

## Article

# Degradation of Polyvinyl Chloride (PVC) Waste with Supercritical Water

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**Abstract:** The chemical degradation of PVC waste in SCW between 400 and 425 °C and reaction times from 30 to 60 min was studied. The PVC waste in SCW decomposed into the gas, oil, water soluble, and solid phases. The highest yield of the gas and oil phases was achieved at the temperature of 425 °C after 60 min. By increasing the reaction time at 400 °C, the yield of chloride ions in the aqueous phase increased and reached the maximum at 60 min. The gas and oil phases contained many valuable compounds similar to crude oil. Alkanes and chloroalkanes; alkenes, alicyclic, and aromatic hydrocarbons; as well as alcohols were the main groups of hydrocarbons in the oil phase, while the gas phase contained only light hydrocarbons (C<sub>1</sub>–C<sub>6</sub>), CO<sub>2</sub>, and small amounts of H<sub>2</sub>. This confirmed that the largest chlorine content remains in the aqueous phase and does not pass into the gas phase. It can be concluded that SCW presents effective decomposition media for plastic waste.

**Keywords:** polyvinyl chloride; supercritical water; chemical recycling; plastic waste



**Citation:** Čolnik, M.; Kotnik, P.; Knez, Ž.; Škerget, M. Degradation of Polyvinyl Chloride (PVC) Waste with Supercritical Water. *Processes* **2022**, *10*, 1940. <https://doi.org/10.3390/pr10101940>

Academic Editors: Dimitris Zagklis and Georgios Bampos

Received: 28 August 2022

Accepted: 22 September 2022

Published: 26 September 2022

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## 1. Introduction

Plastic is one of the most important materials in our daily lives. Synthetic materials are very useful and convenient, with many positive properties (good chemical resistance, technically sophisticated, lightweight, innovative, and inexpensive) [1]. Global world production of plastics and plastic products has increased twenty times since 1960, and by 2036 this number is expected to double [2]. On the other hand, the environmental impacts resulting from the accumulation of plastic waste are increasingly huge. The data show that by the end of 2020, about 585 million tons of plastic waste were generated by over 7.7 billion people globally [3]. The information about plastic waste is alarming. Additionally, plastic debris affects wildlife, human health, and the environment [4]. Recently, society has been increasingly inclined toward cleaner production and the reuse of industrial and municipal waste. Chemical recycling, which is becoming increasingly popular, breaks down plastics into valuable products (crude oil, fuel) or depolymerizes them back into monomers or chemicals. Such processes are still in the early stages, although several projects are already underway, which provides hope that dependence on naphtha can be reduced in this way. Since 2007, the company APChemi has been focusing on developing sustainable pyrolysis technology for the disposal of plastic waste and tires. It has established more than 35 pyrolysis plants in India, Kenya, Indonesia, the UK, etc. [5]. In 2018, the Austrian energy company OMV started to turn plastic waste back into crude oil. The ReOil pilot plant successfully recycled 200,000 kg of plastic waste in two years [6]. The tire manufacturer Michelin is establishing the first tire pyrolysis plant in collaboration with Enviro, a Swedish company that has developed a patented tire pyrolysis technology to recover carbon black, oil, steel, and gas from end-of-life tires [7]. Exxon Mobil and TotalEnergies opened two recycling centers in France. Loop Industries (Canada) and Eastman Chemicals (USA) plan to open two plants in France to process PET by 2025 [8].

Hydrothermal processing is one of the attractive chemical degradation methods in which sub- or supercritical water (SubCW and SCW) is used and can act as a solvent, reactant, or catalyst. Hydrothermal processes can be divided into four main processes according to the type of product: hydrothermal carbonization [9], water reforming, hydrothermal liquefaction, and hydrothermal gasification [10]. The main hydrothermal processes for breaking down biomass and plastic into syngas, bio-oil, or crude oil are supercritical water gasification [11–15] and hydrothermal liquefaction [16–18]. These processes are more energy efficient than thermal processes that produce the same products (pyrolysis and thermal gasification). The drying step of feedstock is not required [19]. This leads to higher energy efficiency, especially for biomass with high moisture content. Temperature, pressure, feedstock concentration (plastic/biomass to water ratio), and reaction time are the important parameters that affect the desired products of the SCW processes [12,20,21]. The operating temperature ranges of supercritical liquefaction and gasification are from 350 °C to 800 °C and depend on the feedstock type, reactor configuration, catalyst, and desired products [10,11,14,16,18,22–25]. The use of SCW techniques exhibits many advantages, such as high yields of the selected products, very clean gas products that contain very low concentrations of NO<sub>x</sub> and SO<sub>x</sub>, reduced levels of CO, and inhibited tar and char formation. However, the method has some disadvantages, especially for biomass processing: the problems include plugging, corrosion, catalyst deactivation, and high production costs [14,26].

Polyvinyl chloride (PVC) is a synthetic polymer prepared from vinyl chloride monomer [27]. PVC is a universal polymer, and it is the third most commonly produced synthetic polymer in the world. It can be processed into a wide range of short-life products, as well as for longer-life products [28]. PVC polymer is composed of 56.8% chlorine [27], which causes the biggest problem in environmental pollution and recycling. PVC can be recycled using various recycling techniques (material and energy recovery methods). Secondary (mechanical) recycling has been used for years for PVC waste. Here, the recycling of PVC is preferred when pure PVC with a known composition and history is available. Incineration with energy recovery is an undesirable recycling technology used to remove PVC waste. Due to the high chlorine content, PVC is quite resistant to combustion, and toxic pollutants are also formed during recycling [28,29]. In general, by thermal decomposition of PVC, high amounts of HCl are produced, which can cause corrosion in furnaces and release harmful gases, which in turn can cause serious environmental and health problems [30]. In addition, PVC is not used as a pure polymer, but many additives (plasticizers, stabilizers, lubricants, and fillers) are added to improve its properties [31]. Huge problems arise in landfills, where PVC slowly decomposes (oxidative degradation of PVC), and heavy metals and phthalates from additives can contaminate the groundwater [32].

In recent years, the chemical recycling of PVC materials has attracted increased attention from researchers. One of the common approaches to the chemical recycling of PVC waste is pyrolysis, including hydrocracking, thermal cracking, and catalytic cracking [28]. The thermal degradation of PVC waste was performed in a batch (vessel, autoclave) and continuous process (fluidized bed reactor) [33–37]. The thermal degradation of PVC also encompasses catalytic and noncatalytic processes [38–40]. In general, during the thermal decomposition (250–525 °C) of PVC, the mass loss and dechlorination reaction occur in the temperature range between 250 and 350 °C, depending on the PVC material, the stabilizers, and the additives. Under these conditions, up to 99.5% of chlorine was removed from the PVC molecule [33]. Moreover, organohalogen compounds, chlorinated dioxins, furans, volatile components (benzene, toluene, and hydrocarbons), and char were also formed during the pyrolysis reaction [28], while the main intermediate product of the thermal degradation is a polyene. At higher temperatures (500–900 °C), PVC waste pyrolyzed to hydrocarbons (oil), HCl, and chlorinated hydrocarbons, where the HCl needs to be removed from the gas products. The main product of PVC pyrolysis is oil for the oil industry [29]. Despite the fact that the thermal degradation of PVC has been studied for years, the mechanism of the PVC thermal degradation is still not fully developed [37].

Compared to thermal degradation, during hydrothermal degradation of virgin PVC, 100% of chlorine was removed at a temperature higher than 300 °C [30,41]. Numerous different catalysts have also been used for more efficient dechlorination. The NaOH solution accelerated the dechlorination of flexible PVC between 150 and 250 °C. The degree of dehydrochlorination of flexible PVC increased with an increasing reaction temperature, and was of about 100% at 250 °C and after 5 h [42,43]. In some other studies, several other organic solvents (ethylene glycol [44], dimethylsulfoxide [43]) were added, which also improved the efficiency. Most of these studies focused on the successful hydrothermal dechlorination of PVC and on the hydrochar characteristics. However, the use of cosolvents and catalysts leads to problems such as solvent recycling and the use of large amounts of inorganic salts, which increase process costs and damage the equipment [30]. The degradation of virgin PVC in SubCW and SCW was studied by Takeshita et al. (2004) and Sato et al. (1998). The decomposition of PVC in SubCW produced a mixture of aromatic and aliphatic compounds (CO<sub>2</sub>, benzene, acetone, benzoic acid) in the water and gas phases [31,45]. At a higher temperature of over 350 °C, the light hydrocarbons (C<sub>1</sub>–C<sub>5</sub>), CO<sub>2</sub>, acetone, benzene, benzoic acid [31,45], phenol, naphthalene, acetic acid (Sato et al., 1998) in liquid and gas phases were obtained during the degradation of virgin PVC. The obtained residual solid after hydrolysis at 300 °C has a high combustion enthalpy and consequently exhibits good potential for use as a fuel ingredient [31,45]. However, despite a very detailed investigation, Takeshita et al. [31] did not report the yield of the obtained oil phase and its chemical composition, which is very important for understanding the recycling of PVC by hydrothermal processes.

According to the literature review, previous studies addressing the hydrothermal decomposition process of PVC have been conducted on virgin PVC. The aim of this research work was to study the decomposition of the real PVC waste (colorless PVC packaging bags) in SCW at different temperatures (400 and 425 °C), reaction times (30 min and 60 min), and without any catalyst. The main goal was to determine the yield and chemical composition of the obtained products. The chemical components generated in the oil and gas phases during the degradation of PVC in SCW have the potential to be used as fuel blends or feedstock for chemicals. The presented degradation mechanism plays an important role and will contribute significantly to a better understanding of the degradation of PVC in SCW and the simultaneous recycling of several types of plastic waste by this method.

## 2. Materials and Methods

### 2.1. Materials

Postconsumer colorless PVC packaging bags were collected from the local market (Maribor, Slovenia). Nitrogen (N<sub>2</sub>) (99.5%) as an inert gas was supplied by Messer (Ruše, Slovenia). Potassium chromate (99.0%), silver nitrate solution, and n-hexane (97%) were obtained from Merck (Darmstadt, Germany) and Sigma-Aldrich (Steinheim, Germany). All standards and solvents were of analytical grades.

### 2.2. Degradation of PVC Waste in SCW

First, the colorless PVC waste (packaging for clothes) was cut into equal-sized particles of 1 × 1 cm. The hydrothermal degradation experiments were performed in a high-temperature and high-pressure batch reactor (Parr Instruments, Moline, IL, USA) [17], presented in Figure 1 at 400 °C and 425 °C for a reaction time of 30 min and 60 min. The reactor was filled with material (~4.5 g) and water (~22.5 mL), so that the water/PVC waste ratio was 5/1 (mL/g). The filled reactor was sealed, and then it was purged with nitrogen (N<sub>2</sub>) to avoid the oxidation of the products. In order to enter the supercritical region when heating to the desired temperature (400 or 425 °C), the initial pressure in the reactor was set to 5 bar (N<sub>2</sub>). The reactor was wrapped with an electrical wire and covered with glass wool in order to prevent heat losses. Afterwards, the reactor was first heated to the desired temperature and then maintained at that temperature for a certain time. Temperature, pressure, and reaction time are very important reaction parameters for hydrothermal degradation

processes. For this reason, pressure and temperature changes during reactor temperature increases were precisely monitored. The heating rate in the temperature range from room temperature to 160 °C was 28 °C/min  $\pm$  0.5 °C/min, followed by periods of slightly slower heating rate of 18 °C/min  $\pm$  0.5 °C/min (to 250 °C), 16 °C/min  $\pm$  0.5 °C/min (to 350 °C), 14 °C/min  $\pm$  0.5 °C/min (to 400 °C), and 8.3 °C/min  $\pm$  0.5 °C/min (to 425 °C), and the average heating rate was 17 °C/min. At the same time, the pressure increased during the heating of reactor from initial 5 bar to 10 bar at 160 °C, to 45 bar at 250 °C, to 145 bar at 350 °C, to 255 bar at 400 °C, and to 320 bar at 425 °C. While the reaction proceeded at a constant temperature, the pressure still increased slightly due to the decomposition of PVC and was 260 bar after 30 min and 270 bar after 60 min at 400 °C, while at 425 °C it increased to 325 bar after 60 min. After the hydrothermal degradation of PVC waste, the reactor was immediately quenched in a water bath to cool down to room temperature. The generated gases were collected through a control valve into a Tedlar sampling bag (Supelco, Bellefonte, PA, USA). The total volume of the gas phase was measured with a volume of water disposed in a measuring chamber, and then the yield of the gas phase was estimated based on the ideal gas law equations. After collecting the gas phase, the reactor was opened, and the post-reaction mixture was transferred into the beaker. The reactor was washed with n-hexane to remove any solid particles and prevent possible losses. The reaction mixture from the reactor consisted of three phases: solid particles, aqueous phase, and oil phase. The solid particles in the aqueous phase were separated by filtration, while the n-hexane was evaporated from the oily phase. The yield of oil and solid phase was calculated by Equations (1) and (2) and it was expressed in weight percentage (%). The experiments were conducted in duplicate, and the error bars in Figure 2 indicate the standard deviation.

$$\gamma_{\text{oil}} = \frac{m_{\text{oil}}}{m_{\text{PVC waste}}} \times 100\% \quad (1)$$

$$\gamma_{\text{SP}} = \frac{m_{\text{SP}}}{m_{\text{PVC waste}}} \times 100\% \quad (2)$$

where,  $\gamma_{\text{oil}}$ ,  $\gamma_{\text{SP}}$  present yields of oil and solid phases, respectively.  $m_{\text{oil}}$  and  $m_{\text{SP}}$  are masses of oil and solid phases obtained by SCW degradation of PVC waste plastics.  $m_{\text{PVC waste}}$  is the initial mass of colorless PVC waste loaded in the reactor.

### 2.3. Decomposition Products Analysis

The oily and gaseous products were analyzed by GC–MS while the content of chloride ions in aqueous phase was determined by the titration method. Solid phase was analyzed by Fourier-transform infrared spectroscopy (FTIR). All analyses of oil, gas, and aqueous phases were performed in triplicate and the results were expressed as their mean value  $\pm$  standard deviation.

#### 2.3.1. FTIR Analysis of PVC Waste and Solid Residue

Functional groups contained in solid residue after degradation of PVC waste in SCW were determined by ATR-FTIR (attenuated reflection method) spectrometry and compared with specific functional groups of non-degraded PVC waste. The spectra of individual samples were recorded in the range of wavenumbers between 4000 and 400  $\text{cm}^{-1}$ , at a resolution of 16  $\text{cm}^{-1}$  and a total of 30 co-added scans. The background measurement against air was conducted with the same settings. The obtained data were analyzed with high-performance IRsolution software.

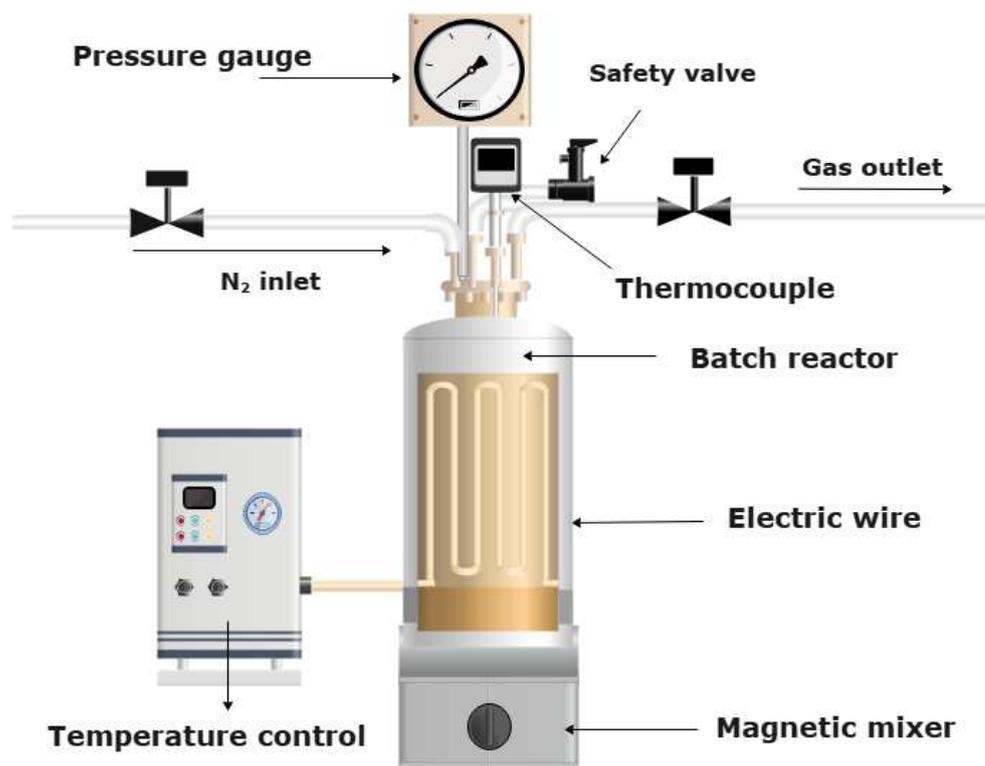


Figure 1. SCW batch reactor system for the chemical degradation of PVC waste in SCW.

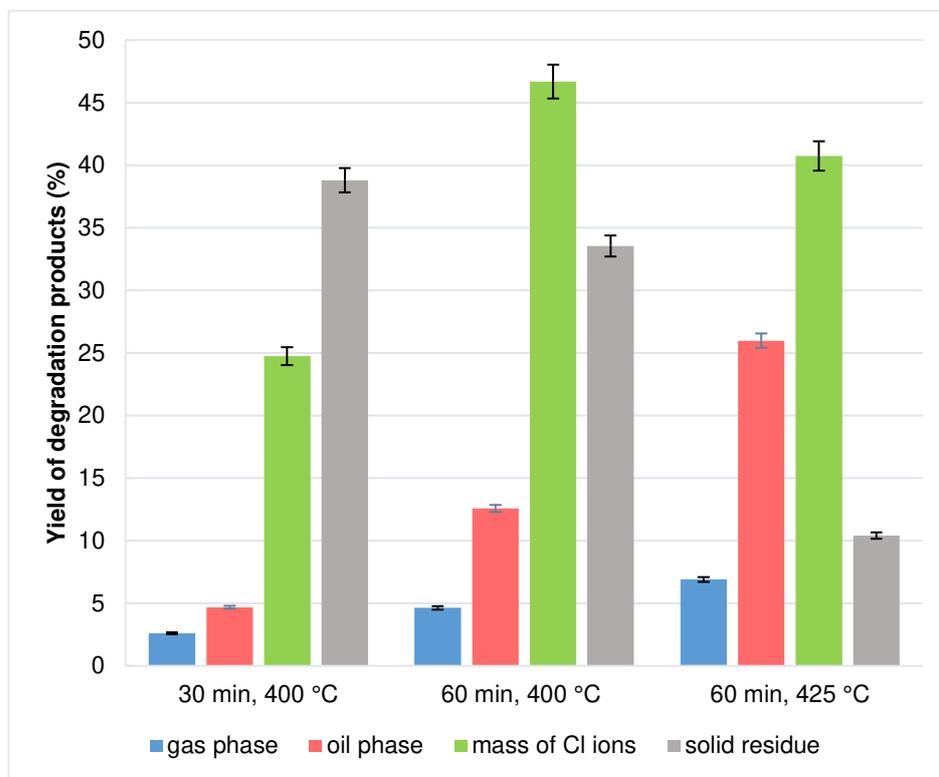


Figure 2. Yield of generated products after degradation of colorless PVC waste in SCW. Error bars in the figure indicate the standard deviation among the duplicate measurements.

### 2.3.2. Analysis of the Oil and Gas Phase Composition after SCW Degradation

A Shimadzu GCMS-QP2010 Ultra system with a mass spectrometer was used to determine the chemical composition of the gas and oil phase (Shimadzu, Tokyo, Japan). The GC-MS analysis of the oil phase was performed on HP-1 column (30 m × 0.25 mm × 0.25 μm) using temperature gradient from 40 °C to 230 °C in 27.5 min, while the analysis of the gas phase was performed on HP-PLOT/Q column (30 m × 0.32 mm × 20 μm) using temperature gradient from 35 °C to 200 °C in 30 min, where helium was used as a carrier gas. All compounds were identified using NIST library. A detailed description of the methods is presented in our previous study [17].

### 2.3.3. Determination of Chloride Ions in the Aqueous Phase

The mass of chloride ions in the aqueous phase was determined using the silver nitrate volumetric method [46]. Titrations were performed by adding potassium chromate indicator solution to the diluted aqueous phase sample and titrated with 0.1 M AgNO<sub>3</sub>. In this case, silver ions reacted with chloride ions, and thus a white precipitate (AgCl) was first formed. In the following procedure, a reddish-brown precipitate (Ag<sub>2</sub>CrO<sub>4</sub>) was formed between the indicator and the standard solution. The mass of chloride ions ( $m_{\text{Cl ion}}$ ) in the aqueous phase was calculated from the consumption of AgNO<sub>3</sub>. The yield of chloride ions in the aqueous phase ( $\gamma_{\text{Cl ion}}$ ) after degradation of PVC waste in SCW was determined by Equation (3).

$$\gamma_{\text{Cl ion}} = \frac{m_{\text{Cl ion}}}{m_{\text{PVC waste}}} \times 100\% \quad (3)$$

### 2.3.4. The Energetic Aspect of the Laboratory Process

For a laboratory batch reactor, energy consumption for the heat transfer ( $Q = P \times t$ ) was roughly estimated.  $Q$  (kWh) is energy consumption,  $P$  (kW) is the power consumption of heater (0.5 kW for laboratory heater) and  $t$  (h) heating time. Heat losses during heating were neglected.

## 3. Results and Discussion

### 3.1. The Yield of Degradation Products after Hydrothermal Decomposition of Colorless PVC Waste

After the hydrothermal degradation in SCW at 400 and 425 °C and reaction times of 30 and 60 min, the PVC waste material decomposed into four phases: oil, gas, water soluble phase, and solid residue (Figure 2). In the study of Takeshita et al. [31], in which virgin PVC was degraded in sub- and supercritical water at various temperatures (200–600 °C) for one hour, only three phases (solid, liquid, and gas) were found and there are no data about the yield of the oil phase. In the present work, it was observed that with an increasing temperature (from 400 to 425 °C) and reaction time (from 30 to 60 min), the yield of gas and oil phases increased, while the yield of solid residue decreased from 39.0 ± 0.9% to 10.0 ± 0.3%. Most likely, the PVC molecule was dechlorinated during the heating of the reaction mixture to the desired temperature. At temperatures between 250 and 300 °C, PVC dechlorination occurred, in which the Cl ion was cleaved from one monomeric unit of two carbons, forming the polyene [47]. Polyene is an organic compound containing alternating double and single carbon bonds. By further decomposition of polyene in SCW at 400 and 425 °C, various hydrocarbons were likely formed in the oil phases via hydrogen abstraction, cyclization, aromatization, and hydration reaction, and consequently, the yield of the oil phase increased. Similarly, with the degradation, gasification, and decarboxylation reactions, gas components were formed in the gas mixture, and as a result, the yield of the gas phase increased. Namely, the physical properties of water at temperatures higher than 300 °C change significantly with temperature and pressure; therefore, under these conditions, water has a low ionic product, low dielectric constant, low viscosity, and high diffusivity. The highest yield of the oil and gas phases was found at 425 °C and 60 min, where the yield of the oil phase was 26.0 ± 0.6% and the yield of the gas phase was 7.0 ± 0.2%. An increase in the yield of the gas phase and a decrease in the yield of

the solid phase with increasing temperature (200–450 °C) was also found in the work of Takeshita et al. [31]. In our work, the yield of chloride ions in the aqueous phase at a temperature of 400 °C increased with time, which is consistent with the decreasing pH of the post-reaction mixture. The pH of the aqueous phases after the PVC degradation in SCW decreased from 3.14 at 400 °C and 30 min to 2.38 at 400 °C and 60 min. In these conditions (400 °C and 60 min), the maximum concentration of chloride ions in the aqueous phase was determined as  $47.0 \pm 1.4\%$  (Figure 2). As the temperature increased to 425 °C, the mass of chloride ions in the aqueous phase began to decrease slightly, as the halogenation of alkanes in the oil phase was most likely to occur. The pH of the aqueous phase was the lowest in this case and amounted to 2.1.

### 3.2. Chemical Composition of the Gas Phase

The chemical composition of the gas phase was determined using the GC–MS method (depending on the peak area (%)). During the degradation of PVC waste H<sub>2</sub>, CO<sub>2</sub> and C<sub>1</sub>–C<sub>6</sub> saturated and unsaturated aliphatic hydrocarbons were mainly formed (Table 1), most likely due to the decomposition of shorter hydrocarbons into gases. CO<sub>2</sub> is also the most represented component in all cases. The concentration of CO<sub>2</sub> in the gas phase decreased with increasing time and temperature. CO<sub>2</sub> was formed due to decarboxylation, where intramolecular and intermolecular Diels–Alder polyene reactions occurred during the benzene formation [31,45]. Similar to the degradation of polyolefins (PE) in SCW [17], the alkane concentration increased, while the alkene concentration decreased when the temperature and reaction time increased. Among the light hydrocarbons formed at 425 °C and 60 min, propane is the most abundant component in the gas phase. During the pyrolysis (530 °C and 25 min) of a plastic mixture of PVC, HDPE, PP, and PS, similar light hydrocarbons (C<sub>1</sub>–C<sub>4</sub>) were determined, among which the main compounds in the gas mixture were propene and propane. In contrast to hydrolysis, pyrolysis also produced chlorinated compounds in the gas mixture, of which HCl was the dominant component and its concentration increased with the PVC content in the plastic mixture [48]. The gaseous hydrocarbons C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> are versatile products which may be used as a fuel, in electric power generation, for the production of platform chemicals, for polyolefin synthesis, etc. [16]. Similarly, CO<sub>2</sub>, which was the main component in the gas phase after the degradation of PVC in SCW, is widely used for food processing, in the chemical industry, agriculture, for methanol production, etc. [49].

**Table 1.** Composition of the gas phase (peak area (%)) at different temperatures and reaction times.

Components	400 °C, 30 min Peak Area (%)	400 °C, 60 min Peak Area (%)	425 °C, 60 min Peak Area (%)
Hydrogen	2.82 ± 0.08	1.00 ± 0.01	0.82 ± 0.01
CO <sub>2</sub>	40.52 ± 1.10	36.71 ± 0.78	17.93 ± 0.45
Methane	2.24 ± 0.06	3.00 ± 0.01	3.10 ± 0.05
Ethene	1.50 ± 0.04	1.50 ± 0.02	0.52 ± 0.01
Ethane	5.80 ± 0.12	5.40 ± 0.13	10.71 ± 0.28
Propene	5.01 ± 0.12	3.10 ± 0.06	1.01 ± 0.01
Propane	7.43 ± 0.11	6.60 ± 0.17	17.41 ± 0.43
Isobutane	5.42 ± 0.16	1.10 ± 0.01	14.94 ± 0.21
2-Methyl-1-propene	4.41 ± 0.07	6.02 ± 0.12	1.40 ± 0.02
Butane	5.60 ± 0.12	5.60 ± 0.07	11.21 ± 0.22
2-Butene	7.10 ± 0.18	0.0 ± 0.0	0.0 ± 0.0
2-Methylbutane	0.90 ± 0.02	1.10 ± 0.01	8.40 ± 0.09
2-Pentene	2.50 ± 0.01	1.10 ± 0.02	0.221 ± 0.006
Pentane	0.0 ± 0.0	0.0 ± 0.0	4.21 ± 0.06
1-Methylcyclopentene	0.0 ± 0.0	12.52 ± 0.21	5.3 ± 0.11
Benzene	2.40 ± 0.05	6.54 ± 0.06	1.72 ± 0.04

### 3.3. Chemical Components in the Oil Phase

Components in the oil phase were determined by the GC–MS method and quantified according to the peak area (%). Six main groups of compounds were detected, i.e., saturated and unsaturated aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and alcohols (Table 2). At the temperature of 425 °C and at 60 min, the oil phase is mainly composed of aromatic hydrocarbons ( $39.31 \pm 0.93\%$ ). This indicates that some alkenes and alicyclic hydrocarbons are probably converted via the aromatization reaction to aromatic compounds. Consequently, the concentration of alkenes ( $3.80 \pm 0.11\%$ ) and alicyclic hydrocarbons ( $0.61 \pm 0.013\%$ ) was quite low. The most represented aromatic components in the oil phase at 425 °C and 60 min are benzene derivatives ( $18.70 \pm 0.39\%$ ) and naphthalenes ( $12.40 \pm 0.19\%$ ), as well as small amounts of polycyclic aromatic hydrocarbons ( $2.61 \pm 0.06\%$ ) (fluorenes and anthracenes). In addition, quite high concentrations of alkanes ( $24.41 \pm 0.51\%$ ) and chloroalkanes ( $15.33 \pm 0.38\%$ ) were detected in the oil phase. Pentadecane ( $6.04 \pm 0.05\%$ ) and 1-chloro-undecane ( $5.40 \pm 0.15\%$ ) were the most represented components in this group. Alkanes were produced during the hydrogen abstraction of polyene, after which the chlorine was eliminated from the PVC molecule into the aqueous phase. During the same period, the halogenation of alkanes took place, where radical substitution occurred, and hydrogen was replaced by chlorine. In the following, alcohols were formed during the alkene hydration [17]. Among alcohols ( $5.23 \pm 0.12\%$ ), 3,7-dimethyl-1-octanol ( $1.20 \pm 0.02\%$ ) is the most common component. The results obtained in this study differ from the results obtained by Sato et al. [50], who studied the decomposition of virgin PVC in SCW at higher temperatures, i.e., at 450 °C and 600 °C, and only aromatic compounds and acetic acid were detected in the oil phase. In comparison, the thermal degradation of PVC (at 500 °C) caused the PVC to be decomposed to 30% of the liquid fraction which was rich with aromatic compounds (88%) of which the major part was benzene (80%), while alkanes, alkenes, and alicyclic hydrocarbons which represented 2.47%, 1.52%, and 1.20% of the liquid, respectively. The content of the chlorinated hydrocarbons in the liquid fraction was 1.75% [36]. At a lower degradation temperature (300 °C), only HCl, benzene, and anthracene were detected after the thermal degradation of PVC due to the dehydrochlorination reaction [37]. The obtained oil phase after the degradation of colorless PVC waste in SCW contained valuable chemical components which are very similar to the components in the crude oil. Namely, crude oil is mainly composed of three types of hydrocarbon components (paraffins, cycloparaffins, and aromatics) [51].

**Table 2.** Composition of the oil phase (peak area (%)) at 425 °C and 60 min.

Main Groups	Most Represented Components (Peak Area (%))
Saturated aliphatic hydrocarbons ( $24.41 \pm 0.51\%$ )	Octanes (methyl, ethyl, dimethyl) ( $5.3 \pm 0.09\%$ )
	Decane ( $2.1 \pm 0.03\%$ )
	Tridecane ( $4.2 \pm 0.11\%$ )
	Pentadecane ( $6.04 \pm 0.05\%$ )
	Hexadecane ( $1.3 \pm 0.01\%$ )
	Octadecane ( $1.7 \pm 0.03\%$ )
	Heneicosane ( $1.2 \pm 0.01\%$ )
Halogenated hydrocarbons (chloroalkanes) ( $15.33 \pm 0.38\%$ )	1-chloro-nonane ( $4.8 \pm 0.12\%$ )
	1-chloro-decane ( $4.9 \pm 0.09\%$ )
	1-chloro-undecane ( $5.4 \pm 0.15\%$ )
Unsaturated aliphatic hydrocarbons ( $3.80 \pm 0.11\%$ )	3,3,5-trimethyl-1-hexene ( $1.8 \pm 0.04\%$ )
	2,4-dimethyl-1-heptene ( $1.9 \pm 0.01\%$ )
Alicyclic hydrocarbons ( $0.609 \pm 0.013\%$ )	Cyclopentane ( $0.32 \pm 0.011\%$ )

Table 2. Cont.

Main Groups	Most Represented Components (Peak Area (%))
Aromatic hydrocarbons (39.31 ± 0.93%)	Benzene derivatives (18.7 ± 0.39%)
	Naphthalene derivatives (12.4 ± 0.19%)
	Polycyclic aromatic hydrocarbons (2.6 ± 0.06%)
Alcohols (5.23 ± 0.12%)	2-methyl-1-butanol (0.7 ± 0.012%)
	6-methyl-1-heptanol (1.1 ± 0.014%)
	3,7-dimethyl-1-octanol (1.2 ± 0.02%)
	1-nonanol (1.1 ± 0.019%)

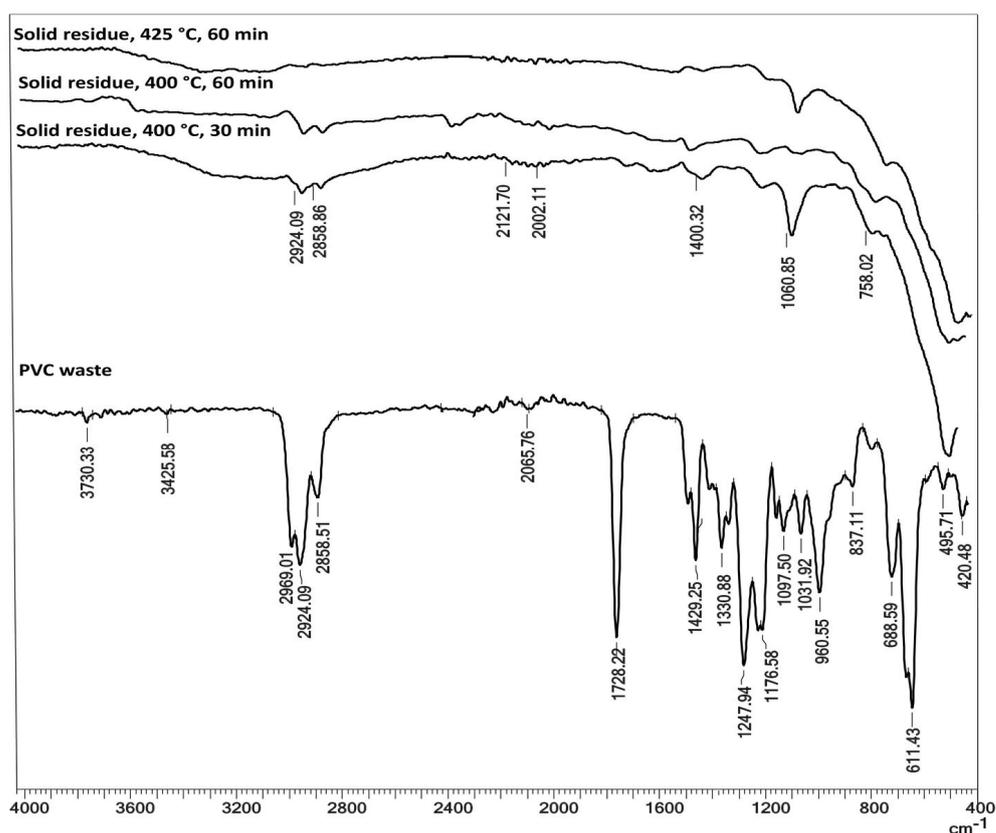
### 3.4. FTIR Analysis of Colorless PVC and Solid Residue after Hydrolysis

FTIR analysis of PVC waste was performed before and after the degradation in SCW (Figure 3). The FTIR spectrum for PVC waste shows strong absorption bands at 2924  $\text{cm}^{-1}$  and 2858  $\text{cm}^{-1}$  [52], which were attributed to the asymmetric and symmetric elongation of the  $-\text{CH}_2$  group, which confirmed the existence of the methylene group ( $-\text{CH}_2-$ ). In comparison, after the hydrothermal decomposition of the PVC waste at 400 °C for 30 and 60 min, the absorption bands for solid residues at 2924  $\text{cm}^{-1}$  and 2858  $\text{cm}^{-1}$  were visibly weakened, while at 425 °C and 60 min these absorption bands completely disappeared. Furthermore, the C–H band on the adjacent  $\text{CHCl}$  groups at 2969  $\text{cm}^{-1}$  and the absorption bands at 1429  $\text{cm}^{-1}$  and 1330  $\text{cm}^{-1}$ , which were attributed to the oscillation and bending of C–H vibrations, also disappeared after the hydrothermal process in all cases. The band for undegraded colorless PVC waste at 1247  $\text{cm}^{-1}$  corresponded to skeletal vibrations (Cl–C–H), while for solid residues after hydrothermal degradation, this band disappeared in all three cases. The bands at 1097  $\text{cm}^{-1}$  and 964  $\text{cm}^{-1}$  were attributed to C–C elongation and  $-\text{CH}_2$  oscillation. In addition, the bands at 611  $\text{cm}^{-1}$ , 688  $\text{cm}^{-1}$ , and 837  $\text{cm}^{-1}$  can be attributed to C–Cl tensile vibrations. For the solid residues obtained after SCW degradation of PVC, these absorption bands were not present anymore. The presence of an additive (plasticizer) in PVC waste may be attributed to the absorption bands at 495  $\text{cm}^{-1}$  and 420  $\text{cm}^{-1}$  [30], and it was also present in solid residues after hydrolysis at 400 °C and 30 min. With an increase in temperature to 425 °C and a reaction time of 60 min, the absorption bands for the plasticizer were weakened or disappeared. It can be concluded that after hydrothermal decomposition of the PVC waste in all three cases, the absorption bands characteristic for Cl ions disappeared. It was confirmed that all chlorine was removed from the polymer molecule during the hydrothermal degradation reaction, and the remaining solid carbonaceous material could find many potential applications, e.g., as a solid fuel, as adsorbent, in catalysis, energy storage, sensor industry, etc.

### 3.5. Degradation Mechanism of PVC Waste in SCW

Based on the obtained results, the decomposition of PVC waste in SCW was proposed (Figure 4). During the heating to the supercritical conditions, HCl was cleaved from the PVC molecule by the “zipper” mechanism. The loss of each HCl molecule from the polymer led to the formation of a double bond, which activated the adjacent chlorine and caused the propagation of the degradation reaction along the polymer chain [53]. As is known from the literature, the dechlorination of PVC waste occurs in the SCW area at about 300 °C and 30 min [30,41]. By further heating the reaction mixture to the supercritical region, the polyenes were broken down into lower molecular weight molecules by the  $\beta$ -cleavage reaction of the C–C bond and by the transformation of hydrogen, resulting in the formation of saturated and unsaturated aliphatic hydrocarbons. Most alkenes were converted by the cyclization reaction to alicyclic hydrocarbons, by the aromatization reaction to aromatic components, and by the hydration reaction to alcohols [16,17] at the reaction temperature of 425 °C. In the same period, the polycyclic aromatic hydrocarbons formed via the polymerization reaction of aromatic hydrocarbons. After the separation of HCl from the PVC molecule, the degradation pathway of PVC waste is very similar to

that of polyolefins [17], except that in the case of PVC, a large amount of chloroalkanes ( $15.33 \pm 0.38\%$ ) appears in the oil phase, while the chlorine components do not pass into the gas phase. The halogenation of alkanes takes place at high temperatures, where radical substitution occurs, and hydrogen is replaced by chlorine. Gases are also formed during the decomposition of PVC waste in SCW. Namely, with increasing temperature and time, long hydrocarbons are decomposed into shorter ones ( $C_1$ – $C_6$ ). The decarboxylation reaction of benzene produces  $CO_2$ , which is the most abundant component in the gas phase.



**Figure 3.** FTIR spectra of colorless PVC waste before and after hydrothermal degradation under different reaction conditions.

### 3.6. Electricity Cost for Laboratory Scale Hydrothermal Process

For the laboratory-scale hydrothermal decomposition of 1 kg of PVC waste (75 mL) at 400 °C for 30 min, the electricity cost was estimated to be 92.6 kWh. By extending the reaction time and increasing the temperature, the energy consumption would increase to 148.1 kWh per kg of PVC at 400 °C and 60 min and to 153.7 kWh per kg of PVC at 425 °C and 60 min. The energy consumption was calculated based on the actual material consumption for the reaction. Energy costs could also be reduced by optimizing the PVC and water masses in the reactor and by increasing the capacity of the reactor. Chemical recycling using SCW has several advantages compared to other chemical recycling techniques, e.g., faster process rates and higher process efficiency, no required material drying, it is more environmentally acceptable, the reaction temperature is much lower than in the pyrolysis process, but its implementation requires a higher investment and high operating costs due to the considerable energy consumption to heat the water to the reaction temperature, as can also be seen from our study. Thus, the implementation still depends on the economics of the process. However, the advanced recycling company Mura Technology has developed an innovative recycling process, Hydro-PRT<sup>SM</sup> (Hydrothermal Plastic Recycling Technology). HydroPRS<sup>TM</sup> utilizes SCW to convert waste plastics, including flexible and multi-layered

materials, into high yields of stable hydrocarbon products for use in manufacturing new plastics and other materials [54].

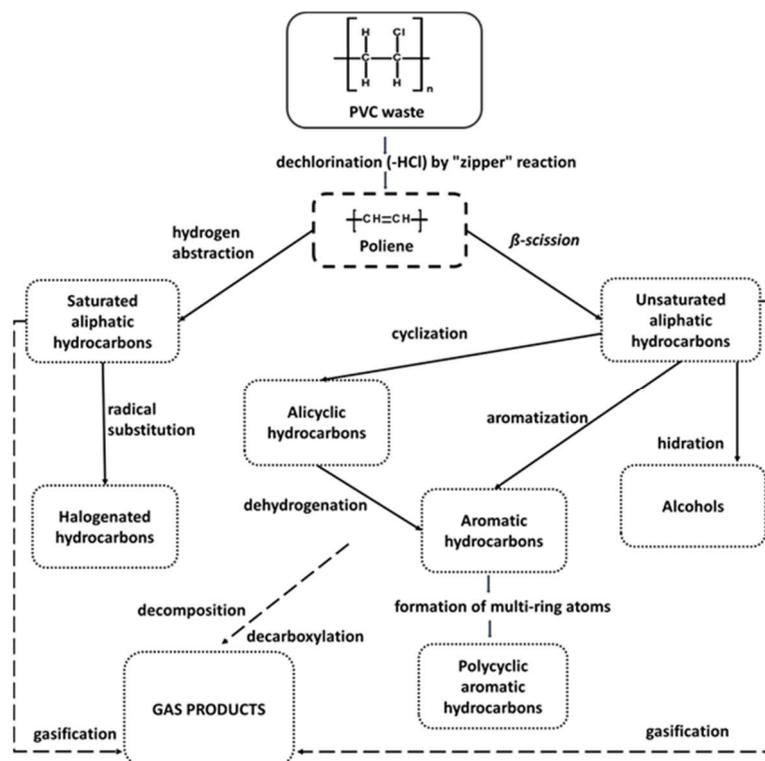


Figure 4. Degradation mechanisms of PVC waste in SCW.

Figure 4. Degradation mechanisms of PVC waste in SCW.

#### 4. Conclusions

The decomposition of colorless PVC waste in SCW at temperatures from 400 to 425 °C and reaction times from 30 to 60 min was investigated. It was found that chlorine was first released from the PVC molecule during degradation, and HCl was formed in the aqueous phase. After the degradation of PVC waste in SCW, an oil, gas, aqueous, and solid phase were obtained. The highest chlorine content ( $47.0 \pm 1.4\%$ ) in the aqueous phase was achieved at 400 °C and at a reaction time of 60 min. As the temperature and reaction time increased, the amount of solid residue decreased, while the yield of the oil and gas phases increased up to 425 °C in 60 min. The highest yield was achieved under these conditions, namely  $7.0 \pm 0.2\%$  for the gas phase and  $26.0 \pm 0.6\%$  for the oil phase. GC–MS analysis was used to determine the chemical composition of the oil and gas phases. PVC waste in SCW at 425 °C and 60 min decomposes into six main groups of compounds, i.e., saturated and unsaturated aliphatic hydrocarbons, alicyclic and aromatic hydrocarbons, alcohols, and halogenated hydrocarbons (chloroalkanes), of which the highest concentration was detected for aromatic hydrocarbons ( $39.31 \pm 0.93\%$ ) where benzene derivatives ( $18.7 \pm 0.39\%$ ) were the most common. The presence of polycyclic aromatic hydrocarbons ( $2.61 \pm 0.06\%$ ) in the oil phase was also detected. In the gas phase, CO<sub>2</sub>, alkanes, and alkenes of light hydrocarbons (C<sub>1</sub>–C<sub>6</sub>) were determined, among which the most common component was propane ( $6.60 \pm 0.17\%$ – $17.41 \pm 0.43\%$ ). It was found that oil and gas phases obtained from colorless PVC waste after hydrothermal degradation in SCW are composed of many valuable chemical components, and that the composition of the oil phase is similar to the composition of crude oil. Additionally, the advantage of this recycling method was also that most of the chloride ions remained in the aqueous phase and did not pass into the gas phase. As a result, however, the pH of

the aqueous phase also dropped significantly, which may cause damage to the equipment. The effect of corrosion depends on the behavior of the material and its ability to resist acid. Metals such as aluminum, cast iron, steel, copper, and titanium will be rapidly attacked by HCl at all concentrations and temperatures. Most types of stainless steel will be exposed to corrosion because their chromium content is not sufficient to form a passive protective layer. Nickel alloys have better resistance than stainless steel but are still not completely resistant to corrosion at different concentrations of HCl. Nickel molybdenum alloys have good resistance at all concentrations and temperatures. However, oxidizing contaminants can change nickel molybdenum alloys from very resistant to very susceptible to attack, and it is difficult to eliminate these oxidizing contaminants from practice. Reactive metals (zirconium and tantalum) offer the best resistance to HCl [55,56]. Considering the problem of corrosivity of the material, the selection of appropriate equipment would be very important if PVC were to be recycled into SCW on a larger scale.

The energy consumption of the process performed in the laboratory autoclave (75 mL) was also analyzed in this study. It was found that at the reaction conditions (425 °C, 60 min) where the highest oil (26.0 ± 0.6%) and gas yield (7.0 ± 0.2%) was detected, the cost of electricity would be 153.7 kWh per 1 kg of PVC waste. The cost of electricity could be reduced by increasing the capacities of the reactors as well as by optimizing the PVC waste and water amounts in the reactor.

The decomposition pathway of PVC waste in SCW provides a significant contribution to the eventual recycling of PVC waste in SCW. Based on the results, it can be concluded that the innovative SCW treatment process is suitable for the chemical degradation of plastic waste into valuable chemicals.

**Author Contributions:** M.Č.: Formal analysis, Investigation, Conceptualization, Writing—original draft, Writing—review and editing. P.K.: Formal analysis, Writing—review and editing, Ž.K.: Funding acquisition, Review of draft, M.Š.: Investigation, Conceptualization, Writing—review and editing, Supervision. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Slovenian Research Agency (No. P2-0421, No. P2-0046, and No. J7-3149).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors would like to acknowledge the Slovenian Research Agency (research core funding No. P2-0421, No. P2-0046, and project No. J7-3149) for financing this research.

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

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