

Dechlorination of polyvinyl chloride electric wires by hydrothermal treatment using K_2CO_3 in subcritical water

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ABSTRACT

Polyvinyl chloride (PVC) waste generation has significantly increased in recent years and their disposal is considered a major environmental concern. Removal techniques of chlorine from PVC waste are being studied to minimize a negative environmental impact. In this work, the use of K_2CO_3 as an alkaline additive to improve the dechlorination efficiency (DE) in the hydrothermal degradation of PVC wires was studied. Different experiments were carried out varying both temperature (175 °C, 200 °C, 225 °C, 235 °C and 250 °C) and K_2CO_3 concentration (0.025 M, 0.050 M and 0.125 M), using a solid/liquid ratio of 1:5 in order to determine the evolution of the dechlorination efficiency with time. About 4.66, 21.1, 24.4, 45.7 and 92.6 wt. % of chlorine in PVC wire was removed during hydrothermal dechlorination (HTD) with an additive/chlorine ratio of 1:25 (K_2CO_3 solution of 0.050 M) at 175, 200, 225, 235 and 250 °C, respectively. Optimal additive/chlorine ratio decreased to 1:50 (K_2CO_3 solution of 0.025 M) at 250 °C, obtaining a dechlorination degree of 99.1% after 4 hours without the need of metallic catalysts. Concerning the solid phase behavior during dechlorination, a linear correlation between the DE reached and the weight loss of PVC was found including every experiment performed in this work.

Keywords: Hydrothermal process; Dechlorination efficiency; PVC electric wires; alkaline additive; potassium carbonate.

24 1. INTRODUCTION

25 Polyvinyl chloride (PVC) has been widely employed in industry, construction, signage, toys, packing
26 material, electronic applications, etc. (Moulay, 2010; Sabaa et al., 2009; Zhu et al., 2016). PVC is the most
27 common thermoplastic used as insulation in electric wires (Morsy et al., 2003), due to its easy processing,
28 good insulation capacity, high chemical resistance and low flammability (Akovali, 2012; Zabłocka-
29 Malicka et al., 2015). PVC products have long useful life in comparison with other plastic materials.
30 However, a large amount of PVC products becomes solid waste every year.

31 PVC waste generation has significantly increased in recent years and their disposal is nowadays
32 considered a major environmental risk (Yao and Ma, 2017). Traditional waste treatment and disposal
33 methods are accumulation in landfills and thermal treatment for energy recovery. Landfilling can lead to
34 soil and groundwater contamination by the leachates of the toxic substances present in PVC waste
35 (Baishya and Mahanta, 2013). Thermal treatment is considered as a potential source of emission of toxic
36 and harmful pollutants such as chlorinated organic compounds (Suresh et al., 2017), which can cause
37 serious environmental problems if no efficient pollutant remediation techniques for gases are present in
38 the facilities. Emissions of chlorophenols (ClPhs), chlorobenzenes (ClBzs), and polychlorodibenzo-*p*-
39 dioxins and furans (PCDD/Fs) were detected during the thermal decomposition of PVC (Aracil et al.,
40 2005) and PVC electric wires (Conesa et al., 2013).

41 Consequently, it is necessary to develop removal techniques of chlorine from PVC waste prior to their
42 utilization to avoid a negative environmental impact. In order to remove chlorine from PVC waste,
43 catalytic dechlorination and hydrothermal dechlorination (HTD) are the main methods used. Catalytic
44 dechlorination entails the selective break of one or more C-Cl bonds, giving rise to less toxic and reusable
45 materials (Yu et al., 2016). This phenomenon is due to addition of high volume of catalyst. The main
46 problems of catalytic dechlorination are the catalyst poisoning, high operation temperature (400-1000 °C),
47 non-uniform heat transfer, low yields obtained and excessive formation of char and gas (Wang and Zhang,
48 2012). HTD has become an effective and environmentally friendly method for the chlorine removal of
49 PVC waste (Kubátová et al., 2002; Poerschmann et al., 2015; Soler et al., 2018; Xiu et al., 2014; Yao and
50 Ma, 2017; Zhao et al., 2018, 2017) because it presents simple and fast reaction rates, and homogeneous

51 reactions without limitations of mass transfer occur, which give rise to excellent process efficiency (Soler
52 et al., 2017).

53 Poerschmann et al. (2015) subjected PVC to subcritical water treatment at different temperatures (180-260
54 °C) and they observed that dechlorination increased with the increase of process temperature. Qi et al.
55 (2018) carried out HTD for PVC waste using subcritical water and their results showed that 10 % the
56 chlorine of PVC waste was transferred into water at 200 °C, 85.5 % was transferred at 250 °C and
57 approximately 95 % was transferred at 300 °C. Higher pressure and temperature could accelerate the
58 removal of the chlorine from PVC waste as HCl. Yao and Ma (2017) also observed a decrease of the
59 chlorine content in the residue and an increase of the carbon and hydrogen content as the dechlorination
60 temperature increased due to reactions of elimination and substitution. In order to improve the
61 dechlorination efficiency of the HTD process applied to PVC waste, some catalysts (Lv et al., 2009; Zhao
62 et al., 2017) and alkaline additives (Yoshioka et al., 2008; Zhao et al., 2018) were used. Zhao et al. (2018)
63 investigated the effect of different alkaline additives in the HTD of PVC, which was performed in
64 subcritical Ni²⁺-containing water at 220 °C. The results showed that the alkaline additives significantly
65 improved the dechlorination efficiency and concluded that the most effective additive was Na₂CO₃ from
66 among those studied.

67 In another work (Soler et al., 2018), PVC wires were also subjected to subcritical water treatment at
68 different temperatures (200, 250 and 300 °C). It was observed that the dechlorination efficiency increased
69 with the increase of the reaction temperature as it was concluded in the study performed by Poerschmann
70 et al. (2015), obtaining a maximum efficiency higher than 95 % at 300 °C. The chlorine removed from
71 PVC was transferred to the water as HCl (main compound), apart from other compounds such as phenol,
72 benzoic acid, benzaldehyde, cyclohexanone and methyl cyclopentane. Thus, in line with the previous
73 research of Soler et al., the aim of the present work was to improve the dechlorination efficiency of
74 hydrothermal degradation of PVC wires at lower temperatures, using K₂CO₃ as alkaline additive in order
75 to decrease the costs of energy and treatment required by the process.

76 **2. MATERIALS AND METHODS**

77 K_2CO_3 used in this study as a “stimulant medium additive” during the subcritical water treatment, was
78 reactive-quality grade with a minimum purity of 99% and was supplied by Merck (Darmstadt, Germany).
79 The electric wire employed for the experiments was supplied by General Cable, Co. This wire was
80 composed of three fractions: a cover made of PVC, an insulation material of reticulated polyethylene (PE)
81 and the copper conductor. For this study, only the non-metallic fraction (cover and insulation material)
82 was used after manual separation from the copper. Once separated, they were mixed in a proportion of
83 82.8% cover and 17.2% insulation (that represents the electric wire as it is) and the mixture was crushed
84 into a particle size (<1 mm) small enough to have a homogeneous material using a cutting mill RETSCH
85 SM200.
86 This electric wire was previously characterized using an elemental microanalyzer (Thermo Finnigan Flash
87 1112 Series) to provide total content (wt. %) of carbon, hydrogen, nitrogen and sulfur, and a sequential X-
88 ray fluorescence spectrometer (Philips Magix Pro PW2400) to obtain the rest of elements (Soler et al.,
89 2018).

90 **2.1. EXPERIMENTAL SET-UP**

91 The dechlorination process was performed in a 1 L high-pressure batch stirred reactor using a K_2CO_3
92 solution in water as subcritical fluid. This reactor RS1000-SMH model from ILSHIN AUTOCLAVE CO,
93 LTD. can safely work up to a maximum temperature of 350 °C and a maximum pressure of 20 MPa.
94 The efficiency of this dechlorination process was controlled mainly by the following parameters:
95 temperature, K_2CO_3 concentration, residence time and solid/liquid (S/L) ratio.

96 **2.2. EXPERIMENTS AND CONDITIONS**

97 The degree of dechlorination achieved depends on diverse factors such as temperature, reaction time at set
98 temperature, solid/liquid (S/L) ratio and additive concentration in the solution used as dechlorination
99 agent, which corresponds to potassium carbonate in the whole study. The will to apply K_2CO_3 as diluted
100 additive in subcritical water for HTD treatment was based on the good behavior of sodium carbonate
101 already proved (Zhao et al., 2018) and the possible activity of potassium higher than that of sodium (Xiao
102 et al., 2014).

103 In this work, the residence time was set to 4 h and the ratio of PVC wire/ K_2CO_3 solution was fixed in 1:5
104 g/mL to assure that neither the S/L ratio nor the treatment time were limiting factors, as mentioned in
105 previous works for similar conditions (Soler et al., 2017; Xing and Zhang, 2013), so that the
106 dechlorination efficiency (DE) was only influenced by the most important factors of interest for this work:
107 temperature and K_2CO_3 concentration-

108 In order to observe the influence of both temperature and K_2CO_3 concentration in the dechlorination
109 process, different experiments were carried out varying these two parameters: temperature treatment at
110 175 °C, 200 °C, 225 °C, 235 °C, 250 °C and K_2CO_3 concentration with solutions at 0.025 M, 0.050 M and
111 0.125 M. Every set temperature was reached under a temperature gradient of 2.5 °C/min approximately. In
112 the same way, the stirrer was fixed at a rotating speed of 100 rpm in each run to assure that the sample and
113 temperature were homogeneous in the batch during the whole process.

114 On the one hand, temperatures were chosen to obtain a wide range around the apparently middle range
115 temperature of 200 °C-300 °C which had been employed during PVC treatment in subcritical water
116 conditions by others researchers (Poerschmann et al., 2015; Xiu et al., 2014).

117 For all the experiments, 50 g of the non-metallic fraction of the electric wire (chlorine content: 22.57 wt.
118 %, particle size <1 mm) were introduced into the reactor together with 250 mL of K_2CO_3 solution. The
119 K_2CO_3 concentrations of 0.025 M, 0.050 M and 0.125 M, with a very small amount of additive (much
120 smaller than the stoichiometric in regard to chlorine), correspond to a molar anionic content about 1:50,
121 1:25 and 1:10 of the total molar PVC chlorine content, respectively, which are comparable to those ratios
122 studied before with other additives (Zhao et al., 2018).

123 On the other hand, in order to assess the evolution of the dechlorination with time, the liquid phase was
124 sampled every hour extracting a fixed amount of solution from inside the reactor (starting from the
125 moment when the reaction mixture reached the set temperature) and preventing the S/L ratio from
126 declining at every moment below the limiting 1:4 g/mL ratio reported by (Soler et al., 2018; Xing and
127 Zhang, 2013). The remaining liquids were collected once the autoclave cooled down to room temperature.
128 The liquid samples were analyzed by ion chromatography searching for chlorine concentrations. The
129 evolution of the dechlorination efficiencies with time that would be reached for each condition in an
130 identical process with no extractions was determined. This was done taking into account that the

131 concentrations measured needed to be corrected because of the reduction of mass solution with time inside
132 the reaction chamber. Therefore, the corresponding mass of chlorine $m_{Cl,Liq,t}$ (in mg) obtained in the
133 residual liquid at time t (in hours) with the correction mentioned was calculated according to the following
134 formulas:

$$m_{Cl,Liq,t}(t=0) = [Cl]_{t=0} \cdot m_{Sol}$$

$$m_{Cl,Liq,t}(\forall t \geq 1) = [Cl]_t \cdot \left(m_{Sol} - \sum_{\tau=1}^t m_{Ext,\tau-1} \right)$$

135
136
137
138 where $[Cl]_t$ is the concentration of chlorine in the liquid of extractions at time t (in mg/kg), m_{Sol} is the
139 weight of solution (in kg) initially introduced and that remains the same at the end for a process without
140 extractions and $m_{Ext,t-1}$ is the weight of liquid sample (in kg) extracted at time $t-1$ (in hours).

141 The DE, which represents the amount of chlorine content removed from the solid and transferred to the
142 liquid phase at time t (in hours), can be calculated as:

$$DE(\%, t) = \frac{m_{Cl,Liq,t}}{m_{Cl,i}} \cdot 100$$

143
144 where $m_{Cl,i}$ is the initial weight of chlorine content in the PVC wire inside the reactor (11285 mg, in this
145 work) and $m_{Cl,liq,t}$ is the weight of chlorine (in mg) in the residual liquid obtained at time t (in hours) in a
146 process without extractions.

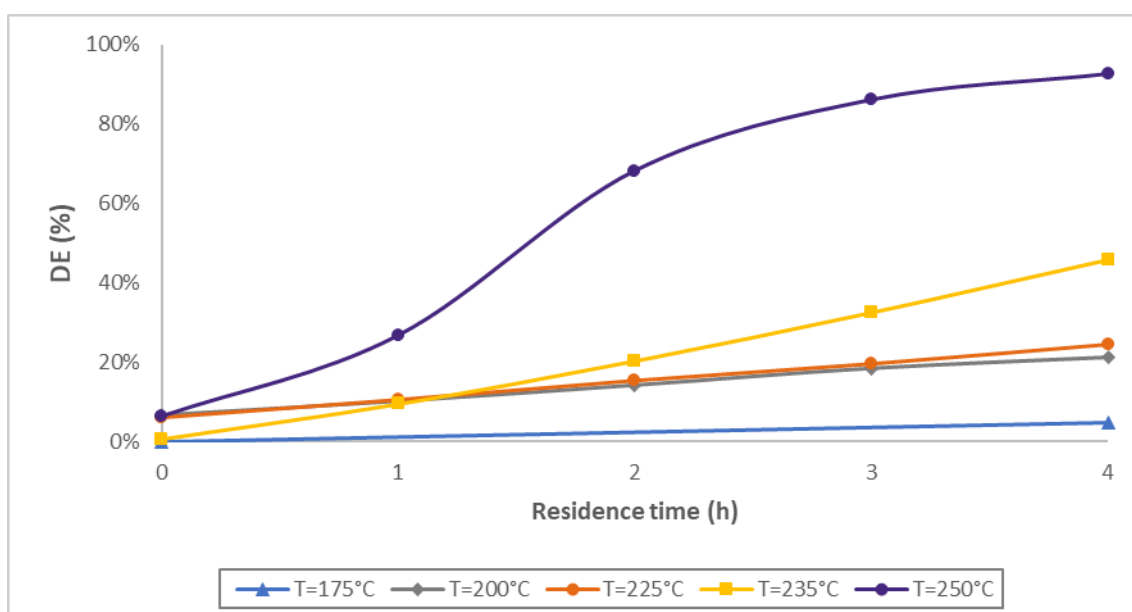
147 Finally, the solid residues (hydrochars) obtained were weighed and their elemental content and net
148 calorific value were determined, after being dried at 105 °C, in order to know their characteristics for a
149 possible later use as fuel for energy outcome and energetic raw material savings.

150 3. RESULTS AND DISCUSSION

151 3.1. EFFECT OF K_2CO_3 ADDITIVE ON HTD BEHAVIOR

152 The HTD process, which provided a partial degradation of the original PVC wire, took place at the
153 following water vapor pressures for each temperature: approximately 1.0 MPa at 175 °C, 1.5 MPa at 200
154 °C, 2.5 MPa at 225 °C, 3.0 MPa at 235 °C and 3.8 MPa at 250 °C.

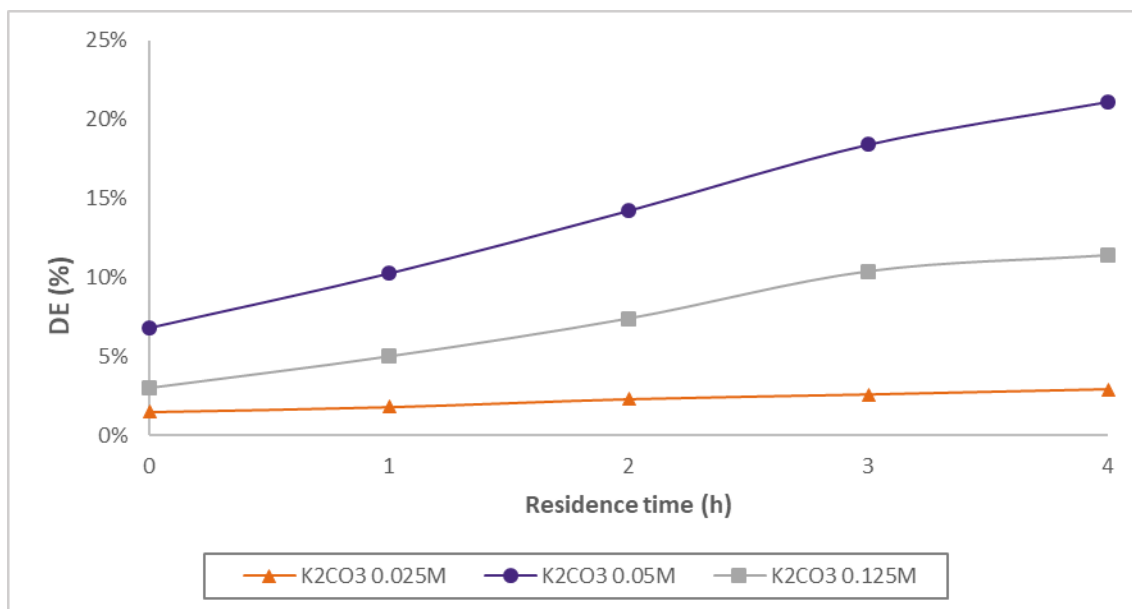
155 Figure 1 shows the DE of PVC after the HTD process for several reaction times between 0 (t_0) and 4 hours
156 (t_4) at various set temperatures using a K_2CO_3 concentration of 0.050 M, except at 175 °C were only t_0 and
157 t_4 were sampled in order to avoid obstructions on the extraction system that occurred possibly because of
158 the ductile nature of this material at that temperature.
159 Concerning the effect of temperature and residence time, both induced an increase of DE. At the lowest
160 temperature (175 °C), the dechlorination was almost non-existent arriving only to a DE of 4.7%. However,
161 a DE of 21.1% and 45.7% was reached after 4 hours of reaction time at low (200 °C) and mid-range (235
162 °C) temperatures, respectively. A huge gap between the temperature of 250 °C (high temperature in this
163 study) and the rest of temperatures was observed because of the closeness to the range of temperature
164 where thermal degradation of PVC starts really to take place (Xiu et al., 2014), presenting in addition an
165 inflection point around 1 hour of residence time, when DE quickly increased compared to the other
166 temperatures. Nevertheless, the rate started to decrease particularly after 3 h, revealing that dechlorination
167 completion of PVC was approaching.



168
169 *Figure 1. DE obtained with K_2CO_3 at 0.050 M for several temperatures and reaction times (corresponding to a molar anionic*
170 *content about 1:25 of the total molar chlorine content).*

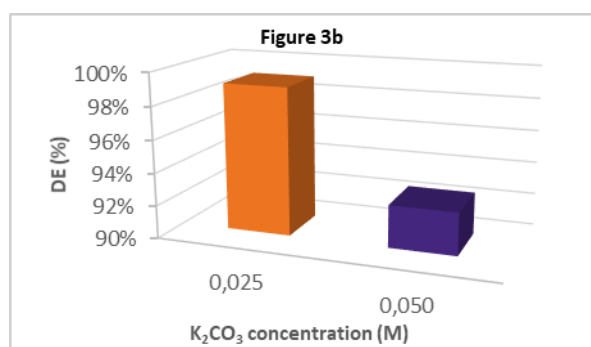
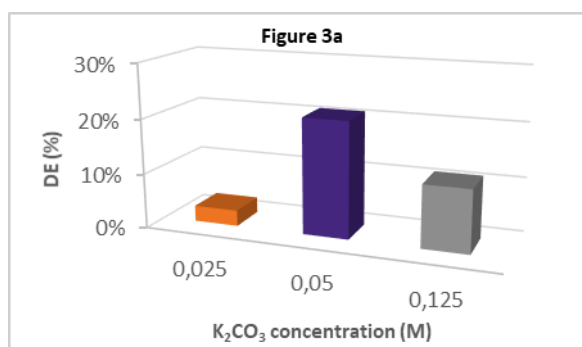
171 Figure 2 shows the evolution and behavior of DE at a low temperature ($T=200$ °C is the lowest
172 temperature studied from which no sample extraction obstructions were found) with different additive
173 concentrations (0.025 M, 0.050 M and 0.125 M). It was observed that between t_0 and t_3 , DE increased with

174 a greater pitch as K_2CO_3 concentration increased, but this slope starts decreasing for higher K_2CO_3
175 concentrations than 0.050 M. After 3 hours of reaction (t_3) we observed the same behavior but less
176 sharply, revealing that DE started to brake its increase and even being able to stop it after 4 hours of
177 reaction with K_2CO_3 at 0.125 M.



178
179 *Figure 2. DE of PVC at 200°C for several additive concentrations and reaction times (concentration of 0.025 M, 0.050 M and*
180 *0.125 M, corresponding to a molar anionic content about 1:50, 1:25 and 1:10 of the total molar chlorine content, respectively).*

181 That optimum intermediate K_2CO_3 concentration at low temperatures can be clearly visualized in Figure
182 3a, after a HTD process of 4 hours. So, DE firstly increased and then decreased when K_2CO_3
183 concentration changed from 0.025 M to 0.125 M, presenting an apparent optimum around 0.050 M. The
184 fact that a maximum was observed at an intermediate concentration has been also reported in the literature
185 for Na_2CO_3 (Zhao et al., 2018) and NaOH (Li et al., 2017). These authors explained this behavior
186 considering that at high dosage, the alkaline additive might block the dechlorination process. Moreover,
187 linked to a longer residence time, this could promote the formation of pores and swelling in solid residue
188 which should facilitate the diffusion of released chlorine in the solid (Hashimoto et al., 2008) but could
189 also be responsible, at high DE, of the reduction of final DE because of a possible re-absorption of water-
190 soluble chlorine (Li et al., 2017). That was the case for the two experiments carried out at 250 °C, where
191 the highest DE was obtained (higher than 90% for both concentrations studied), as shown in Figure 3b.
192 For these experiments, the chlorine content of the liquid collected once the reactor was cooled down to
193 room temperature was lower than that of the liquid sampled at time 4 hours.

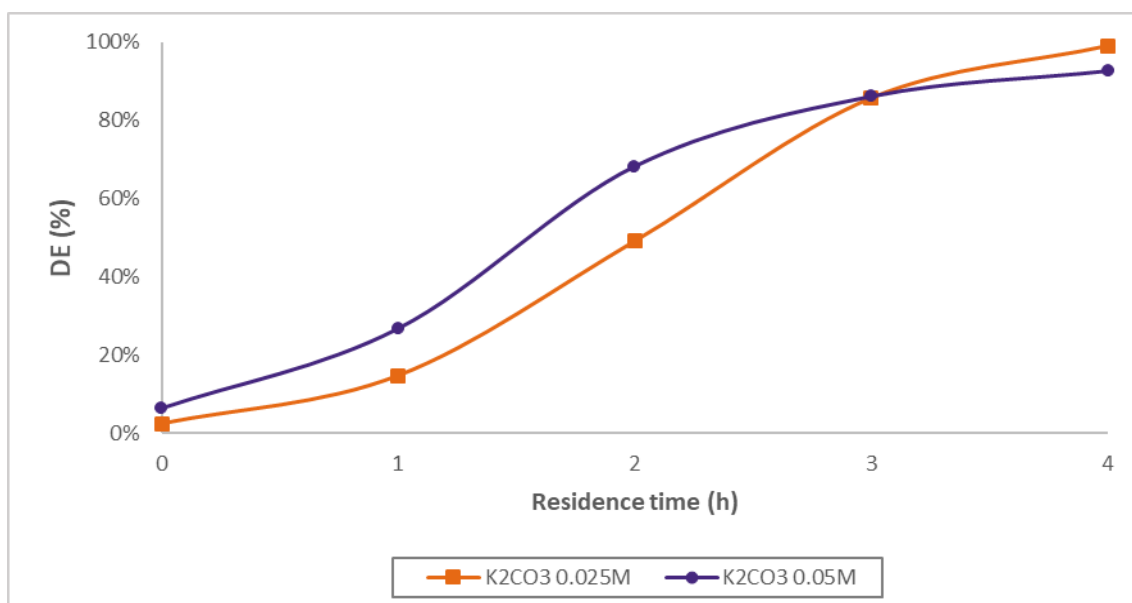


194

195 *Figure 3a. DE of PVC at 200°C after 4 hours of residence time for several additive concentrations (0.025M, 0.050M and 0.125M,*
 196 *corresponding to a molar anionic content about 1:50, 1:25 and 1:10 of the total molar chlorine content).*

197 *Figure 3b. DE of PVC at 250°C after 4 hours of residence time for several additive concentrations (0.025M, 0.050M*
 198 *corresponding to a molar anionic content about 1:50, 1:25 of the total molar chlorine content).*

199 Referring to the evolution and behavior of DE at the highest temperature studied (250 °C) and with
 200 additive concentrations of 0.025 M and 0.050 M, two different cases were found, too. For reaction times
 201 between 0 (t₀) and 3 hours (t₃), the behavior observed was the same as for low range temperatures,
 202 whereas 3 hours onwards (corresponding to a DE around 86%), the DE obtained with 0.025 M was higher
 203 than that with 0.050 M, as shown in Figure 4. In fact, the DE reached after 4 hours with K₂CO₃ 0.025 M
 204 was 99.1%, while it was only 92.6% with K₂CO₃ 0.050 M.

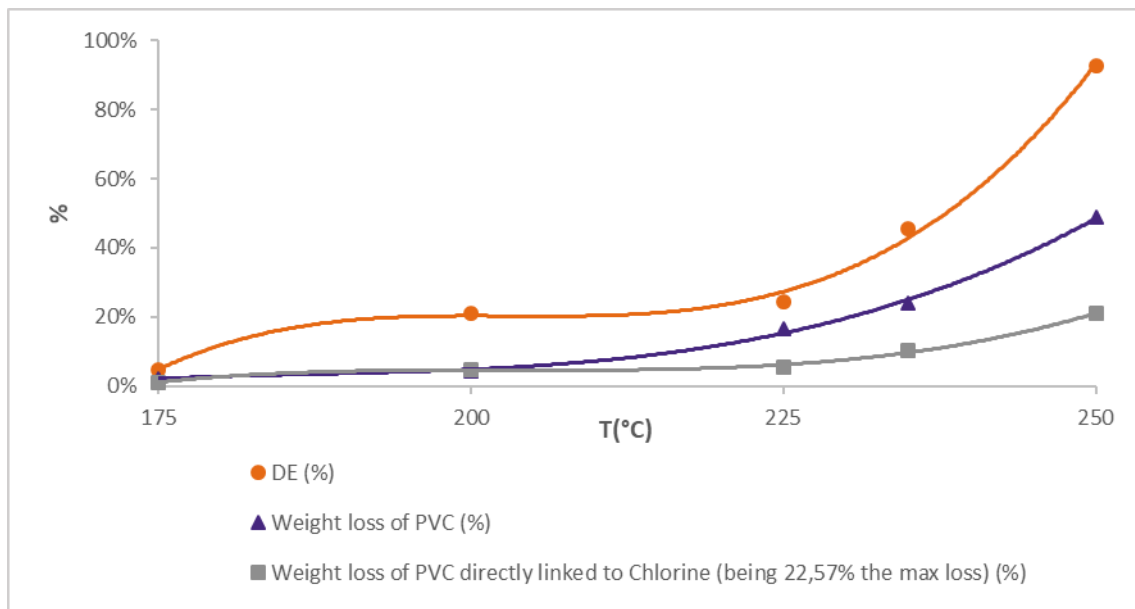


205

206 *Figure 4. DE of PVC at 250°C, for several reaction times and 0.025 M and 0.050 M concentrations (corresponding to a molar*
 207 *anionic content about 1:50 and 1:25 of the total molar chlorine content, respectively).*

208 After HTD, the initial chlorine content of PVC (22.57 wt. %) is mainly converted into HCl gas (Takeshita
 209 et al., 2004) and then this compound dissolves in the liquid as chlorine ions (Yu et al., 2016), thus deriving

210 in a weight loss of the solid directly related to the chlorine content. In addition, the solid recovery ratio
211 decreases further more due to PVC thermal degradation which is inappreciable at 200 °C but starts to be
212 appreciable at 225 °C, where a 10% of weight loss can be observed besides the 5.5% of weight loss
213 directly linked to chlorine. As shown in Figure 5, after 4 h of residence time at 250 °C with a 0.050 M
214 K_2CO_3 concentration, a total weight loss of 48.8% was obtained of which almost half (20.9% of the total
215 PVC weight loss), was directly linked to the chlorine removal achieved (corresponding to a DE of 92.6%).
216 Thus, by decreasing the temperature needed for a relatively complete dechlorination, the amount of PVC
217 lost by thermal degradation could be reduced, and therefore this would avoid the generation of toxic
218 chlorinated organic compounds and producing an aqueous liquid residue more easily treatable.



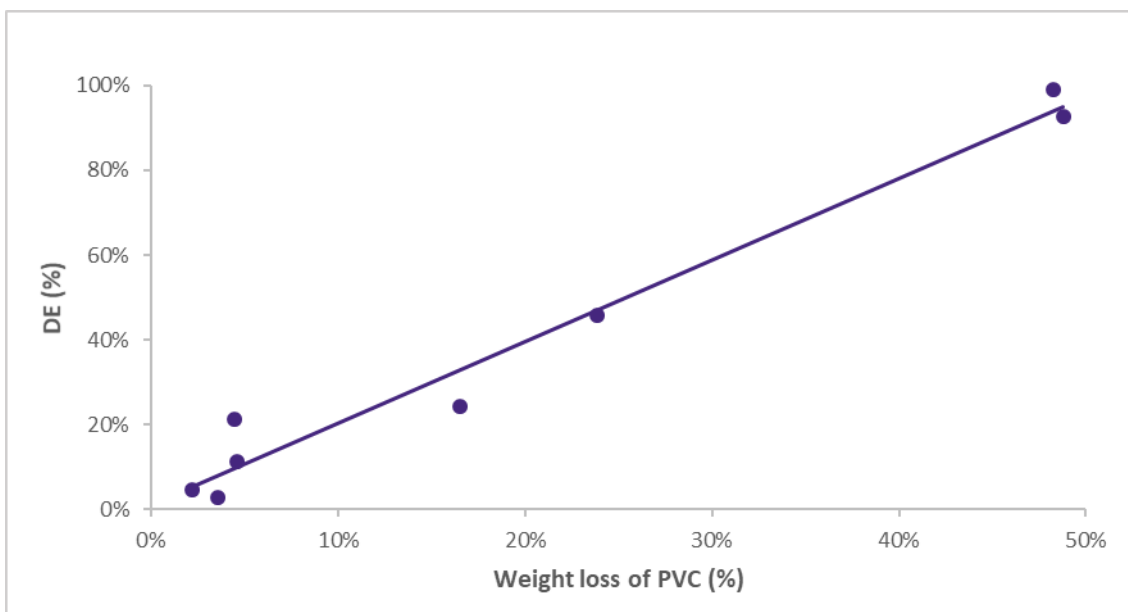
219
220 *Figure 5. DE, weight loss directly linked to chlorine and total weight loss of PVC with K_2CO_3 0.050 M after 4 h of residence time*
221 *for several temperatures*

222 Concerning the solid phase behavior during dechlorination, a linear correlation between the DE reached
223 and the weight loss of PVC (once the solid residue was dried) was found after including every experiment
224 performed in this work (with every temperature and K_2CO_3 concentration employed). Specifically, the
225 results from Figure 6 show that the experimental data fitted quite well to a straight line, with a correlation
226 coefficient of 0.9744.

227 The plotted values represent the experimental data obtained from every solid residual after 4 hours of
228 residence time and the blue solid line designates the calculated values disposed empirically through the
229 following formula:

$$DE = 1.9223 \cdot (1 - w_{PVC,f}) + 0.0115$$

230
231 where DE is the dechlorination efficiency reached at time 4 hours (in %) and $w_{PVC,f}$ corresponds to the
232 remaining weight of PVC (in %) after being properly dried. In this way, this could avoid the need for
233 analysis by ion chromatography when no accuracy is required.



234
235 *Figure 6. DE as a linear function of PVC weight loss after 4 h of residence time at several temperatures and K_2CO_3*
236 *concentrations.*

237 3.2. Features of the HTD solid residue

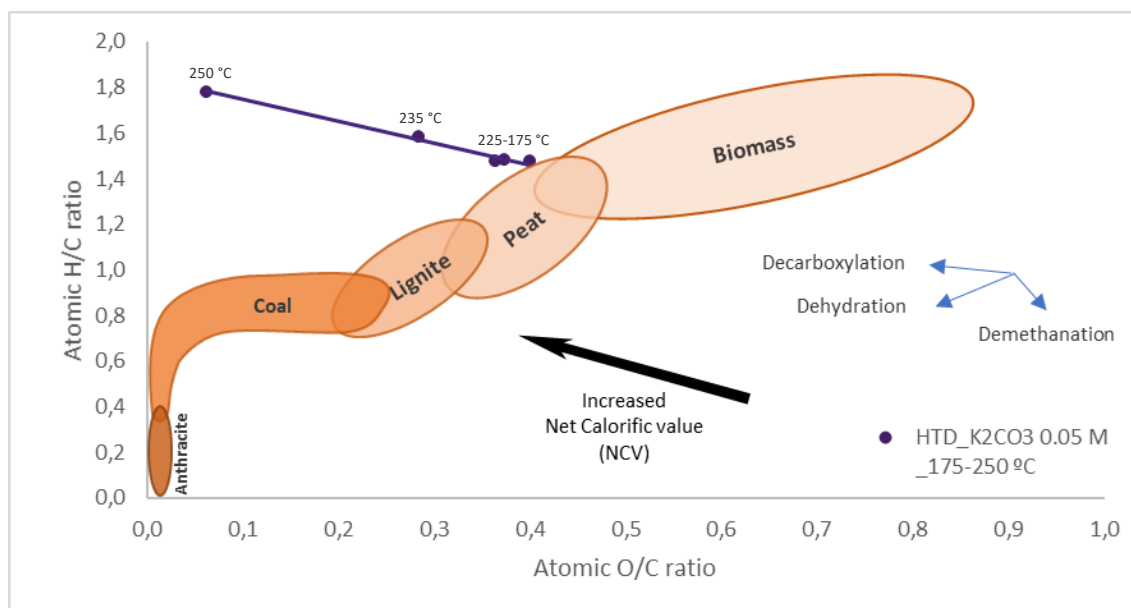
238 Table 1 shows the elemental composition of the solid residues obtained after the dechlorination process
239 using 0.050 M K_2CO_3 solution. It can be observed that the hydrogen content in the solid residue increased
240 as the dechlorination temperature rose, while the oxygen content decreased with this increase of
241 temperature and, consequently, the carbon content increased from 39.15 % to 69.95 % for the residues.
242 Sulfur and nitrogen content were significantly low for all the samples analyzed, as they were under the
243 detection limit of the elemental microanalyzer used in all cases.

Table 1. Elemental composition and heat value of solid residues using 0.050 M K₂CO₃ solution.

ID [RT (M)]	sample (°C)-C _{solution}	C (wt. %)	H (wt. %)	S (wt. %)	N (wt. %)	O (wt. %)	Ash (wt. %)	H/C	O/C	NCV (MJ/kg)
R175_0.05		39.15	4.82	n.d.	n.d.	20.87	35.17	1.48	0.40	21.61
R200_0.05		40.89	5.05	n.d.	n.d.	20.36	33.71	1.48	0.37	21.71
R225_0.05		45.34	5.58	n.d.	n.d.	22.00	27.08	1.48	0.36	24.02
R235_0.05		49.71	6.56	n.d.	n.d.	18.78	24.95	1.58	0.28	26.27
R250_0.05		69.95	10.38	n.d.	n.d.	5.72	13.95	1.78	0.06	34.51

245 As mentioned earlier in this study, although the chlorine content in the solid residue decreased with the
 246 increase of the operating temperature, the hydrogen content did not decrease accordingly due to hydrolysis
 247 reaction. In this case, the hydrolysis reaction of PVC includes the cracking of C-C chain and the
 248 replacement of chlorine by the base (Lu et al., 2002). The use of alkaline solvents could support these side
 249 reactions.

250 From the elemental composition data, H/C and O/C atomic ratios were calculated. The results were plotted
 251 in a Van Krevelen diagram to illustrate the effect of the hydrothermal carbonization process over solid
 252 residues (Figure 7). Both H/C and O/C ratios linearly moved from lower right to upper left when HTD
 253 conditions became harder (increase of temperature), which indicates that dehydration and decarboxylation
 254 reactions could occur during HTD process. In this case, the evolution of the experiments with K₂CO₃
 255 0.050 M observed for an increasing temperature treatment, seemed to follow the path of a decarboxylation
 256 process (Funke and Ziegler, 2010), which could explain why the atomic O/C ratio decreases instead of
 257 increasing when hydrolysis reactions take place.



258

259 *Figure 7. Van Krevelen diagram representing solid residues obtained after HTD treatment using 0.050 M K₂CO₃ solution and*
 260 *comparison with other fuels.*

261 The net calorific value (NCV) of the solid residues obtained after dechlorination treatment increased with
 262 the increase of process temperature (represented as a bolded dark arrow on Figure 7). The minimum value
 263 of 21.61 MJ/kg was obtained for the solid residue collected after the dechlorination at 175 °C, and the
 264 maximum value of 34.51 MJ/kg for solid residue collected at 250 °C. Soler et al. (2018) concluded that the
 265 temperature of the dechlorination process using subcritical water also increased the net calorific value of
 266 the solid residues collected, obtaining similar net calorific values for the residues than those of the present
 267 work (17.3 MJ/kg at 200°C and 37.8 MJ/kg at 300 °C, respectively). Thus, these solid residues can be used
 268 as high-quality fuel for blast-furnace or a feedstock for producing activated carbon, etc. (Takeshita et al.,
 269 2004) because their net calorific value is comparable to those of mineral and vegetal coal (21.3-35.5
 270 MJ/kg and 29.0-35.0 MJ/kg respectively).

271 4. CONCLUSIONS

272 In order to investigate the role of potassium carbonate as chemical additive in the HTD process of PVC,
 273 several conditions were carried out juggling between the main HTD controlling factors: temperature,
 274 residence time and K₂CO₃ concentration.

275 In general, the dechlorination efficiency increased with the increase of both HTD temperature and
 276 residence time, as expected. However, that was not the case for K₂CO₃ concentration.

277 At low temperatures around 200 °C, an optimum dechlorination efficiency (21.1%) was found with an
278 additive molar anionic content about 1:25 of the total molar chlorine content. That optimal
279 additive/chlorine ratio decreased at higher temperatures near 250 °C and above, when reaching a high DE
280 value (upon 90%), contributing to reduce by half and maybe more the amount of additive needed for a
281 complete dechlorination (1:50 additive/chlorine ratio).

282 The low price and abundance of K₂CO₃, plus the generation of an aqueous liquid residue easily treatable
283 and a solid residue with high quality fuel features, makes this compound a promising additive to be used
284 for PVC dechlorination in HTD treatments.

285 In this way, it can be concluded that the HTD treatment with K₂CO₃ can be considered as an
286 environmentally friendly pretreatment for PVC waste before its potential use as a fuel, able to reach a
287 degree of dechlorination of 99.1% after 4 hours at 250 °C with a solid/liquid ratio of only 1:5 (close to the
288 limiting ratio of 1:4, so avoiding as far as possible the use of water in excess) and an additive/chlorine
289 ratio of 1:50 (minimizing the amount of additive and operating costs required), thus avoiding the
290 employment of metallic catalysts.

291 In order to improve its viability and to reduce the time needed for a complete dechlorination in optimal
292 conditions using the lowest reaction temperature as was previously mentioned, larger solid/liquid ratios
293 should be analyzed further on.

294 **ACKNOWLEDGEMENTS**

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