Article

Debromination and Reusable Glass Fiber Recovery from Large Waste Circuit Board Pieces in Subcritical Water Treatment

Gerard Gandon-Ros, Ignacio Aracil, María Francisca Gomez-Rico, and Juan A. Conesa*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The great economic, social, and environmental interest that favors an effective management of the recycling of waste printed circuit boards (WCBs) encourages research on the improvement of processes capable of mitigating their harmful effects. In this work, the debromination of large WCBs was first performed through a hydrothermal process employing potassium carbonate as an additive. A total of 32 runs were carried out at 225 °C, various CO_3^{2-}/Br^- anionic ratios of 1:1, 2:1, 4:1, and 6:1, treatment times from 30 to 360 min, proportion of submerged WCBs in the liquid of 100, 50, and 25% that corresponded with the use of three WCB sizes of 20 mm × 16.5 mm, 20 mm × 33 mm, and 80 mm × 33 mm, respectively, and solid/liquid ratios of 1:2 and 1:1 g/mL without other metallic catalysts. A debromination efficiency of 50 wt % was reached at only 225 °C (limited by mechanical reasons) and 360 min, using a CO_3^{2-}/Br^- anionic ratio of 4:1 and a solid/liquid ratio of 1:2 for a large WCB with only 25% of its volume submerged in the liquid. This means conservation of water and energy compared to previous studies. A muffle furnace was used later to thermally treat a total of 101 debrominated samples, at constant temperature or following a temperature scaling program. An estimated decrease in resistance to rupture of glass fibers of only around 50% was accomplished by following a temperature scaling program up to 475 °C, obtaining clean glass fibers of large size. The simple techniques proposed to obtain reusable glass fibers from WCBs as large as the size of the reactor allows (as it might be in their original size) could significantly improve interest in the industry.
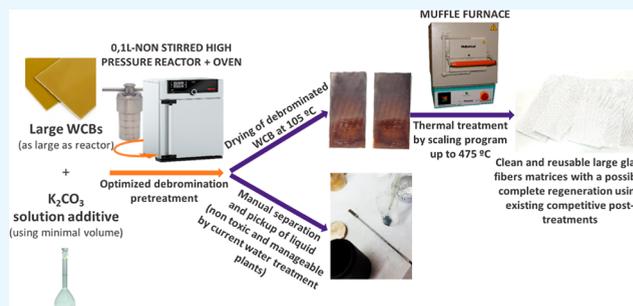
1. INTRODUCTION

Large amounts of waste electric and electronic equipment (WEEE) are generated every year. With 53.6 million metric tons (Mt) generated globally in 2019 and only a 17.4% officially documented as properly recycled,[1] our electronic-dependent civilization is producing a vast and growing amount of electronic waste, which is being reputed as the world's fastest growing domestic waste stream of the moment. This waste contains dangerous substances, and the WEEE Directive of Europe promotes their reuse, recycling, and other forms of recovery.[2] In particular, waste printed circuit boards (WCBs), mainly coming from mobile phones, computers, and televisions, represent around 8% of all electronic waste and are causing a lot of concern these days.[3] They contain metals such as copper, lead, iron or precious metals, organic compounds such as thermosetting resins or brominated flame retardants (BFRs), and glass fibers.[4,5] The resin acts as an insulator and the glass fibers act as reinforcement, forming both of them a substrate used to mechanically support the electronic components. The resin used in the WCBs is made of plastic material acting as an insulator containing BFRs. The analysis of this resin results in about 71 kt from the not documented flows of e-waste generated in 2019 that account for 82.6%.[1]

WCB recycling is scarce and consists of separating the metallic and non-metallic fractions by using mechanical or chemical techniques and recycling of both parts separately. Usually, the metal powders are purified and re-smelted. However, the re-using technique for the non-metallic part has not been well-developed. The resin powders have been used as fillers for construction materials, epoxy resin products, or decorating agents among others, but the profit obtained is not economically attractive.[6] Over 90% WCBs in Europe are land-filled or incinerated.[7] Pollution caused by the presence of BFRs such as tetrabromobisphenol A (TBBPA) in the non-metallic fraction is particularly remarkable. BFRs represent between 5 and 15% of the total weight of WCBs.[8] During thermal treatments such as incineration, highly toxic compounds such as polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) can be emitted from

BFRs,[9−11] even under controlled conditions to obtain fuels or recover valuable materials.[12]

Thermal treatments normally used to process the non-metallic fraction of WCBs could also be used to recover the fiber part (its most valuable component that makes up approximately 50% by weight),[13] if this was profitable. Therefore, great efforts should be made to previously remove bromine present in BFRs, thus avoiding the formation of toxic brominated compounds during treatment. In this sense, debromination of WCBs under hydrothermal treatment using subcritical or supercritical fluids is a promising technique that has gained more and more relevance during the last years over other processes because of the excellent debromination efficiencies obtained.[14] In fact, in the last decade, supercritical water has been introduced as an environmentally friendly method to recycle organic polymers due to its extraordinary properties, such as high mass transport, high diffusivity, penetrability, and solubility.[15] In addition, using water at temperature around 200 °C and under pressure as subcritical fluid produces a solvent more similar to less-polar organic solvents such as methanol or ethanol[16] but with the benefit of using an environmentally friendly solvent. Thanks to the changes in the viscosity and density of the water with temperature and pressure, the molecules in the water are able to participate in chemical reactions with the organic compounds present in polymer matrices such as BFRs or lignin (biopolymer of biomass).[17] Wang and Zhang[18] obtained a maximum debromination efficiency of 97.6% with water at 400 °C in 60 min after comparing various supercritical fluids (water, methanol, isopropanol, and acetone) to treat BFRs and BFR-containing waste computer housing plastic. Soler et al.[14] obtained an efficiency of 63.6% with subcritical water at 275 °C for 3 h when treating WCBs and also observed a decrease in the emissions of brominated compounds during subsequent thermal treatment. Gandon-Ros et al.[19] improved these results by adding potassium carbonate to subcritical water, favoring the reaction conditions using a CO_3^{2-}/Br^- ratio of 1:1 and a S/L ratio of 1:2 g/mL, to achieve a quasi-complete debromination (99.6%) of small particles of WCBs (0.84 mm × 0.84 mm) at only 225 °C for 2 h. No papers related to debromination of large pieces of WCBs without total submersion in liquid have been found, and the studies used them only in the powder form.

Recovering the fiber fraction from the non-metallic part of WCBs would decrease the damage to the environment and meet the EU legislation for the disposal of WEEE,[2] thereby saving natural resources. For example, the replacement of pristine glass fiber products with recycled ones from thermoset-based composites would equate to a global reduction in CO_2 emissions of 400,000 tons per year from reduced melting energy requirements alone.[20] Furthermore, such a development would also reduce the need for an annual landfill disposal of 2 million tons of composites.[20] The separation of the fiber fraction from the matrix in these materials is always challenging since thermosetting matrixes such as resins present in WCBs cannot be melted and reformed. Nevertheless, processes such as chemical or thermal degradation are available for recycling such composites.[21,22] A major disadvantage of chemical degradation is the need of washing to remove residual chemicals and solvents from the surface and therefore the production of a large amount of waste, thus making this less environmentally friendly.[23] Thermal recycling normally involves a treatment in the absence of air (pyrolysis) at 400−500 °C. The recovered fibers covered with char require further subsequent combustion to remove any solid residue left.[23] Combustion could be used

directly, where the polymer is broken down and combusts, releasing the fibers and any filler.[24]

However, heating tends to cause a significant degree of strength loss in glass fibers (80−90%) that should be restored with additional treatments.[25,26] When recycling glass fibers, this effect occurs at significantly lower temperatures than those used for the manufacturing of this material (1150−1250 °C). Thomason et al.[20] studied different recycling temperatures up to 600 °C and found up to 70% strength loss in glass fibers after thermal conditioning, noting losses above 250 °C.

The objectives of this work were to remove bromine from WCBs presented in large pieces with a solution of potassium carbonate in subcritical water and to recover the glass fiber fraction by subsequent combustion with the lowest loss of properties. Different conditions for bromine removal and combustion were compared. The ultimate goal was to find the most suitable conditions for future industrialization of the process, prioritizing simplicity, water and energy savings, and the lowest loss of fiber properties so that this material could be re-used later without much additional cost. This treatment makes it easier for recycled fibers to compete with new glass fibers. In addition, when performing the treatment using large WCBs or even using them in their original size, an intact glass fibers matrix is obtained avoiding later the spread of powdered glass fibers, classified as possible carcinogenic in humans by the International Agency for Research on Cancer (IARC).

2. MATERIALS AND METHODS

2.1. Materials. Metal-free WCBs were used to ensure the absence of metallic catalysts, beneficial for dehalogenation purposes but whose presence is not environmentally friendly.[27] These were composed of high-quality standard FR-4 epoxy fiberglass substrates, were supplied by CISA (Circuitos Impresos S.A., Spain), and had a thickness of 1 mm in which five overlapping laminates of cross-linked glass fibers were bonded with the resin. Previous studies[14] already used this material and confirmed by Raman spectroscopy that these FR-4 WCBs contained TBBPA as BFR. WCBs were cut into 20 mm × 16.5 mm, 20 mm × 33 mm, and 80 mm × 33 mm pieces using pliers. The largest size was selected in order to debrominate the biggest pieces of WCBs that fit into the 0.1-L reactor employed. A Thermo Finnigan Flash 1112 Series elemental analyzer revealed an elemental composition of 27.5 wt % C, 2.5 wt % H, 1.1 wt % N, and 24.6 wt % O. In accordance with the UNE-EN-14775:2009 standard,[28] an ash content of 44.3 wt.% was obtained at 550 °C. US EPA methods 5050[29] and 9056A[30] by oxygen combustion bomb-ion chromatography (under a Dionex DX-500) were employed to measure an averaged bromine content of 4.0 wt %.

K_2CO_3 with a minimum purity of 99% (Merck, Darmstadt, Germany) was employed in this work.

2.2. Subcritical Water Debromination and Clean Glass Fiber Recovery Setup. All debromination runs were performed at 225 °C in a high-pressure non-stirred batch reactor of 0.1 L, using several dilute solutions of K_2CO_3 in water as subcritical fluid. This reactor, built with a 304 stainless-steel shell and PTFE chamber, was supplied by Baoshishan (China). This low-cost reactor is able to resist a limit temperature of 225 °C under acid and alkali atmospheres for a maximum pressure of 3 MPa. An oven model UF30 supplied by Memmert (Germany) was used to manage the temperature inside the reactor at a heating rate of 3.5 °C min^{-1} approximately until the established temperature.

The parameters studied to measure the efficiency of the debromination were the operating temperature (constant in this work), K_2CO_3 concentration of dilute solution, residence time, solid/liquid (S/L) ratios, sample size, and submerged proportion of WCBs. After the debromination process, the solid residues were treated by controlled thermal combustion in an electric muffle furnace (Hobersal 12 PR/300 series, Spain) in order to remove the resin and obtain clean fibers. The process was studied by varying temperature, residence time at set temperature, and heating rates, in order to control the efficiency of the resin removal process and to minimize the loss of mechanical properties. In this way, the study maximizes the future usability of WCBs, a waste causing great concern, to give it a second life.

2.3. Runs and Conditions. *2.3.1. Debromination Process in Subcritical Water.* In the present work, a total of 32 debromination runs were performed at 225 °C (the limit safe temperature of the reactor) during 30 to 360 min, with CO_3^{2-}/Br^- ratios of 1:1, 2:1, 4:1, and 6:1 and three different WCB sizes and S/L ratios of 1:2 and 1:1 g/mL, as shown in Table S1 of the Supporting Information However, for large WCB pieces, stronger conditions are required and were therefore investigated, testing, for example, values for the S/L ratio higher than 1:2. Minimizing the amount of liquid required for a complete debromination achievement is essential because less amount of energy will be needed to reach a certain temperature and more WCBs will be debrominated by a run. Each sample size had a proportion of submerged WCBs in the liquid of 100, 50%, or 25%, as indicated in Table S1. Replicate runs were carried out in order to check reproducibility, obtaining a relative experimental error below 2%, very similar to what was already previously measured for this equipment[19] when working under analogous conditions.

The remaining liquid from the reaction chamber after hydrothermal debromination (HTD) treatment was collected and manually separated from solid residue once the reactor cooled down to room temperature and then analyzed for bromine content by ion chromatography. The instrument used was an ion chromatograph Metrohm 850, ProfIC AnCat-MCS, with chemical suppression and conductometric detection.

The debromination efficiency (DE) was defined as the fraction of bromine content transferred from the solid to the liquid phase and was calculated as follows

$$DE(\%) = \frac{m_{Br,\ liq}}{m_{Br,i}} \cdot 100 \tag{1}$$

where $m_{Br,i}$ is the initial weight of bromine content in the WCB inside the reactor (in mg) and $m_{Br,liq}$ is the weight of bromine (mg) in the residual liquid. In fact, more than 99% bromine is emitted in the form of HBr according to previous studies.[14,31,32] In parallel, water has high solubility for HBr and dissolves it in the aqueous phase as bromide ions, as occurred with HCl.[33,34]

A proposal of the reactions and mechanisms involved in this process will be detailed in future research. Basically, organic bromine present in WCBs reacted with potassium that subcritical water contained, following two consecutive steps:

1 First, mass transfer of bromine occurred from the surface of the WCB particles to the subcritical water, where it gets solved.

2 Second, the reaction between bromine and potassium occurred to form KBr.

Although bromine was turned from its organic form inside the WCBs to an inorganic non-toxic form (KBr), the liquid waste left by this process could contain some toxic brominated compounds. The analysis of volatile and semivolatile organic brominated compounds should be part of a detailed study conducted aside. In previous similar research,[15,35] when a quasi-complete debromination by subcritical water oxidation was achieved from printed circuit boards, all of the released Br was transferred into water as HBr, which avoided the formation of toxic brominated organic compounds. Nevertheless, the partial removal of precursors of halogen derivatives and the removal of compounds causing water color and turbidity, including carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), is already achieved during the coagulation step in water treatment plants.[36,37] A recent study[38] shows that in the coagulation process of water treatment plants (with the purpose of obtaining drinking water), the effectiveness achieved in the elimination of PAHs can reach around 95% when using simple activated carbon. Moreover, prevention of the formation of halogen organic bonds is possible too by using current advanced oxidation (chemical, photochemical, and catalytic) processes.[39]

The solid residues obtained in this work were separated manually using tweezers and dried at 105 °C. In this way, the solid residues composed of glass fibers dipped in debrominated resin were ready for their subsequent heat treatment for reusable fiber release.

2.3.2. Experimental Optimization of the Thermal Degradation Process to Recover Clean Glass Fibers. For this part of the study, a total of 13 sets of runs, each one with three to eight samples (i.e., a total of 101 samples), were performed under different conditions in order to find the best combination of temperature and residence time to obtain clean glass fibers by thermal treatment. In addition, the runs permitted to assess which parameters of the entire process (resin debromination + resin removal) had a significant influence on the efficiency of the thermal process used to remove the debrominated resin.

The parameters studied with a possible significant impact on the removal efficiency of resin were as follows: temperature (constant vs scaling program), time, size of WCBs pieces, previous HTD residence time, CO_3^{2-}/Br^- ratio, S/L ratios, and percentage of submersion of WCBs during previous debromination treatment, as shown in Tables S2 and S3.

The temperature range for this study (350−550 °C) was chosen attending in parallel to two facts. First, this temperature should be high enough to obtain a complete resin removal. Second, this temperature needed to be as low as possible in order to avoid large losses in the mechanical properties of glass fibers for their potential future reuse.

In fact, the glass fibers obtained from thermal recycling of plastic wastes lose generally their mechanical properties and are of no value because the typical temperatures (400−550 °C) used to incinerate these wastes result in a strength loss of 80−95%.[24] Moreover, the time spent at this temperature also influences the deterioration of the mechanical properties of the glass fibers. The effect of temperature and time on recycled glass fibers was already modelized by Feith et al.,[40] concluding that their results for glass fiber bundles (where the percentage of strength loss was more pronounced than for a single fiber) were fully applicable to thermal recycling of fiberglass laminates composites, as WCBs are. This model avoids the need to perform strength tests, whose results are highly difficult to obtain in cases like this. On one hand, the initial properties of the fibers
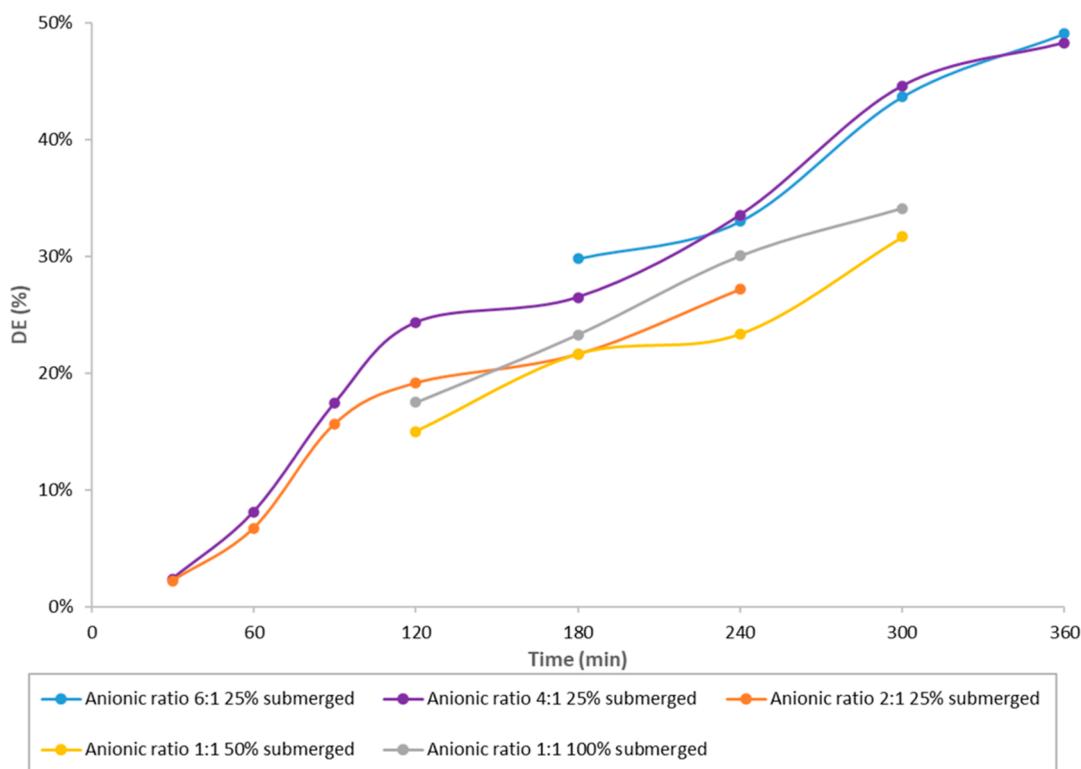
Figure 1. DE obtained at 225 °C with solid/liquid ratio 1:2 for several CO_3^{2-}/Br^- ratios and submerged WCB proportions (corresponding to the three different WCB sizes studied).

before treatment, necessary to calculate the strength loss, are unknown unless manufacturers give these data. Fibers are embedded in the resin, and strength tests are not possible. On the other hand, the damage suffered by glass fibers during previous conditioning for the experiments could reduce their strength, and results could be questioned.

In the present work, the evolution of glass fiber strength (inside WCBs) over time at different temperatures was calculated using Feith et al.'s model,[40] shown in Figure S1 of the Supporting Information, in order to have a first estimation of the possible reuse of the fibers obtained. Detailed parameters for the model used are shown in Table S2.

A complete qualitative macromorphological study was carried out for every set of runs in order to estimate the degree of resin removal obtained from the debrominated resin. For this purpose, a photographic analysis with standardized basis was performed using a Canon 800d + Canon EF-S 24 mm f/2.8 STM system. In addition, a Thermo Finnigan Flash 1112 Series elemental analyzer was employed to evaluate the carbon content of the solid residues coming from the most remarkable set of runs (the last ones). This allowed to support the evolution of residual resin observed from the qualitative macromorphological study.

3. RESULTS AND DISCUSSION

3.1. Debromination of WCBs and Optimal HTD Parameters when Using K_2CO_3.
The effect of the solid/liquid ratio on the DE of the runs performed using potassium carbonate when feeding the HTD process with the largest WCB pieces was studied (Figure S2 shows the details). According to this figure, DE was lower using a solid/liquid ratio of 1:1, regardless of time and anionic ratios employed. This fact actively suggests that the optimal solid/liquid ratio is still near 1:2,

corroborating what was previously established by Gandon-Ros et al.[19] using small particles instead of large pieces.

In addition, DE increased when going from 180 to 240 min of treatment time and when the anionic ratio was increased from 2:1 to 4:1 (Figure S2).

On the other hand, Figure 1 shows the evolution of DE over time including all the debromination runs carried out at 225 °C and for the solid/liquid ratio of 1:2, taking the average value when duplicates were available. As can be observed, degradation of large pieces of WCBs occurred in two stages: First, DE increased over time following an elongated "S"-shaped curve as was already shown in previous studies using K_2CO_3, where small particles completely submerged in liquid during the whole hydrothermal treatment were dechlorinated[27] and debrominated.[19] This part of the process takes place once the minimum temperature for the thermal degradation of the material is reached around 250 °C for PVC[35,41,42] and for WCBs.[19] In the present study, much larger sample sizes were employed compared to those of Gandon-Ros et al.,[19] and the DE achieved was lower due to more difficult reaction conditions. In the second stage, the evolution continued over time with another elongated "S"-shaped curve. For the runs using smaller size, performed with total submersion of the pieces in the liquid, this behavior was not observed.

Corresponding to the second elongated "S"-shaped curve, after enough time (120 min at an anionic ratio 2:1 or 180 min at an anionic ratio 1:1), the pressurized steam formed during the HTD process began to debrominate the non-submerged part of WCBs. This curve was more stretched over time with a smoother increase (maybe the reaction through gaseous contact could somehow be slower than that with liquid contact).

Figure 1 also shows the evolution of DE with CO_3^{2-}/Br^- anionic ratios. DE increased when CO_3^{2-}/Br^- ratios increased.
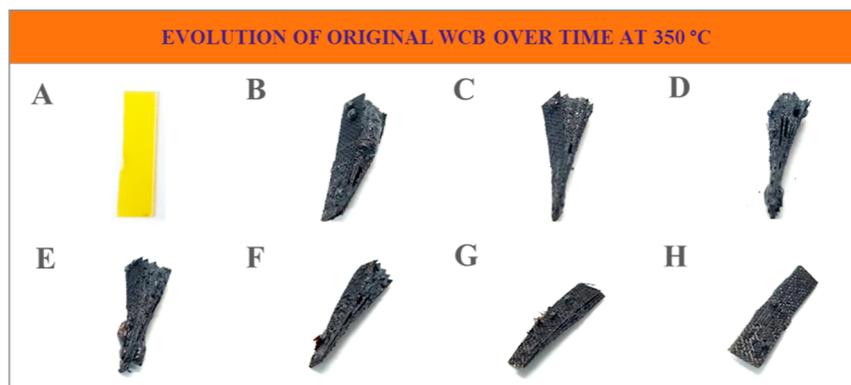
Figure 2. Thermal degradation over time at 350 °C of original WCBs (A, B, C, D, E, F, G, and H for 0, 60, 120, 180, 270, 360, 390, and 420 min, respectively).

The appreciable asymptotes not reached suggests that an increase in temperature would improve the results. It was observed that when the anionic ratio increased, the reaction started earlier in time and increased more promptly until reaching a certain DE.

Considering the runs performed at a CO_3^{2-}/Br^- ratio of 4:1 (all performed with 25% submerged), the maximum accomplishable DE was around 50%, and the increase in the amount of additive (to an anionic ratio of 6:1) did not introduce any improvement at the end. Therefore, the optimum parameters are a solid/liquid ratio of 1:2 and a CO_3^{2-}/Br^- ratio of 4:1, where the temperature of treatment should be slightly increased to achieve a complete debromination.[19] In Table S3, a comparison table with our previous results on the debromination of smaller WCB particles[19] is presented, where runs of both investigations with identical experimental conditions (except the size of WCB) were compared to study to what extent the global potential of the process was being exploited. For these comparisons, experiments using the previously optimized parameters (225 °C, CO_3^{2-}/Br^- of 1:1, and a solid/liquid ratio of 1:2) from Gandon-Ros et al.[19] were taken for a WCB size of 20 × 33 × 1 mm of the present work with the same conditions being applied. Likewise, experiments from the previous work where the new provisional (because no complete debromination was achieved for the moment due to the mechanical limitations of the reactor) optimized parameters for large WCBs of this work were applied (225 °C, CO_3^{2-}/Br^- of 4:1, and a solid/liquid ratio of 1:2) were taken for the size 80 × 33 × 1 mm of the present work with the same conditions being applied. The value of the total surface of contact was calculated as the sum of the surface area of all the particles of WCBs that make up each reactant sample, assuming that these particles follow a quadrangular prismatic structure. The total surface of contact ratio was calculated as the ratio between the total surface of contact of powder particles from our previous research (0.84 × 0.84 × 0.84 mm) and the total surface of contact of large WCB sizes (20 × 33 × 1 mm and 80 × 33 × 1 mm) used in this current research. The total surface of contact of the WCBs in this work is between 3.3 and 3.4 times lower than that of the powdered WCBs. This provokes the reaction to be much more difficult in the present situation.

Also, in comparison with our previous results with smaller particles, the impact in bebromination efficiency due to sample size (IDESS) was calculated as the ratio between the debromination efficiencies obtained for powder and large WCB sizes under identical HTD treatment conditions. In this work, IDESS was 6.2 for 20 × 33 × 1 mm pieces when previously optimized parameters for powder WCB size were used and 4.1 for 80 × 33 × 1 mm pieces when new provisional optimized parameters for large WCB size were used. IDESS decreased when larger WCB size pieces were used because although larger sizes (with lower total surface of contact) hindered the reaction, the reaction conditions were improved in such a way that compensated the size effect, going from using previously optimized parameters to using new provisional optimized parameters. According to these comparative results, it can be seen that the evolution of IDESS due to WCB size was not linear.

Finally, the process improving factor was introduced in order to visualize and estimate to what extent the overall potential of the debromination process was affected by increasing the sample size of WCBs. The process improving factor was calculated as the ratio between the total surface of contact ratio and IDESS. In this work, the process improving factor was 0.5 (the total surface of contact ratio was 3.3 and IDESS was 6.2) when previously optimized parameters were used, meaning that the overall potential of the process was halved in this case. In the same way, the process improving factor reached 0.8 (the total surface of contact ratio was 3.4, but at this time, IDESS was only 4.1) when new provisional optimized parameters were used, meaning that the overall potential of the process was only decreased by 20% in the end. Therefore, the overall potential of the process was reduced by only 20% even after having more than tripled the total surface of contact and increased by almost 4500 times the volumetric particle size.

3.2. Cleaning of Glass Fibers and Experimental Optimization of Combustion Treatment. The set of runs carried out for this part of the study after the debromination step was evaluated in two different groups. First, runs performed at constant temperature were performed, considering their evolution over time. Second, runs carried out using an increasing temperature program were studied.

3.2.1. Evolution of Glass Fiber Cleaning Using a Constant Temperature Program. Thirty four runs under different experimental conditions were performed (Table S4 shows details of the runs). Figure 2 shows some pictures of the evolution of the WCB pieces with time at 350 °C. We can observe that this low temperature was not enough to clean up the glass fibers of an original WCB piece of 0.5 cm × 3.3 cm. However, the amount of resin decreased over time as it can be seen how the resin, between the glass fiber layers, gradually disappeared. Although special consideration was given to keep the lighting conditions constant for the entire photographic
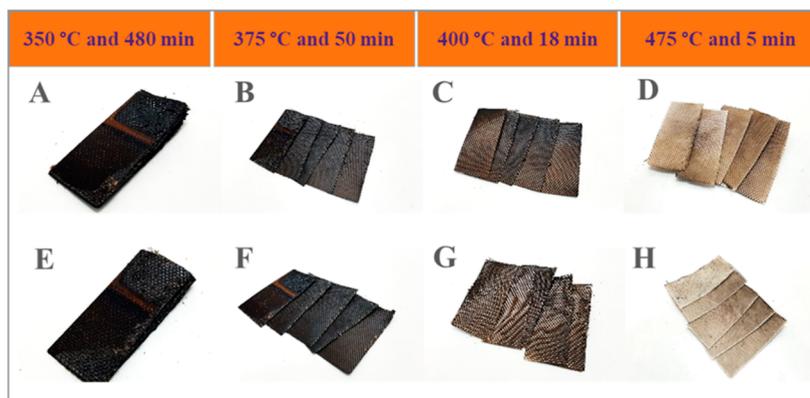
Figure 3. Thermal degradation over time of resin within two solid residues R_18 (A,B,C, and D) and R_21 (E,F,G, and H) with similar low DE from the HTD process, using a scaling program temperature from 350 to 475 °C according to the conservative scenario.

reportage, as well as the brightness and contrasts in postprocessing to compare tones between experiments), for this particular case shown in Figure 2, since the solid residue was so dark, the brightness was enhanced in order to be able to observe its better textures.

Figure S3 of the Supporting Information shows how a slightly higher temperature of 400 °C applied to bigger WCB pieces of 1.65 cm × 4.0 cm could reduce 390 min to only 60 min. After only 120 min and 180 min, the different laminates started to separate from themselves and started to appear slightly clean, respectively.

Figure S4 shows how a low temperature of 350 °C was almost but not enough to clean up the glass fibers of smaller solid residues of 0.5 cm × 1.65 cm with similar low DE coming from a previous HTD treatment. It took around 420 min for the different laminates to start to separate from themselves, and glass fibers appeared not clean enough after 480 min. However, compared to the original WCB, where glass fibers were almost not visible yet (Figure 2), the improvement due to the previous debromination treatment was noticeable.

In Figures S5 and S6 of the Supporting Information, glass fiber laminates started to separate from themselves after 180 min at 375 °C and 120 min at 400 °C, respectively. Similarly, mostly clean fibers were obtained after 300 min at 375 °C and only 330 min at 400 °C, respectively.

Depending on the required level of cleaning of the fibers, an acceptable clean and small glass fiber laminate with an approximated strength retention of 38% could be obtained after 300 min at 400 °C (Figure S1). Nevertheless, we have not obtained completely clean glass fibers in the runs performed at constant temperature. An application of higher temperatures, apparently necessary to obtain complete clean glass fibers, would result in an approximated strength retention of only 26, 18, and 12% at 450 °C, 500, and 550 °C, respectively.

3.2.2. Evolution of Glass Fiber Cleaning Using an Increasing Temperature Program. Sixty seven runs were performed to optimize the temperature program (Table S5 shows the details). Note that in these runs, temperature programs are additive, in the sense that each run in a group has been subjected to the temperature program of the previous runs and one more step has been added. For example, the temperature program of the last run of the set 6 (sample R_21) was 480 min at 350 °C, followed by 50 min at 375 °C, 18 min at 400 °C, and 5 min at 475 °C. The oven used in these runs was capable of heating at a gradient of 40 °C/min when the difference between temperatures was large, but it was only of 3.2

°C/min when the step between temperatures was lower than or equal to 100 °C.

As can be observed in Figure S1, there is a time at a given temperature to reach a steady-state minimum strength from which the properties do not change. In this way, a specific strength for a glass fiber can be achieved by using a temperature program in which time and temperature combinations do not exceed a specified strength loss. The minimum heat treatment temperature of 350 °C was selected for this reason, where more than 50% of the specific resistance was retained over time as shown in Figure S1. This temperature was increased to 355 °C (exactly 50% of the specific resistance was retained over time) for the last four sets of runs performed in order to maximize the possible improvement of the scaling programs from the low temperatures. For higher temperatures of the scaling programs, the treatment times were always chosen at each said temperature so that its retained specific resistance did not drop below 50% (when achievable due to the muffle heating rate limitations).

A classification of runs was carried out attending to the final % of strength retention achieved after a complete temperature program application. Conservative, neutral, and optimistic scenarios were established as 20−40, 40−55, and >55%, respectively. Conservative is what usually could remain when a treatment is performed to remove the resin (in fact, the most common in the literature is 15−20%), neutral needs less effort and expense later to recover properties through existing regenerating chemical treatments, and optimistic would be even better. The limit of 20% was the worst result obtained for one of the experiments using the scaled temperature program when trying to obtain completely clean large-sized glass fiber laminates. A higher limit of 55% was obtained for small-sample size WCBs but not large pieces.

Figures 3, S7, S8, and 4 show the aspect of the materials treated according to a conservative scenario, with final percentages of strength retention in the order of 20−40%. Similar results were obtained after thermal treatment of samples with similar DE, regardless of the HTD conditions applied previously to solid residues of 4.0 cm × 1.65 cm. In this way, Figure 3 shows the same results for two samples with similar low DE but different HTD conditions being applied.

In the same way, Figure S7 shows that similar results were obtained too for solid residues from HTD with similar DE when residence times of HTD were varied. Therefore, comparing results from solids with similar DE but different HTC conditions should be like comparing replicates. Nevertheless, Figure S8 of

Figure 4. Thermal degradation over time of resin within a unique solid residue from the HTD process, using a scaling program with the highest temperature going from 355 to 550 °C according to the conservative scenario (A,B,C,D,E,F,G, and H for original solid residue R_30, 480 min at 355 °C, 60 min at 375 °C, 30 min at 400 °C, 20 min at 425 °C, 12 min at 450 °C, 1 min at 500 °C, and 1 min at 550 °C, respectively).
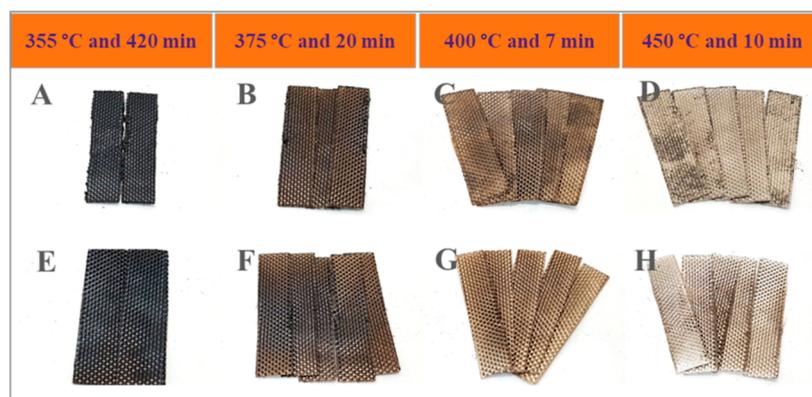
Figure 5. Thermal degradation over time of resin within a unique solid residue from the HTD process (R_29) differentiating its submerged (A,B,C, and D) and non-submerged (E,F,G, and H) parts when using a scaling program temperature from 355 to 450 °C according to the neutral scenario.

Figure 6. Thermal degradation over time of resin within a unique non-submerged part of a solid residue from the HTD process (R_23) differentiating between the smallest size of 0.50 cm × 1.65 cm (A,B,C, and D) and the biggest size of 3.30 cm × 4.00 cm (E,F,G, and H) used in this work when using a scaling program temperature from 355 to 450 °C according to the neutral scenario.

the Supporting Information shows the consistency of the results after resin removal by comparing HTD replicates.

Although the temperature program applied in Figure 3 was not enough to degrade completely the resin, it was close to a clean fiber obtention when using the temperature programs shown in Figures S7 and S8 (set of experiments 7 and 8).

In Figure 4 the scaling program with the highest temperature according to the conservative scenario of this study was applied to a unique sample with great debromination efficiency results, obtaining a completely clean glass fiber even for a size of 4.0 cm

× 1.65 cm (Figure 4H). However, the damage caused to glass fibers in this case was the greatest in the whole study with a strength retention around 20%. In Figure 4A, as an example, a submerged part of a WCB after a debromination process can be easily differentiated as it remains much darker (right side) compared to the non-submerged part (left side).

On the other hand, Figures 8−8 show the resulting materials with the final percentage of strength retention being around 50% (neutral scenario). The figures show that the size of the solid residue and the submerged/not submerged effect during HTD
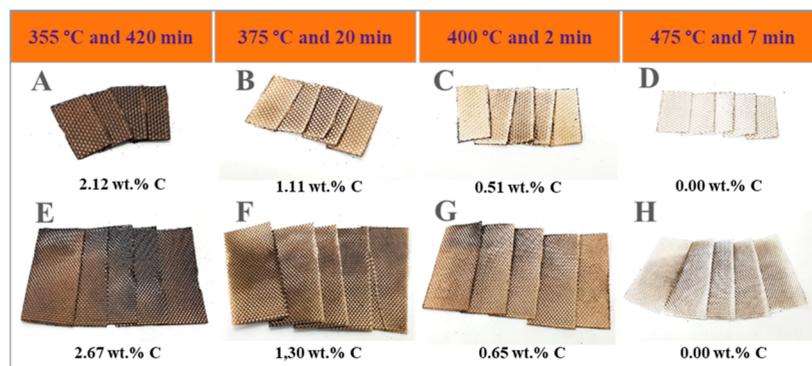
Figure 7. Thermal degradation over time of resin within a unique non-submerged part of a solid residue from the HTD process (R_28, with an initial carbon content of 25.8 wt %) differentiating between the smallest size of 0.50 cm × 1.65 cm (A,B,C and D) and the biggest size of 3.30 cm × 4.00 cm (E,F,G and H) when using a scaling program temperature from 355 to 475 °C according to the neutral scenario.
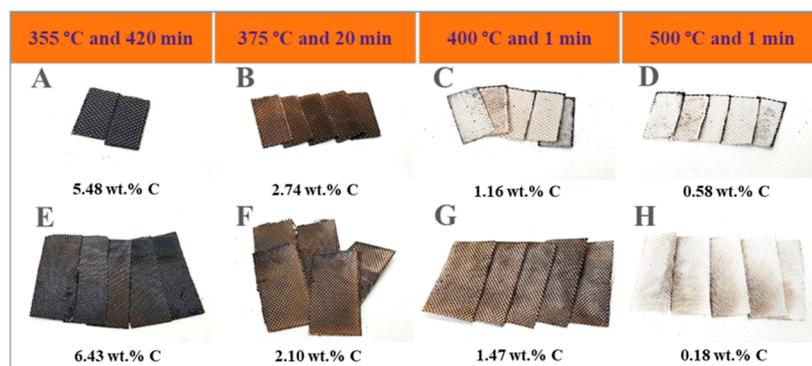
Figure 8. Thermal degradation over time of resin within a unique non-submerged part of a solid residue from the HTD process (R_32 with a carbon content of 26.6 wt %) differentiating between the smallest size of 0.50 cm × 1.65 cm (A,B,C and D) and the biggest size of 3.30 cm × 4.00 cm (E,F,G, and H when using a scaling program temperature from 355 to 500 °C according to the neutral scenario.

treatment were the main parameters influencing the thermal degradation of the resin. In this way, Figure 5 shows how from a temperature of 375 °C, the non-submerged solid residue of 0.5 cm × 3.3 cm started to offer a slightly cleaner glass fiber. At the end, the non-submerged glass fiber was cleaner as expected according to what was previously observed in Figure 4A.

Figure 6 shows the materials treated with an identical scaling program temperature as used in Figure 5 but different sizes. We can see how the size (the smallest and biggest sizes used in this work with a difference factor of around 16 times) of the solid residue was crucial during this thermal treatment. In this way, clean glass fibers were obtained with a strength retention close to 50% for both sizes. Depending on the level of cleaning required, this temperature program could be a good option to obtain clean glass fibers with 50% of their original strength from WCBs up to 0.5 cm × 1.65 cm.

Figures 7 and 8 correspond to the same comparative strategy of sizes but the maximum temperature reached in the scaled program temperature was increased in order to obtain cleaner glass fibers even with larger pieces of WCBs. For these cases, the carbon content of each solid residue is given under each photograph in order to support the results of resin degradation observed in the photographs. Figure 7 shows a completely clean and almost clean glass fiber (considering the photographs) with a retained strength of around 50% obtained for solid residues of 0.5 cm × 1.65 cm and 3.3 cm × 4.0 cm, respectively. In addition, the results of elemental analysis, which showed a null value of carbon content, suggested a complete removal of the resin even in Figure 7H, where the small levels of unburned resin observed

should be insignificant. Table S6 in the Supporting Information shows the detailed CHNS analysis results of all samples A, B, C, D, F, G, and H, corresponding to the resin thermal degradation shown in Figures 7 and 8. In this way, this temperature program could be an excellent option to obtain complete clean fibers from WCBs up to 3% of the maximum size that fits in the reactor (0.5 cm × 1.65 cm) and apparently enough from WCBs up to 50% of the maximum size that fits in the reactor (3.3 cm × 4.0 cm).

In Figure 8, for the smallest size, the results were worse (according to the photographs), and the edges appeared to be burned. However, for the largest size, the results were even better than before, obtaining a quasi-clean fiber. The carbon content supports these findings, resulting in close to zero for the material shown in Figure 8H (taking into account the detection limit of the instrument). Depending on the level of cleaning required, this temperature program could be a good alternative to obtain clean fibers with 50% of their original strength from WCBs up to 50% of the maximum size that fits in the reactor. It was observed that the size of WCB solid residues seemed to have an influence on the final result obtained. This could be caused in some way due to limitations in energy and mass transfer and kinetic aspects (in the degradation reaction of the resin during the heat treatment) as the volume of WCBs increases.

In addition, according to Thomson et al.,[26] a regeneration of the strength of thermally degraded glass fibers close to 75% could be obtained by chemical treatments after a thermal conditioning of glass fibers was performed at 500 °C for 25 min (with a final strength retention only between 15 and 20% approximately). Also, in the case of recycled glass fibers obtained

from plastic wastes where the fibers are protected within a resinous matrix during a part of the thermal treatment, the expected results could be even better.

As in this work a strength retention of 50% was obtained, 30% above the final strength retention of the conditioned glass fibers used by Thomson et al.,[26] a quasi-complete regeneration close to 100% of the original strength could be expected so that these recycled glass fibers could compete with new ones.

Once the potential reuse of the fibers obtained in this work has been estimated, a subsequent detailed mechanical study would be recommended with data from printed circuit boards manufacturers in order to analyze the data of strength before and after treatments (considering all the limitations related to the measurements mentioned before) in order to confirm the good results obtained.

The findings of this work could benefit the printed circuit board industry and the environment by saving raw materials and especially energy. Previously, a rigorous verification of the results on a pilot scale should be performed. The glass fiber manufacturing process was achieved in ovens at temperatures around 1200 °C according to Thomson et al.,[20] significantly higher than the recycling temperatures employed in this work. The process proposed in this work for resin removal could be carried out using some of the glass fiber manufacturing equipment but at temperatures significantly lower. Furthermore, a certain percentage of the weight composition of the glass fiber part of the printed circuit boards could be added as recycled during manufacturing. On the other hand, the debromination process proposed without total submersion in subcritical water minimizes the use of water and indirectly the pressure inside the reactors. In addition, without the need of stirring nor decreasing the original WCB size, simpler reactors with more modest mechanical properties can encourage companies to debrominate WCBs and recover glass fibers.

4. CONCLUSIONS

Considering the results obtained from the debromination of WCB pieces, a standard non-stirred reactor allows a sample size treatment as large as the inside of the reactor since the proportion of submerged WCBs in liquid during debromination treatment had not perceptible influence on efficiency. In addition, it was preferable that the amount of liquid was minimum in order to obtain more easily a clean glass fiber for later reuse. Stronger conditions are required for the debromination of large WCB pieces (a CO_3^{2-}/Br^- ratio of 4:1 vs 1:1, a treatment time of 6 h vs 2 h, and a treatment temperature higher than 225 °C to obtain a complete debromination, compared to small-size WCBs). However, the potential of the global process of debromination of WCB pieces was only decreased by 20% with regard to the debromination of small WCBs when using a simple laboratory equipment for debromination, which limited, for mechanical reasons, the possible improvement that was actually achievable. Alternatively, there is evidence and sufficient scientific basis to anticipate that a complete debromination should be accomplished by increasing slightly the temperature of treatment in a more robust reactor. Therefore, it is encouraged to continue with the research through the use of a reactor which allows to work at higher temperatures to optimize the actual provisional debromination parameters found for a complete debromination of large or even fully of its original-size WCBs.

According to glass fiber recovery, combustion with temperature scaling programs represents a valid alternative to obtain reusable (with half of its original mechanical properties) and clean glass fibers of large size. With temperature programs up to 475−500 °C, reusable fibers up to a certain limit size around 50% of the maximum size that fits in the reactor can be obtained. Fully reusable large glass fibers with close to 100% of their original strength could be obtained with the help of the existing treatments to improve the properties of glass fibers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02368.

> Experimental conditions of the runs performed during debromination, parameters used, comparison with previous optimization studies, runs carried out for the thermal degradation of the resin, complete CHNS content of all the samples, Phenomenological model, DE obtained, thermal degradation over time of original WCBs and resin within solid residues (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Juan A. Conesa − *Institute of Chemical Process Engineering, University of Alicante, Alicante E-03080, Spain; Department of Chemical Engineering, University of Alicante, Alicante E-03080, Spain;* ⓞ orcid.org/0000-0001-7981-440X; Email: ja.conesa@ua.es

Authors

Gerard Gandon-Ros − *Institute of Chemical Process Engineering, University of Alicante, Alicante E-03080, Spain; Department of Chemical Engineering, University of Alicante, Alicante E-03080, Spain;* ⓞ orcid.org/0000-0001-5866-3702

Ignacio Aracil − *Institute of Chemical Process Engineering, University of Alicante, Alicante E-03080, Spain; Department of Chemical Engineering, University of Alicante, Alicante E-03080, Spain;* ⓞ orcid.org/0000-0001-5382-4386

María Francisca Gomez-Rico − *Institute of Chemical Process Engineering, University of Alicante, Alicante E-03080, Spain; Department of Chemical Engineering, University of Alicante, Alicante E-03080, Spain*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c02368

Author Contributions

G.G.-R.: conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing−original draft, writing−review and editing, visualization, and project administration. I.A.: writing−original draft, writing−review and editing, and visualization. M.F. and G.-R.: writing−original draft, writing−review and editing, and visualization. J.A.C.: writing−original draft, supervision, and funding acquisition.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

ABBREVIATIONS

WCBs, waste printed circuit boards; DE, debromination efficiency; WEEEwaste electric and electronic equipmentBFRs, waste electric and electronic equipmentBFRsbrominated flame retardants; TBBPA, tetrabromobisphenol A; PBDD/Fs, polybrominated dibenzo-p-dioxins/furans; HTD, hydrothermal debromination; IDESS, impact in debromination efficiency due to sample size

REFERENCES

(1) Forti, V.; Balde, C. P.; Kuehr, R.; Bel, G.. *The Global E-Waste Monitor 2020: Quantities, Flows and the Circular Economy Potential*; (UNU)/United Nations Inst. Train. Res. −co-: Bonn/Geneva/ Rotterdam, 2020; Vol. *1*−119.

(2) European Parliament and Council. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). (accesed March 10, 2022).https://rod.eionet.europa.eu/instruments/651.

(3) Maurice, A. A.; Dinh, K. N.; Charpentier, N. M.; Brambilla, A.; Gabriel, J. C. P. Dismantling of Printed Circuit Boards Enabling Electronic Components Sorting and Their Subsequent Treatment Open Improved Elemental Sustainability Opportunities. *Sustain* 2021, *13*, 10357.

(4) Goosey, M.; Kellner, R. Recycling Technologies for the Treatment of End of Life Printed Circuit Boards (PCBs). *Circuit World* 2003, *29*, 33−37.

(5) Guo, J. J.; Guo, J. J.; Xu, Z. Recycling of Non-Metallic Fractions from Waste Printed Circuit Boards: A Review. *J. Hazard. Mater.* 2009, *168*, 567−590.

(6) Peng Muo, P.; Wa Layiding, L.; Dong Xiang, D.; Jiangang Gao, J.; Guanghong Duan, G. A Physical Process for Recycling and Reusing Waste Printed Circuit Boards; *IEEE International Symposium on Electronics and the Environment*, 2004, pp 237−242..

(7) Recycling Ltd, *Composite PCBRec Process: Waste Printed Circuit Board (WPCB) Recycling with Molten Salts*; CORDIS EU research results, 2017.

(8) Chien, Y.-C.; Paul Wang, H.; Lin, K.-S.; Huang, Y.-J. J.; Yang, Y. . W. Fate of Bromine in Pyrolysis of Printed Circuit Board Wastes. *Chemosphere* 2000, *40*, 383−387.

(9) Sakai, S.; Watanabe, J.; Honda, Y.; Takatsuki, H.; Aoki, I.; Futamatsu, M.; Shiozaki, K. Combustion of Brominated Flame Retardants and Behavior of Its Byproducts. *Chemosphere* 2001, *42*, 519−531.

(10) Altarawneh, M.; Dlugogorski, B. Z. Formation of Polybrominated Dibenzofurans from Polybrominated Biphenyls. *Chemosphere* 2015, *119*, 1048−1053.

(11) Barontini, F.; Marsanich, K.; Petarca, L.; Cozzani, V. Thermal Degradation and Decomposition Products of Electronic Boards Containing BFRs. *Ind. Eng. Chem. Res.* 2005, *44*, 4186−4199.

(12) Dangtungee, R.; Somchua, S.; Siengchin, S. Recycling Glass Fiber/Epoxy Resin of Waste Printed Circuit Boards: Morphology and Mechanical properties. *Mech. Compos. Mater.* 2012, *48*, 325−330.

(13) Li, J.; Zeng, X. Recycling Printed Circuit Boards. *In Waste Electrical and Electronic Equipment (WEEE) Handbook*; Elsevier Inc., 2012, pp 287−311.

(14) Soler, A.; Conesa, J. A.; Ortuño, N. Emissions of Brominated Compounds and Polycyclic Aromatic Hydrocarbons during Pyrolysis of E-Waste Debrominated in Subcritical Water. *Chemosphere* 2017, *186*, 167−176.

(15) Xing, M.; Zhang, F.-S. Degradation of Brominated Epoxy Resin and Metal Recovery from Waste Printed Circuit Boards through Batch Sub/Supercritical Water Treatments. *Chem. Eng. J.* 2013, *219*, 131−136.

(16) Daneshvar, S.; Salak, F.; Ishii, T.; Otsuka, K. Application of Subcritical Water for Conversion of Macroalgae to Value-Added Materials. *Ind. Eng. Chem. Res.* 2011, *51*, 77−84.

(17) Çolak, U.; Durak, H.; Genel, S. Hydrothermal Liquefaction of Syrian Mesquite (Prosopis Farcta): Effects of Operating Parameters on Product Yields and Characterization by Different Analysis Methods. *J. Supercrit. Fluids* 2018, *140*, 53−61.

(18) Wang, Y.; Zhang, F. S. Degradation of Brominated Flame Retardant in Computer Housing Plastic by Supercritical Fluids. *J. Hazard. Mater.* 2012, *205−206*, 156−163.

(19) Gandon-Ros, G.; Soler, A.; Aracil, I.; Gómez-Rico, M. F.; Conesa, J. A. Improving Efficiency and Feasibility of Subcritical Water Debromination of Printed Circuit Boards E-Waste via Potassium Carbonate Adding. *J. Clean. Prod.* 2021, *319*, 128605.

(20) Thomason, J. L.; Yang, L.; Meier, R. The Properties of Glass Fibres after Conditioning at Composite Recycling Temperatures. *Compos. Appl. Sci. Manuf.* 2014, *61*, 201−208.

(21) Pickering, S. J. Recycling Technologies for Thermoset Composite Materials-Current Status. *Compos. Appl. Sci. Manuf.* 2006, *37*, 1206−1215.

(22) Job, S. Recycling Glass Fibre Reinforced Composites - History and Progress. *Reinf. Plast.* 2013, *57*, 19−23.

(23) Wait, C. F. The Reuse and Recycling of Glass Fibre Waste, Master of research in the science and engineering of materials, University of Birmingham, 2010.

(24) Kennerley, J. R.; Kelly, R. M.; Fenwick, N. J.; Pickering, S. J.; Rudd, C. D. The Characterisation and Reuse of Glass Fibres Recycled from Scrap Composites by the Action of a Fluidised Bed Process. *Compos. Appl. Sci. Manuf.* 1998, *29*, 839−845.

(25) Jenkins, P. G.; Yang, L.; Liggat, J. J.; Thomason, J. L. Investigation of the Strength Loss of Glass Fibre after Thermal Conditioning. *J. Mater. Sci.* 2015, *50*, 1050−1057.

(26) Thomason, J. L.; Nagel, U.; Yang, L.; Sáez, E. Regenerating the Strength of Thermally Recycled Glass Fibres Using Hot Sodium Hydroxide. *Compos. Appl. Sci. Manuf.* 2016, *87*, 220−227.

(27) Gandon-Ros, G.; Soler, A.; Aracil, I.; Gómez-Rico, M. F. Dechlorination of Polyvinyl Chloride Electric Wires by Hydrothermal Treatment Using K2CO3 in Subcritical Water. *Waste Manag.* 2020, *102*, 204−211.

(28) *ECS Solid Biofuels - Determination of Ash Content. Solid Biofuels - Determination of Ash Content.* European Committee for Standardization 2010.

(29) *EPA Method, U. S. Bomb preparation method for solid waste. Method 5050. Bomb Preparation Method for Solid Waste. SW-846*; United States Environmental Protection Agency, Office of Solid Waste: Washington, D.C, 50501994.

(30) US EPA Method 9056A. *Determination of inorganic anions by ion chromatography*; United States Environmental Protection Agency, Office of Solid Waste: Washington, D.C., 2000.

(31) Ortuño, N.; Conesa, J. A.; Moltó, J.; Font, R. Pollutant Emissions during Pyrolysis and Combustion of Waste Printed Circuit Boards, before and after Metal Removal. *Sci. Total Environ.* 2014, *499*, 27−35.

(32) Altarawneh, M.; Dlugogorski, B. Z. Mechanism of Thermal Decomposition of Tetrabromobisphenol A (TBBA). *J. Phys. Chem. A* 2014, *118*, 9338−9346.

(33) Xiu, F. R.; Zhou, K.; Yu, X.; Qi, Y. Co-Treatment of PVC and Used LCD Panels in Low-Temperature Subcritical Water: Enhanced Dechlorination and Mechanism. *Process Saf. Environ. Prot.* 2021, *151*, 10−19.

(34) Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H. Thermal Degradation of PVC: A Review. *Waste Manag.* 2016, *48*, 300−314.

(35) Xiu, F. R.; Qi, Y.; Zhang, F. S. Co-Treatment of Waste Printed Circuit Boards and Polyvinyl Chloride by Subcritical Water Oxidation: Removal of Brominated Flame Retardants and Recovery of Cu and Pb. *Chem. Eng. J.* 2014, *237*, 242−249.

(36) Nowacka, A.; Włodarczyk-Makuła, M. Effectiveness of Priority PAH Removal in a Water Coagulation Process. *Water Supply* 2015, *15*, 683−692.

(37) Dąbrowska, L.; Rosińska, A. Removal of PCBs and Heavy Metal Ions from Surface Water by Coagulation. *Annu. Set Environ. Prot.* 2013, *15*, 1228−1242.

(38) Rosińska, A.; Dąbrowska, L. Selection of Coagulants for the Removal of Chosen PAH from Drinking Water. *Water* 2018, *10*, 886.

(39) Włodarczyk-Makuła, M.; Wiśniowska, E. Halogenated Organic Compounds in Water and in Wastewater. *Civ. Environ. Eng. Reports* **2019**, *29*, 236−247.

(40) Feih, S.; Boiocchi, E.; Mathys, G.; Mathys, Z.; Gibson, A. G.; Mouritz, A. P. Mechanical Properties of Thermally-Treated and Recycled Glass Fibres. *Compos. Part B Eng.* **2011**, *42*, 350−358.

(41) Aracil, I.; Font, R.; Conesa, J. A. Thermo-Oxidative Decomposition of Polyvinyl Chloride. *J. Anal. Appl. Pyrolysis* **2005**, *74*, 215−223.

(42) Kosuda, T.; Okada, T.; Nozaka, S.; Matsuzawa, Y.; Shimizu, T.; Hamanaka, S.; Mishima, S. Characteristics and mechanism of low temperature dehydrochlorination of poly(vinyl chloride) in the presence of zinc(II) oxide. *Polym. Degrad. Stab.* **2012**, *97*, 584−591.