytic cleavage is suspected to be catalyzed by the addition of the acidic hydrochar, as the hydrogen ions are expected to interact with the chlorine atoms in the PVC, weakening the polar bond between the chlorine and the carbon. The C-Cl bond being weakened allows for this bond to be selectively broken first during the degradation reaction, as it has lower bond energies than the other bonds in the PVC molecule. After the heterolytic cleavage has occurred, the negatively charged hydroxyl groups in the water will be bonded with the positively charged carbon formed after the heterolysis. At low temperatures (<~450 °C), the formation of the polyol is preferred compared to direct dehydrochlorination to form polyenes [53]. As such the formation of polyenes in this system is expected to be the result of the dehydration of the initial polyol product rather than direct dehydrochlorination of PVC due to the temperature of the reactions being too low. The dehydration of polyols into polyenes is supposed to be catalyzed by the additional acidic hydrochar, although dehydration will still occur with no additional acid due to the initial hydrochloric acid formation. Additional hydrogen ions can interact with the hydroxyl group in the polyol to form a water molecule, which will then break away from the main polyol chain, catalyzing the dehydration reaction. The dehydration reaction is also suspected to be catalyzed by temperature, which is further backed up by the trend decreasing oxygen concentration in the product at higher temperatures. This effect is further shown by the negative relationship between acidic hydrochar loading and oxygen concentration in the product for hydrochar concentrations above 3%. The dechlorination process is effective, as in the crude oil of all runs, the GCMS results only detect one chlorinated compound, which composed only 0.44 wt% of the total product area for that specific liquefaction experiment. This result agrees with the current literature, which typically states that the dichlorination of PVC has an approximate dechlorination rate of about 100% at temperatures above 300 °C [10]. It can conclude that most chlorine goes to the aqueous phase as HCl because the pH of the aqueous phase samples was

between 1 and 2. There are some systems to treat the acidic wastewater that can regulate pH levels in the aqueous phase [54].

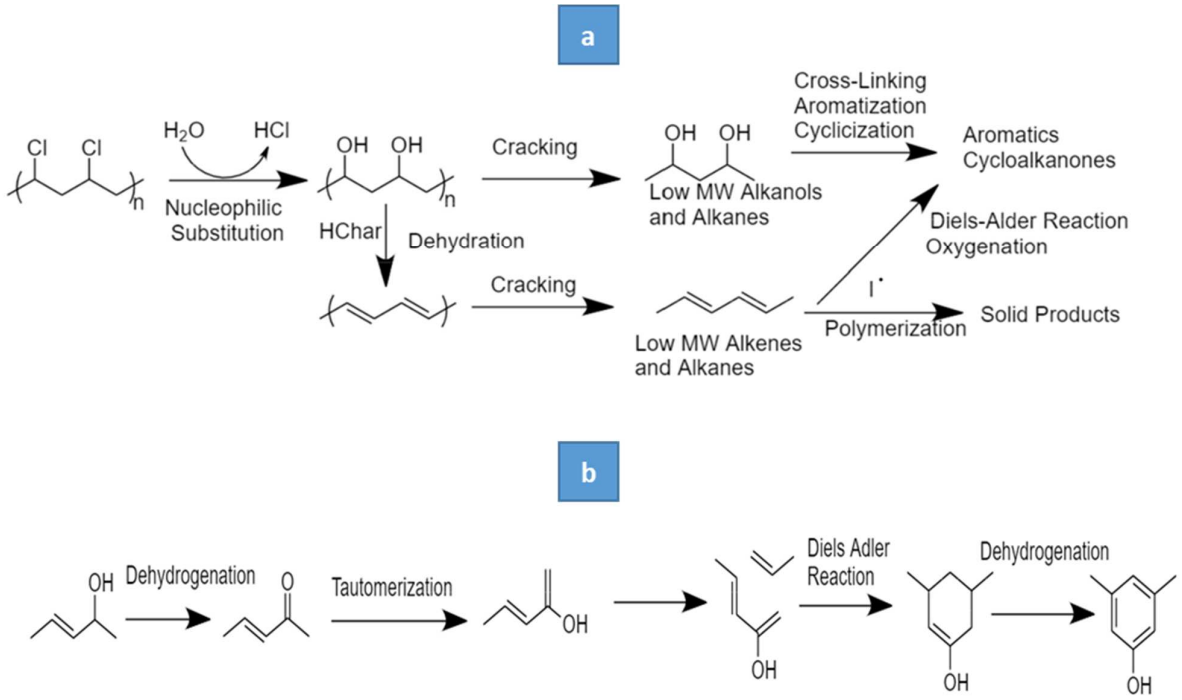

Figure 6. (**a**) Widely accepted reaction mechanism for PVC degradation in water [54], and (**b**) more specific reaction mechanism that could explain the large amount of dimethylphenols detected in the liquid product.

After the initial dechlorination steps, the polymer is expected to undergo thermal cracking, with the breaking down of the polymer chain into smaller molecular alkanes. The low molecular weight hydrocarbons and alkanols produced can undergo further reactions to form aromatic, cycloalkanone, and furan compounds. Polymerization and condensation reactions of this product can form solid hydrochar. Cyclopentanones can be formed via radical cyclization of polyol compounds followed by dehydrogenation of the alcohol functional group. BTX (benzene, toluene, and xylenes) aromatics can be formed during liquefaction by the Diels Alder reaction and dehydrogenation from polyene compounds [55]. Aromatics are also hypothesized to be formed via radical crosslinking and aromatization of hydrocarbons.

The major product of the liquefaction was 3,5 dimethylphenol in all crude oil samples except one. The only exception was when the major product was 3,4-dimethylphenol, which likely could be formed from the same reaction, especially during liquefaction, where there is a significant degree of randomness. The percentage of dimethylphenol produced ranged from 61.4 to 86.4 wt% according to GCMS data. The formation of dimethylphenol is assumed to be formed from a Diels-Alder reaction followed by dehydrogenation to form an aromatic. The diene is thought to be formed by an alkenone that undergoes ketone-enol tautomerization to form an alkadienol. The diene is suspected to have an alcohol group since the atmosphere in the reaction system is inert and incapable of providing oxygen to allow for oxidation after aromatization to form phenols. The dienophile is supposed to be propene formed during the cracking of the polyene molecules. Nucleophilic substitution of methyl/alcohol groups is unlikely as both alcohol and methyl groups are ortho/para directors and the substituents are in the meta direction compared to each other.

4. Conclusions

In this work, the effect of acidic hydrochar loading, reaction temperature, and residence time on the HTL of waste PVC in subcritical conditions were investigated. Loading hydrochar and increasing temperature had positive effects on the HTL conversion. HTL conversion increased when the residence time increased from 0.25 to 1 h and then it reduced by increasing residence time from 1 to 4 h. The maximum HTL conversion was achieved at 350 °C, 1 h and in presence of 5 wt% acidic hydrochar. A crude oil with appropriate HHV (26.91–36.43 MJ/kg) was produced from waste PVC through HTL. Due to its poor qualities, such as viscosity, density, and acidity, crude oil cannot be used directly as fuel [56]. For upgrading the oil product, in the first step, molecule distillation process can be used to separate light fraction, middle fraction, and heavy fraction of crude oil. In the second step, catalytic cracking, hydrodeoxygenation, and emulsification processes can be used for upgrading light fraction, middle fraction, and heavy fraction, respectively [56].

Loading hydrochar and increasing temperature or residence time improved the HHV of crude oils. The main components of crude oil produced from waste PVC were volatilized in the boiling range of gasoline, kerosene, and diesel. Loading acidic hydrochar and increasing temperature and residence time led to a higher conversion into lighter compounds, which are the most preferable components for producing liquid fuels. The GCMS results revealed that phenolic, hydrocarbon, and ketone components made up the majority of the crude oil samples obtained from HTL. The findings demonstrated that acidic hydrochar influences the component relative amounts but does not alter crude oil's chemical composition. Although this study focuses on plastic crude oil synthesis and corresponding characterization, a char and aqueous phase analysis might need to carried out to further understand the process. Based on the low pH of aqueous phase (1 to 2), the main safety concern to future scale up of the HTL process is equipment corrosion. To avoid corrosion, the HTL reactor and pipe lines should be made from material that is persistence against corrosion such as Hastelloy C alloy.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr10122538/s1, Table S1: Inorganic components of waste PVC ash (analyzed by energy-dispersive X-ray spectroscopy (EDAX)). Table S2: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 0 wt% acidic hydrochar. Table S3: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 2 wt% acidic hydrochar. Table S4: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 3 wt% acidic hydrochar. Table S5: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 4 wt% acidic hydrochar. Table S6: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 5 wt% acidic hydrochar. Table S7: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 10 wt% acidic hydrochar. Table S8: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 325 °C and 0.5 h residence time in presence of 20 wt% acidic hydrochar. Table S9: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 300 °C and 0.5 h residence time in presence of 5 wt% acidic hydrochar. Table S10: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 350 °C and 0.5 h residence time in presence of 5 wt% acidic hydrochar. Table S11: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 350 °C and 0.25 h residence time in presence of 5 wt% acidic hydrochar. Table S12: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 350 °C and 1 h residence time in presence of 5 wt% acidic hydrochar. Table S13: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 350 °C and 2 h residence time in presence of 5 wt% acidic hydrochar. Table S14: Identified compounds via GCMS in the waste PVC drive crude oil at a temperature of 350 °C and 4 h residence time in presence of 5 wt% acidic hydrochar.

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