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Article

Application of subcritical water to dechlorinate Polyvinyl Chloride Electric Wires

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Abstract: Polyvinyl chloride (PVC) electric wires were subjected to dechlorination in subcritical water at three different temperatures in a high-pressure reactor. About 2.09, 73.08 and 95.96 wt. % of chlorine in PVC wires was removed during dechlorination at 200, 250 and 300 ºC, respectively. The solid residues were analyzed and characterized by thermogravimetry, at three different heating rates (5, 10 and 20 ºC/min) in inert and oxidizing atmosphere. With the purpose of studying the emission of chlorinated pollutants, pyrolysis experiments at 850 ºC were also performed in a laboratory scale reactor with the dechlorinated materials, as well as with the original PVC electric wire. Polycyclic aromatic hydrocarbons (PAH) formation increased, but chlorobenzenes (ClBz) and chlorophenols (ClPh) formation decreased as the temperature of dechlorination increased; naphthalene was the most abundant PAH and monochlorobenzene and monochlorinated phenols (3-+4-) were the most abundant chlorinated compounds.

Keywords: dechlorination; hydrothermal treatment; thermogravimetric study; pyrolysis; chlorophenols; chlorobenzenes

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1. Introduction

At present, there are more than 20 different types of electric wires available, designed for applications ranging from transmission to heavy industrial use. Electric wires consist of one conductor, which usually is copper or aluminum, covered with insulating material, which can be polyvinyl chloride (PVC), polyethylene (PE), rubber, etc. [1].

Electric wires are designed with a limited useful life [2], normally they work for 10-30 years, so they become obsolete after a certain period of time. Consequently, electric wires waste generation has increased noticeably in recent years. Therefore, it is essential to take appropriate measures about the fate of this waste to avoid a negative environmental impact. Prevention of the generation of this waste, reuse and recycling are essential to preserve the environment and public health [3].

Recycling is crucial, not only to diminish the quantity of waste requiring treatment, but also to recover some of the raw materials such as plastics and base metals, as well as to eliminate the hazardous compounds (heavy metals such as mercury, nickel, lead, cadmium, etc. and brominated flame retardants) [4]. The stages of recycling process are: (1) disassembly, (2) separation of metallic and non-metallic fractions and (3) recycling of both fractions separately. The metallic fraction, which represents 50 % of the total weight of electric wires [5], is considered the most valuable fraction and becomes part of new industrial processes on the one hand and, on the other, the non-metallic fraction is used for recycling for material, chemical or energy recovery [2].

When plastics of electric wires waste are PVC, thermal treatment is turned into a very problematic way of recovery because important quantities of toxic or harmful compounds, such chlorophenols (ClPhs), chlorobenzenes (ClBzs), and polychlorodibenzo-*p*-dioxins and

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furans (PCDD/Fs), are emitted during the thermal decomposition of PVC in an inert and oxidizing atmosphere [6] and the thermal decomposition of PVC electric wires in air [5]. One solution is the development of removal techniques of chlorine from PVC electric wires before its thermal treatment.

Hydrothermal treatment with supercritical or subcritical water has become an effective and promising technique to remove the chlorine contained in PVC-containing wastes [7] and thus the emissions of chlorinated pollutants in thermal treatment of this waste could be reduced. Poerschmann et al. [8] subjected PVC to subcritical water treatment at 180-260 ºC and concluded that dechlorination increased with the increase of treatment temperature. Xiu et al. [9] carried out subcritical water oxidation of waste printed circuit boards and PVC, obtaining a total dechlorination of PVC when treatment temperature exceeded 250 ºC. Kubátová et al. [10] obtained a solid residue that contained less than 1 wt. % of chlorine after subcritical water treatment of PVC at 300 ºC. In the same research line, Endo and Emori [11] examined the hydrothermal degradation of PVC under high pressure and high temperature, concluding that the dechlorination efficiency could reach 100 % at 300 ºC.

In accordance with the previous studies, the objectives of this research are: (1) to assess the dechlorination efficiency of subcritical water treatment on PVC electric wire waste; (2) to identify the pollutants present in the water after the treatment; (3) to study the thermal degradation of the dechlorinated residues, as well as the decomposition of the original PVC electric wire by thermogravimetry; and (4) to analyze pollutant emissions during the thermal decomposition in inert atmosphere of the dechlorinated residues and the original PVC electric wire, with particular focus on the chlorinated pollutants.

2. Materials and Methods

The electric wire was supplied by General Cable, Co. The cover material is PVC, the insulation material is reticulated polyethylene and the conductor is copper [12].

As only the non-metallic fraction (cover and insulation material) was used in this study, this fraction was manually separated from the metallic fraction and it was crushed into small particles (<1 mm) using a cutting mill RETSCH SM200. Then, the sample was characterized. Elemental analysis was performed in elemental microanalyzer (Thermo Finnigan Flash 1112 Series). Oxygen plus ash content was calculated by difference. The analysis of the rest of elements was performed in a sequential X-ray fluorescence spectrometer (Philips Magix Pro PW2400). Table 1 shows the characterization of the cover and the insulation.

Table 1. Characterization of the materials used in the study.

wt. %	**Cover**	**Insulation**	**PVC wire**
Ashes	46.02	0.65	38.23
Elemental analysis			
C	34.58	84.57	43.16
H	4.45	14.68	6.20
N	nd	nd	nd
S	nd	nd	nd
O (by difference)	14.96	0.10	12.41
Fluorescence analysis			
Na	0.05	0.01	0.04
Mg	0.11	nd	0.09
Al	0.14	0.04	0.12
Si	0.06	0.09	0.07
P	0.01	nd	0.01
Cl	27.25	0.07	22.57

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Table 2. *Cont.*

wt. %	Cover	Insulation	PVC wire
Ca	23.45	0.22	19.46
Ti	0.06	nd	0.05
Fe	0.03	0.01	0.02
Zn	0.05	0.03	0.05
Sr	0.01	nd	0.01

nd: not detected

Dechlorination experiments with subcritical water were performed in a high-pressure batch reactor with stirring (volume of 1 L).

The parameters controlling the efficiency of this process are temperature, treatment time and solid/liquid (S/L) ratio [13]. Dechlorination runs were carried out at 200 ºC, 250 ºC and 300 ºC during 180 min, with a solid:liquid ratio (S/L) equal to 1:5 g/mL. In this way, treatment time and S/L ratio were not limiting factors in the dechlorination efficiency, based on the previous work done in a similar reactor working on the debromination of printed circuit boards waste [13].

During the dechlorination experiments, samples from the liquid phase were collected every hour and the remaining liquid from the reaction chamber was also collected after 24 h, in order to evaluate the evolution of the dechlorination process with time. These liquid samples were analyzed for chlorine by ion chromatography, and so it was possible to tally the chlorine balance. In addition, these liquid samples were qualitative analyzed for organic compounds by GC- MS (Agilent GC 6890N/Agilent MS 5976N, Agilent Technologies, USA) following the US EPA method 8270D [14] as reference. Specific conditions of this analysis have been described in detail in a previous study realized by Soler. et al. [15].

The solid residues obtained (that will be referred to as R200, R250 and R300, indicating the temperature of the treatment) were dried at 105 ºC until reaching a constant weight. Elemental analysis and chlorine content of the dechlorinated residues were also determined.

TGA was performed on a Perkin Elmer thermogravimetric analyzer (model STA6000). PVC electric wires (before and after the dechlorination process) were subjected to three different heating rates (5, 10 and 20 ºC/min) from room temperature up to 900 ºC in inert and oxidizing atmospheres. The flow rate of carrier gas was set at 100 mL/min. For each run, approximately 8 mg of sample were used.

Prior to each TGA run, a blank run was carried out using the same experimental conditions but with the crucible empty to ensure the system errors were corrected. So, these weight values recorded for each experimental time were subtracted from the values obtained in the TGA runs with sample.

Duplicated runs were done in the thermobalance to prove the outstanding reproducibility of the thermobalance. Really good reproducibility was obtained for the decomposition of these samples.

Pyrolysis of original PVC and residues R200, R250 and R300 were performed in a moving tubular quartz reactor located inside a horizontal laboratory furnace described by Aracil et al. and Moltó et al. [6, 16]

Once the set-point temperature was reached (850 ºC in all runs), the sample was introduced in the horizontal furnace at constant speed (0.5 mm·s^{-1}) using a quartz boat and maintained inside the reactor for 10 min, while the emitted pollutants were sampled for later analysis. A nitrogen flow of 300 mL/min (measured at 1 atm and 20 ºC) was introduced in parallel to the sample movement during the experiment. The sample weight was 25 mg approximately in each experiment.

Before the experiments, a control run with no sample was realized under the same conditions (blank). The blank values were subtracted from the values obtained in the pyrolysis runs with sample.

To analyze the emissions of inorganic chlorine was carried out by passing the evolved gases through two impingers which contained a dilute sulfuric acid solution (0.1 N) and then other two which contained a dilute sodium hydroxide solution (0.1 N). This experimental setup allows analyzing HCl and Cl_2 by ion chromatography, according to the US EPA method 26 [17].

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The HCl solubilizes in the acidic solution and forms chloride ions, whereas the Cl_2 passes through to the alkaline solution where it is hydrolyzed to form a proton (H^+), the chloride ion (Cl^-) and the hypochlorous acid (HClO). To facilitate formation of a second chloride ion, sodium thiosulfate was added in excess to the alkaline solution. In this way, two chloride ions are formed for each molecule of Cl_2.

A polyaromatic Amberlite® XAD-2 resin (Supelco, Bellefonte, USA) was used to collect the semivolatile compounds generated during the entire experiment. This resin was placed at the exit of the furnace. Three internal standards were added to the resin before the extraction to determine the concentration of PAHs, ClBzs and ClPhs. Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) supplied the deuterated standards used for the analysis of the PAHs and Wellington Laboratories (Ontario, Canada) supplied the 13C-labeled standards for ClPhs and ClBzs.

The next step was to extract the semivolatile compounds adsorbed to the resin with a mixture of dichloromethane/acetone (1:1 v/v) using ASE 100® Accelerated Solvent Extractor (Dionex-Thermo Fisher Scientific, California, USA) following the US EPA method 3545A [18]. The resultant extract was concentrated up to 1.5 mL using a rotary evaporator and straightaway with a moderate stream of nitrogen. Lastly, 3 µL of 2000 µg/mL of anthracene-d10 (AccuStandard, USA) was added as recovery standard.

PAHs, ClBzs and ClPhs were analyzed by GC- MS (Agilent GC 6890N/Agilent MS 5976N, Agilent Technologies, USA) following the US EPA method 8270D [14] as reference. Specific conditions of this analysis just as the identification and quantification of the compounds have been described in detail in a previous work realized by Soler. et al. [15].

3. Results

3.1. Dechlorination treatment

The rate of dechlorination depends on several factors including temperature, time of the treatment and solid/liquid ratio (S/L). The reaction time was set to 3 h and the ratio of PVC wire/water was fixed in 1:5 by weight. In this way, in this study, the most important factor influencing the dechlorination efficiency is the reaction temperature.

The process took place at the water vapor pressure at the corresponding temperature (approximately 1.6 MPa at 200 ºC, 4.0 MPa at 250 ºC and 8.6 MPa at 300 ºC) giving rise to a partial degradation of the original PVC wire.

Figure 1 shows the chlorine concentration in the liquid at different reaction times during the dechlorination treatment carried out at 200, 250 and 300 ºC. The initial chlorine concentration corresponds to the sample from the liquid phase collected when the reaction chamber reached the treatment temperature, after heating up to this temperature at 3 ºC/min approximately.

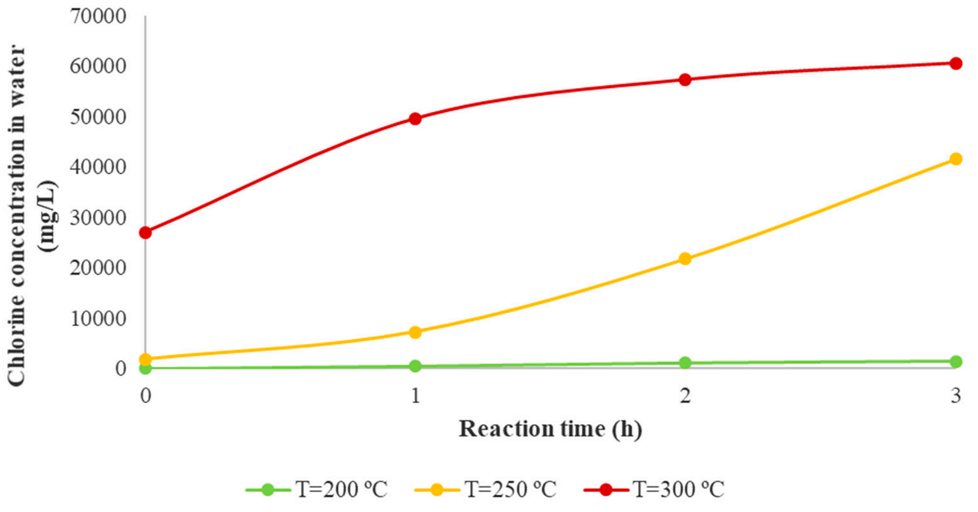

Figure 1. Effects of temperature and time on dechlorination process.

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As can be observed, dechlorination was not almost visible at 200 ºC, whereas dechlorination increased significantly at 250 ºC, because at this temperature region thermal degradation of PVC takes places. Xiu et al. [9] also concluded that dechlorination of PVC was no noticeable below 200 ºC, but the dechlorination reached almost 100 % above 300 ºC. Regarding to the effect of the reaction time, it can be observed that the chlorine concentration in liquid phase at all process temperatures increased with increasing time. Therefore, the dechlorination treatment was more effective as reaction time increased. At 300 ºC the initial dechlorination rate (slope of the curves presented in Figure 1), is quite high. Nevertheless, it seems that after 2 h the rate decreases in an important way, indicating that a maximum level of dechlorination has been reached.

As can be seen in Table 2, all the experiments were carried out with 50 g of PVC wire and a final solid yield of 79.2, 40.2 and 23.9 wt. % was obtained at 200, 250 and 300 ºC, respectively. The chlorine content of the solid residues obtained after the treatment was measured by X-ray fluorescence spectrometry, obtaining 27.9, 15.1 and 3.8 wt. %, at 200, 250 and 300 ºC, respectively. These results show that the chlorine content in the solid residue decreased with the increase dechlorination temperature. As a result, the subcritical water treatment was more effective as the dechlorination temperature increased. Poerschmann et al. [8] also subjected PVC to dechlorination treatment in subcritical water at high temperatures (180-260 ºC) and concluded that dechlorination increased with increasing treatment temperature.

Table 2. Results of dechlorination experiments.

Experiment	**Initial wire (g)**	**Solid residue (g)**	**Cl in solid residue (g)**	**Cl in final liquid (g)**	**DE (%)**
Dechlorination at 300 ºC	50.06	11.98	0.46	10.78	95.96
Dechlorination at 250 ºC	50.01	20.12	3.04	8.25	73.08
Dechlorination at 200 ºC	50.04	39.65	11.06	0.28	2.09

The percentage of chlorine removed can be calculated as:

$$\text{Dechlorination efficiency, DE (\%)} = \frac{m_{Cl\,i} - m_{Cl\,f}}{m_{Cl\,i}} \cdot 100 \qquad (1)$$

where $m_{Cl\,i}$ is the initial weight of chlorine in the PVC wire and $m_{Cl\,f}$ is the weight of chlorine in the solid residue obtained.

According to the chlorine content in the solid residues, hardly any chlorine was removed in the subcritical water treatment at 200 ºC, while a total of 73.08 and 95.96 wt. % of chlorine was removed when the dechlorination treatment was performed at 250 ºC and 300 ºC, respectively. This chlorine should have been removed in the gas or liquid phase.

Yu et al. [19] concluded that the chlorine of PVC was not transferred to gas phase, because it was nearly completely transferred to liquid phase. For this reason, the chlorine content in the gas phase was not analyzed in this study. The dechlorination efficiency (DE) can be also calculated by the following equation:

$$\text{DE (\%)} = \frac{m_{Cl\ in\ liquid}}{m_{Cl\,i}} \cdot 100 \qquad (2)$$

The higher the treatment temperature, the greater was the dechlorination efficiency, being 2.48, 73.06 and 95.45 wt. %, for the runs at 200, 250 and 300 ºC. The dechlorination efficiency values obtained by both previous equations were practically similar; it can be concluded that the chlorine removed of original PVC wire was retained in liquid phase. Therefore, the dechlorination treatment at high pressure and high temperature could break the chemical bonds of the polymeric matrix,

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favoring PVC degradation. Possible decomposition pathways of PVC have been proposed by several authors [20-22].

In this way, the subcritical water treatment proved to be an efficacious method to remove the chlorine present in PVC electric wires. Endo and Emori [11] studied the hydrothermal degradation of PVC under high pressure and concluded that a total dechlorination of the material could be possible at 300 ºC.

Upon hydrothermal treatment, the pH of liquid phase was measured, and it was obtained that the pH dropped progressively with the treatment temperature, obtaining pH values of 7.18, 2.40 and 2.84 at 200, 250 and 300 ºC, respectively, due to the release of HCl in the solution. Phenol, benzoic acid, benzaldehyde, cyclohexanone and methyl cyclopentane were identified in the liquid phase. These compounds were also determined in liquid phase after dechlorination treatment by Takeshita et al. [21], obtaining a total amount of these compounds of 179 mg/L.

Table 3 shows the elemental analysis results of the solid residues. Carbon and hydrogen content in the solid residue increased as the operating temperature increased. The content of H was not decreased due to hydrolysis reaction. Therefore, the chlorine should be replaced by the base [23].

Table 3. Elemental analysis of the solid residue obtained and net calorific values.

wt. %	**C**	**H**	**O**	**Ash**	**H/C**	**Net calorific value (kJ/kg)**
R200	34.46	4.66	19.50	41.38	0.14	17269
R250	63.20	8.08	10.44	18.27	0.13	32281
R300	74.40	8.41	8.72	8.46	0.11	37766

Oxygen content reach to about 8-20% in solid residues, decreasing with the increase of treatment temperature. The net calorific value of the residues also increased gradually, obtaining a maximum value of 37766 kJ/kg in the solid residue obtained after the treatment at 300 ºC. Lu et al. [23] and Takeshita et al. [21] also obtained similar net calorific values of the residual solid after dechlorination treatment (35798 kJ/kg at 260ºC and 38749 kJ/kg at 300 ºC, respectively). Therefore, the solid residues may be employed as high-quality fuel for blast furnace or a feedstock for producing activated carbon, etc. because their net calorific values are as good as coal and coke (18800-33500 and 25100-31400 kJ/kg, respectively) [21]. In addition, the ratio of H/C decreased, indicating that the unsaturation degree of the hydrolysis product increased. It can be concluded that the hydrolysis reaction of PVC includes the cracking of C-C chain and substitution of Cl with -OH [23].

3.2. Thermogravimetric analysis

Thermogravimetric experiments in inert (pyrolysis) and oxidizing atmosphere (combustion) were performed to characterize dechlorinated residues and the original PVC wire. Dynamic runs at 5, 10 and 20 ºC/min were carried out for each material from room temperature up to 900 ºC. Figure S1 shows the details on the TG-curves obtained during the pyrolysis of original PVC wire (only plastic fraction), R200, R250 and R300. Figure S2 presents the thermal decomposition in air.

All samples present mass loss curves moving to the right (towards higher temperatures) with the increase of the heating rate. This is a habitual behavior which has been observed in many materials; this can be explained just taking the kinetic law into consideration [24-26]. On the other hand, thermal decomposition of the materials accelerates in the presence of oxygen, since the oxidation of the final pyrolytic residue occurs, giving rise to out a higher mass loss.

Figure 2 shows a comparison of the curves obtained at 10 ºC/min for the four materials tested in nitrogen, and Figure 3 is the one corresponding to combustion in air. As can be observed (Figure 2), the mass loss curve of the original PVC wire presents three main stages (centered at about 300, 480 and 780 ºC). The decomposition of R200 is very similar to that of the original wire, but there is a great change in the thermal decomposition of R250 and R300. In this case, only the first two stages are

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present. This can be due to the obtaining of a more degraded material when the pretreatment occurred at higher temperature. The declorinated residues begin to decompose at lower temperatures, which means a further degradation of the polymeric matrix when pretreatment temperature increases. The TG runs performed in oxidizing atmosphere (Figure 3) present an analogous variation when comparing the diverse materials tested.

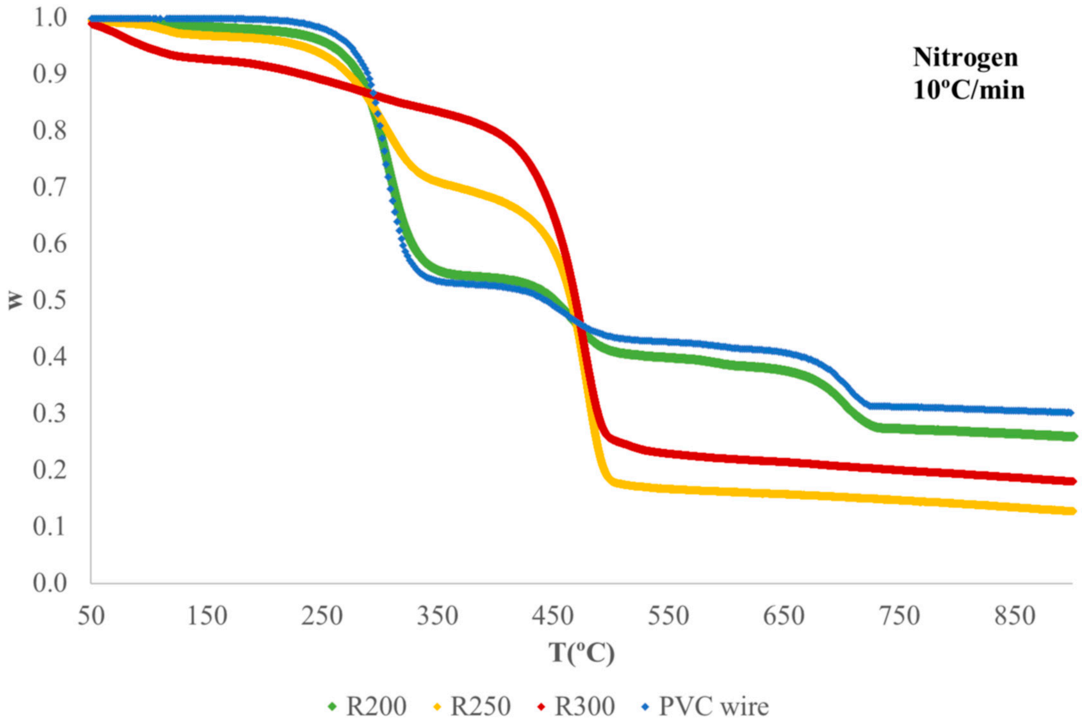

Figure 2. TG-curves obtained during the pyrolysis at 10 ºC/min.

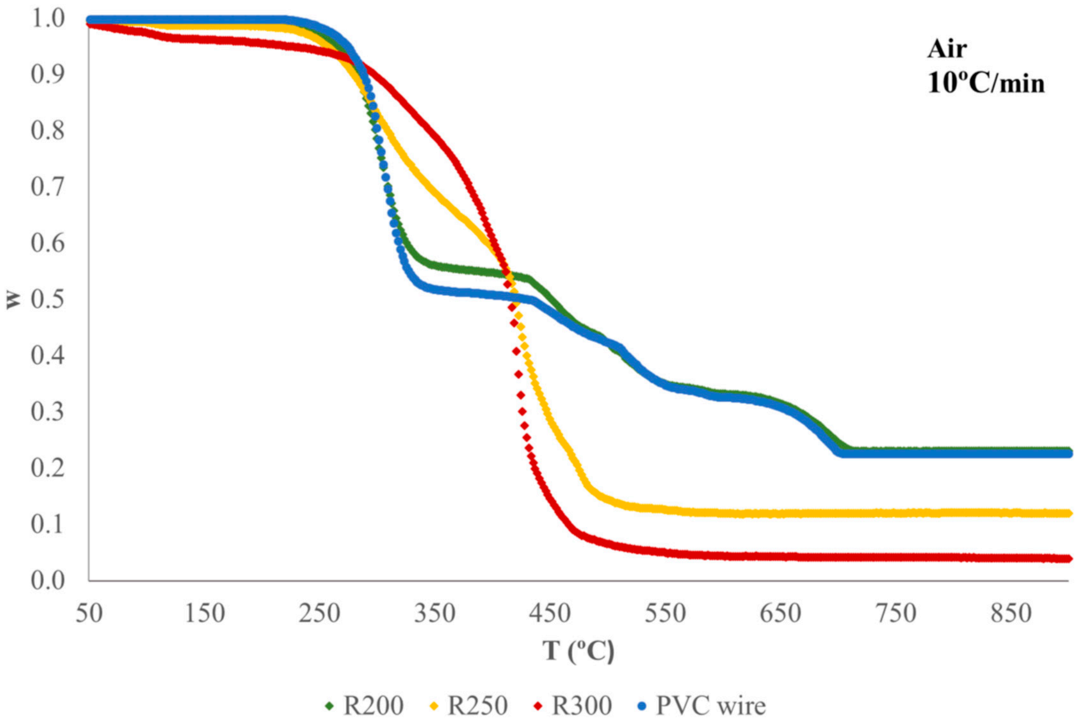

Figure 3. TG-curves obtained during the combustion at 10 ºC/min.

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3.3. Pollutant emissions in pyrolysis runs

As mentioned in the experimental section, pyrolysis of the residues R200, R250 and R300, as well as of the original PVC wire, were carried out in a horizontal furnace at 850 ºC to check for the pollutant formation.

3.3.1. Hydrogen halide and halogen emissions

Inorganic chlorine emissions in the pyrolysis runs are shown in Table 4. Emissions significantly decreased when the material had been subjected to dechlorination process at the higher temperature, i.e., the emission decreased as the dechlorination temperature increased. The materials obtained after dechlorination at 200, 250 and 300 ºC emitted 4.0, 81.9 and 92.4 % less inorganic chlorine than the starting material.

Table 4. Emission of inorganic chlorine during the pyrolysis at 850 ºC.

	PVC wire	**R200**	**R250**	**R300**
Compound	**mg /kg sample**			
HCl	155300	149200	18750	2140
Cl_2	10780	10210	11320	10550

Emission factors of HCl were higher than the ones for Cl_2 for all materials, except the residue obtained in dechlorination treatment at 300 ºC. This behavior was also found for other wastes, such as printed circuit boards (PCBs) [27] and debrominated PCBs [13].

3.3.2. PAHs

Figure 4 shows the emissions of the 16 priority PAHs during pyrolysis at 850 ºC. Data are also provided in Table S1 of Supplementary Material. All the samples presented similar emission pattern of these compounds. The most abundant compound was naphthalene, followed by acenaphthylene, phenanthrene and fluorene.

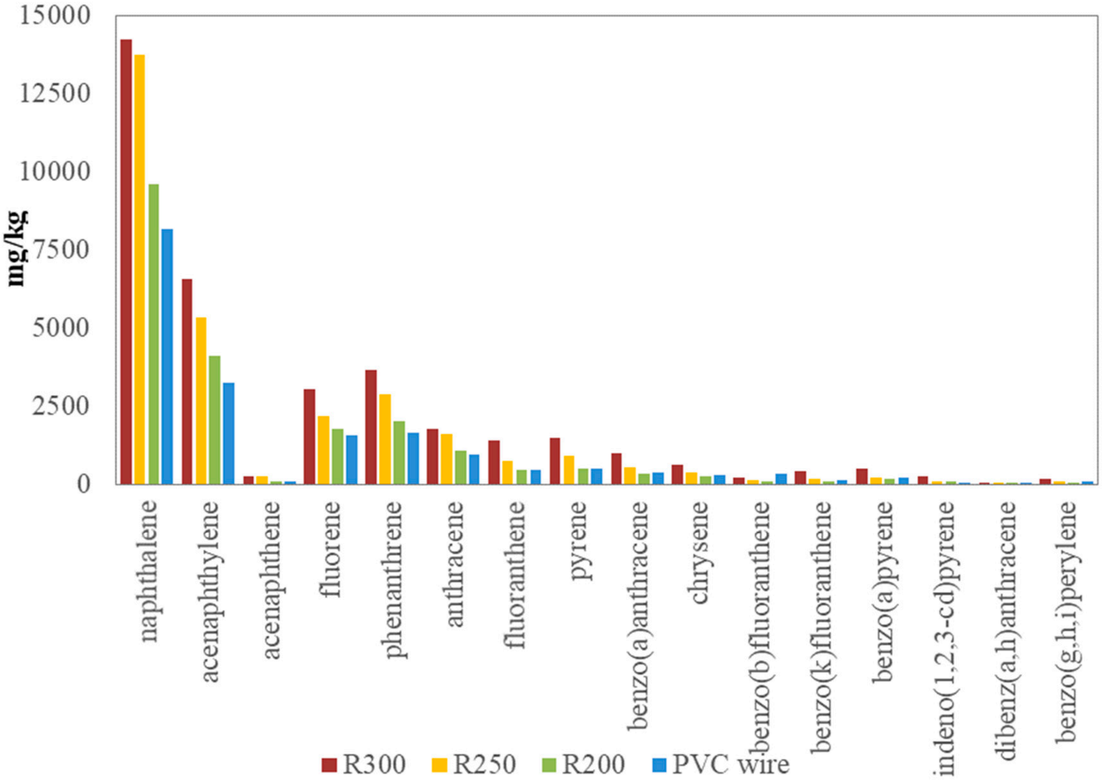

Figure 4. PAH emissions during the pyrolysis at 850 ºC.

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These results coincide with several previous studies [5, 13, 28, 29] where the naphthalene was the principal PAH emitted during the thermal decomposition of different wastes.

PAH formation effectively increased during pyrolysis as the temperature of hydrothermal dechlorination increased, i.e., the emission factors increased when pyrolysis was performed with the dechlorinated residues obtained from the dechlorination process at higher temperatures. PAH formation reached its maximum in pyrolysis at 850 ºC because the thermal decomposition in inert atmosphere was confirmed as the primary source of PAH formation [30] Total PAH yields in pyrolysis were 18070 mg/kg for the original PVC wire, 20690, 29260 and 35710 mg/kg for the dechlorinated materials obtained at 200, 250 and 300 ºC, respectively. These results are of the same order of magnitude as those obtained in a previous study done by Aracil et al. [6], where the total yield was 35000 mg/kg in the pyrolysis of PVC pellets at 850 ºC.

3.3.3. ClBzs

Table 5 presents the detail of ClBz congeners and the total amount of ClBzs in the pyrolysis at 850 ºC. Total yields of ClBzs were 1751 mg/kg for the original PVC wire, 2178, 928 and 500 mg/kg for the dechlorinated materials prepared at 200, 250 and 300 ºC, respectively. The maximum total yield was obtained for the decomposition of the sample dechlorinated at 200 ºC, as it presented the highest chlorine content. Therefore, the total yields of ClBzs decreased with the increase of dechlorination temperature to which the samples had been subjected. This can indicate that the formation of chlorine structures during the pyrolysis is less effective. In this way, the increase in the emission of PAHs from this material can be justified. PAHs could transform into chlorinated species at temperatures between 300 and 1000 ºC [31].

Table 5. Yields of ClBzs during the pyrolysis at 850 ºC.

	PVC wire	**R200**	**R250**	**R300**
Compound		**mg/kg sample**		
mono-	919	1360	125	11.3
1,3-	nd	nd	nd	nd
1,4-	5.48	4.27	1.14	0.26
1,2-	826	814	802	488
1,3,5-	0.03	0.02	0.02	nd
1,2,4-	0.03	0.02	0.02	nd
1,2,3-	0.03	0.03	0.02	0.01
1,2,3,5-+1,2,4,5-	0.02	0.02	0.02	0.01
1,2,3,4-	0.04	0.03	0.02	0.02
penta-	0.04	0.01	0.02	0.01
hexa-	nd	nd	nd	nd
TOTAL	1751	2178	928	500

nd: not detected (<0.01 mg/kg sample)

Respect to the ClBz congener distribution, all samples present the same trend. For all the materials, mono- and dichlorinated congeners were the main products emitted, particularly dichlorinated congeners with chorine in the position 1,2- and 1,4-. Aracil et al. [6] also found a predominance of mono- and dichlorobenzenes in pyrolysis of PVC at 850 ºC.

Conesa et al. [5] analyzed ClBz emissions during thermal treatment of two types of wires (PVC wire and halogen-free wire) and concluded that ClBz formation was higher for the PVC wire, and increased in the presence of metal. Therefore, it can be concluded that hydrothermal dechlorination could reduce the formation of chlorinated compounds in thermal processes, now that the material obtained after dechlorination treatment at 300 ºC emitted 71.4 % less ClBzs than the original PVC wire during the pyrolysis at 850 ºC.

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3.3.4. ClPhs

Table 6 presents the total amount of ClPhs detected in the pyrolysis runs carried out at 850 ºC. ClPh total yields decreased with the increase of dechlorination temperature to which the samples had been subjected. ClPh total yields of all solid residues (100.7 mg/kg, 57.5 mg/kg and 56.9 mg/kg for the solid residue obtained at 200, 250 and 300 ºC, respectively) were lower than total yield from the original PVC wire (113.2 mg/kg). Therefore, subcritical water treatment could decrease the emissions of chlorinated compounds in thermal processes, now that R300 emitted 49.7 % less ClPhs than the original PVC wire.

Table 6. Emission of ClPHs during the pyrolysis at 850 ºC.

	PVC wire	**R200**	**R250**	**R300**
Compound	**mg/kg sample**			
2-	nd	nd	nd	nd
3-+4-	61.7	57.6	55.1	54.5
2,4-	nd	nd	nd	nd
2,5-	0.13	0.07	0.07	0.06
2,3-	nd	nd	nd	nd
2,6-	0.03	nd	nd	nd
3,5-	51.0	42.7	2.15	2.13
3,4-	0.26	0.16	0.10	0.10
2,3,5-	nd	nd	nd	nd
2,4,6-	nd	nd	nd	nd
2,4,5-	nd	nd	nd	nd
2,3,4-	nd	nd	nd	nd
2,3,6-	nd	nd	nd	nd
3,4,5-	nd	0.11	nd	nd
2,3,5,6-	0.04	0.03	0.02	0.02
2,3,4,5-	0.04	0.04	0.02	0.02
2,3,4,6-	0.03	0.03	0.02	0.02
penta-	nd	nd	nd	nd
TOTAL	113.2	100.7	57.5	56.9

nd: not detected (<0.01 mg/kg sample)

Table 6 also shows the detail of ClPh congeners. In all the runs, monochlorinated phenols (3-+4-) were the most abundant congeners, followed by 3,5-dichlorinated phenol. Kaivosoja et al. [32] and Soler et al. [15] also concluded that the most emitted ClPhs were monochlorinated phenols (3-+4-) in their studies about thermal treatment of different wastes.

4. Conclusions

Subcritical water treatment for dechlorination of PVC wire was more effective as the treatment temperature increased. Therefore, dechlorination efficiency increased as the process temperature increased, obtaining a maximum efficiency of 95.96 wt. % at 300 ºC. The concentration of chlorine in solid residue decreased because the chlorine present in PVC wire was nearly completely transferred to the water. In addition, these solid residues obtained high net calorific values, with a maximum value of 37766 kJ/kg for the solid residue obtained after the treatment at 300 ºC, which may be employed as high-quality fuel consequently.

TG curve of the original PVC wire presented three main stages, but as the material was subjected to a more severe dechlorination the TG curve presented fewer stages; the decomposition of R200 was very similar to that of the original wire, while the decomposition of R250 and R300 only presented the first two stages and one stage, respectively. Therefore, dechlorination process produced a more degraded material as the treatment temperature increased.

Regarding pollutant emissions during pyrolysis, emissions of inorganic chlorine significantly decreased when increasing the increase of the dechlorination temperature. R200, R250 and R300 emitted 4.0, 81.9 and 92.4 % less inorganic chlorine than the original PVC wire. PAH formation increased as the temperature of dechlorination process increased. This increase in the emission of PAHs can justify that the formation of chlorine structures was less effective during the pyrolysis. Thus, the emissions of organic chlorinated compounds (ClBzs and ClPhs) decreased with the increase of dechlorination temperature to which the samples had been subjected and total yields originating from the thermal decomposition of dechlorinated residues were lower than the total yield from the original PVC wire. All the materials presented a much more emission of ClBzs than ClPhs. Furthermore, the main chlorinated compounds were monochlorobenzene and monochlorinated phenols (3-+4-).

Therefore, it can be concluded that the subcritical water treatment was an efficient method for dechlorination of PVC wires and could reduce the formation of chlorinated compounds in subsequent thermal processes of this waste.

Supplementary Materials: The following are available online, Figure S1: TG-curves obtained during the pyrolysis of: (a) R200, (b) R250, (c) R300 and (d) original PVC wire. Figure S2: TG-curves obtained during the combustion of: (a) R200, (b) R250, (c) R300 and (d) original PVC wire. Table S1: Yields of PAHs during the pyrolysis at 850 ºC.

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