Segregation of Batteries from Pyrolyzed Entire Smartphones by means of Density Separation

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ABSTRACT

Purpose: In a scenario of excessive use of manual work and poor valorization of the residues, WEEE recyclers urge for novel solutions that promote more automated processes. This study proposes a recycle route for entire smartphones (avoiding the need for manual disassembly) and present a novel method for the segregation of batteries from other components through density separation. **Methods:** Smartphones are firstly pyrolyzed and sieved (2 cm sieve), and then tested for density separation to find a possible density medium that promotes the separation of the batteries. At the end, some different media were tested to validate the applicability of the method. **Results:** Pyrolysis and sieving experiments were conducted successfully, and an ideal density for the separation was found. Into a selected solution, batteries floated and other components sank. Testing the novel method with 50 batteries and 50 other components from diverse brands and models of smartphones, it reached an efficacy of 96%. A possible route for recyclers is provided. **Conclusions:** The processing of entire devices from the beginning of the recycling route may facilitate the work of recyclers, avoiding the costly and time-consuming steps of dismantling, and improving profits and valorizing the residue. This method is cheap, practical, and can be utilized by small and medium recyclers. In terms of products, pyrolysis generates valuable gaseous and liquid sub-products and a rich solid fraction in metals. The step of density separation generates a separated flow for batteries that can be further recovered by specific methods.

Keywords: WEEE, pyrolysis, recycling, gravimetric separation

1. INTRODUCTION

The generation of waste electrical and electronic equipment (WEEE) is currently a global concern due to its constant growth and lack of recycling alternatives that properly satisfy the needs for a circular economy and sustainable patterns of consumption. Among many types of electronic devices, residues of mobile phones deserve special attention by their importance in terms of valuable composition (containing high concentrations of precious and critical elements such as Au, Pd, Ag, Nd and Li) [1] and quantity of waste generated. Approximately, 16 billion units are currently in use globally (6.6 billion of smartphones), with a tendency to grow [2], which means a high generation of this type of residue in the middle term.

The WEEE recycling industry (including for mobile phones) is dominated worldwide by small and medium recyclers that employ processes of low complexity and efficiency (with predominance of manual work and rudimentary tools, sometimes verging informality and wasting valuable components and materials) [3–5], with only a few players that deal with complex and big-scale recovery processes to efficiently extract valuable and critical elements (Abalansa et al., 2021). Basically, formally collected smartphones and other complex electronic residues are manually dismantled, and only specific parts such as the printed circuit boards (PCBs) are separated and sent to appropriate valorization in terms of material recovery (recovery of precious and critical elements) [6,7], while other parts are sent to base metals/polymer recycling and landfill, meaning a huge wasting of valuable material that flows downstream to processes that do not properly valorize the residues.

The study of recycling routes that facilitate the operation of small and medium recyclers towards the automatization of the process and better valorization of the residues are essential to improve the entire recycling chain in terms of quality of provision materials, profitability, and strategic importance, not to mention the social issues such as labor security, promotion of formality, and others. A possible approach for that is to directly process entire mobile phones from the beginning of the recycling route, avoiding the need of dismantling and separating components and materials through manual work and other rudimentary techniques. This may facilitate the processes at the first stage of the recycling chain in small and medium recyclers, since the labor cost of dismantling components is commonly the main expense (Dias et al., 2022), and allow the better valorization of the residues towards the recovery of precious and critical elements that are present in other components than PCBs (such as rare earth elements from screens and magnets, and Li and Co from batteries).

Thermal processes, such as pyrolysis, already have a wide applicability in recycling processes for many types of materials and can generate valuable sub-products (liquid and gas) along with a metal-concentrated solid output. In this case, entire mobile phones (including batteries) can be pyrolyzed, and the main challenge, after pyrolysis, is to provide a further adequate treatment for each component. Metal concentrates (electronic parts and metal plates) can be processed jointly towards the beneficiation and recovery of valuable metals, but batteries require a separate treatment to achieve an efficient recovery of their valuable materials lithium and cobalt (critical elements that are currently highly demanded by the market), as they are totally different components in terms of composition, target elements for recovery, and processes applied in recycling [8]. Thus, considering a scenario of recycling for entire smartphones, a step of battery separation is essential to promote a better valorization of the residue.

The objective of this work is to introduce the idea of recycling entire smartphones through pyrolysis and explore the physical property of density to separate batteries from other components. An ideal density medium can be defined to separate the components by floating or sinking. Through the pyrolysis process and separation of the batteries, it is expected that a simple initial recycling route can be implemented to produce valuable fractions of materials (concentrates of electronic parts and a clean battery fraction) and facilitate the beneficiation work of the recyclers.

2. METHODOLOGY

Pyrolysis experiments, applied to 8 entire smartphones from diverse brands and models, were carried out in a fixed batch reactor under nitrogen atmosphere, 600 °C for 15 minutes, and a heating rate of 300 °C per hour. The temperature of 600 ºC was selected to guarantee the decomposition of the polycarbonate (which occurs until 567 ºC in pyrolysis conditions [9]) and prevent the melting of Al pieces. The smartphones were collected through delivery points and processed as they were received. The brands and models of the smartphones were: Motorola XT1762, Microsoft RM1065, Samsung A307GT, Asus Z00AD, Lenovo 5316, Samsung GTS7390G, Samsung G531F, and Samsung J320FN.

After pyrolysis, a step of granulometric separation in a 2 cm sieve was used to acquire a gross fraction composed of batteries and other components, and to avoid the entering of the fine granulometry in the density separation process. In addition, the agitation from the granulometric separation promotes the disaggregation of carbonaceous materials adhered to the components, facilitating the downstream processes.

An ideal density for the separation of the batteries was tested using a solution of sodium polytungstate (SPT), starting from a solution of density 3.1 $g.cm^{-3}$ (approximately the maximum solubility of the SPT), and decreasing the density in increments of 0.2 $g.cm^{-3}$. The SPT is a high soluble substance used in scientific research for density separation, and has an industrial presence in the field of mining and recycling [10]. In a becker containing one liter of the solution, the pieces were individually tested for floating or sinking through the immersion and holding for 2 seconds. All pyrolyzed components from the 8 smartphones (glass, PCBs, metallic pieces and others) were tested in each increment to find a possible density medium that promotes the separation.

After finding a suitable density for separation, other applicable density media were searched to substitute the SPT, due to its high price in the market. Among many possibilities, solutions of zinc chloride and white-clay (kaolin mineral) were selected to perform additional density separation experiments. Finally, 50 units of pyrolyzed batteries and 50 units of other components, from different brands and models, were tested to confirm the viability of the method. An efficacy index (%) is provided according to the units of batteries floating and other components sinking.

3. RESULTS

3.1 Pyrolysis and the definition of an ideal density

Pyrolysis resulted in approximately 25-30% of mass degradation. Figure 1 shows examples of components of mobile phones after pyrolysis (a) and after granulometric separation (b). Approximately, 77.6% of the materials, in mass, remain in the fraction above 2 cm, and is composed of batteries (8 units), screen glasses (many pieces), metallic parts (many pieces), and PCBs (8 units). The material passing the sieve (< 2 cm) is mainly composed of small components and metallic parts, char from pyrolysis degradation, and broken glass from screens.

Fig 1. Mobile phone components after pyrolysis (a) and after 2 cm sieving (b)

After passing through 2 cm sieving, the gross fraction was sent to density separation experiments in solution of SPT. All components were individually immersed into the solution of SPT to test for floating or sinking, starting from the density 3.1 $g.cm^{-3}$ and decreasing in increments of 0.2 $g.cm^{-3}$ until finding the ideal density medium for the separation of the batteries. Table 1 describes the results of the tests in each increment of density, to analyze the evolution of the experiments.

Table 1. Description of the experiments of density separation in SPT

Medium Density	Description of results
3.1	All components floated. Some metallic pieces sank.
2.9 to 2.3	All components floated. Metallic pieces sank.
2.1	It was perceived a tendency to glasses and PCBs to sinking
1.9	All glasses and two PCBs sank. All batteries still floating
1.7	All other components and one battery sank. Other seven batteries floated
1.5	All other components and five batteries sank. Three batteries floated
Increment to 1.8	All batteries floated and all other components sank

In the highest density (3.1 g.cm^{-3}), all components floated except metallic pieces probably made of high-density metals like iron and copper. Between 2.9 and 2.3 g.cm^{-3}, other metallic pieces sank (probably those made of aluminum and other light metals) while all other components remained floating. When the solution reached the density 2.1 g.cm^{-3}, PCBs and glasses began to sink (however, still in the top-middle of the solution), while the batteries remained floating. In the medium density 1.7 g.cm^{-3}, seven batteries floated and one battery and all other components sank, indicating a possible ideal density to promote the separation of batteries. When the density was decreased to 1.5 g.cm^{-3} other batteries sank, thus the solution density was increased to 1.8 g.cm^{-3} to verify if this density would be more effective than 1.7 g.cm^{-3}. In density 1.8 g.cm^{-3}, all batteries floated and all other components sank, indicating an ideal density in which batteries could be separated from other components of smartphones in high efficacy (100% in this initial experiment).

3.2 Alternative solutions for density separation at 1.8 g.cm^{-3}

3.2.1 Zinc Chloride solution

Although the SPT solution is very suitable for density separation, this chemical compound is costly, hampering its application in real recycling routes. Since this study aims to provide recyclers with solutions to facilitate the manipulation and valorization of the residues, a low-cost option is essential. A literature review on solutions and liquids with densities close to 1.8 g.cm^{-}3 was performed, and, among some alternatives, a solution of zinc chloride and a solution of white-clay were selected for additional experiments due to its low price and absence of toxic substances.

Zinc chloride was added to one liter of distilled water until reaching the density of 1.8 g.cm^{-}3. A possible drawback of this compound is the low pH found in the resultant solution, which may lead to solubilization of some metals when submerged for a certain time. Measuring the final pH of the solution through a pHmeter was not possible due to its high viscosity. Thus, the pH was measured by pH test strips, indicating a final pH between 1 and 2, approximately.

A solution of diluted NaOH was used to increase the pH. When the solution reaches a pH of approximately 4, zinc hydroxide begins to precipitate, limiting the increase of the solution's pH. Diluted HCl was used to decrease the pH of the solution until solubilizing the precipitated zinc hydroxide, and a final optimal pH solution was determined as approximately 3, measured by pH test strips.

Simulating this solution in the software Hydra-medusa (a free software to simulate aqueous solution equilibrium diagrams), the chemical species Zn could be found solubilized until the pH 5, without precipitation (Figure 2). Approximately, in pH higher than 5, a precipitation occurs as the most stable form of a zinc hydroxide, reinforcing the conditions found in the real experiments, also considering the possible errors in the pH measurement through test strips.

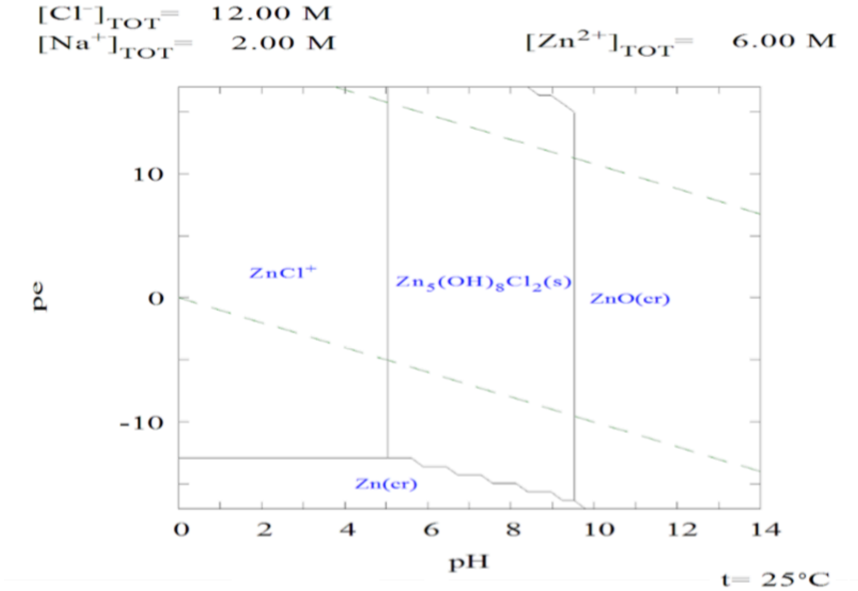

Fig 2. Pourbaix diagram simulated for the conditions of the experiments of density separation

Using this solution of zinc chloride at density 1.8 g.cm-3 and pH 3, all the same smartphone components used in the experiments with SPT were tested again, reaching the same results: all batteries floated and all other components sank. Additional experiments were performed to validate the method with 50 batteries and 50 units of other components (Figure 3). Finally, from 50 batteries, 48 floated and 2 sank, and from 50 units of other components, 48 sank and 2 floated. An efficacy of 96% was reached for the method of density separation of batteries applied to pyrolyzed smartphones.

Fig 3. Batteries floating on the zinc chloride solution with density 1.8 $g.cm^{-3}$ (a) and some tested components (b)

3.2.2 White-Clay Solution

Besides the solution of zinc chloride, a solution of white-clay was experimented as a possible medium. In the density 1.8 g.cm^{-}3, a solution of white-clay is a pasty material (as can be seen in Figure 4a. This solution has a viscosity of 35.7 g/(cm.s), and all components and batteries easily floated on it.

Fig 4. Pasty material of white-clay with density 1.8 g.cm^{-3} and viscosity 35.7 g/(cm.s) (a) Solution of viscosity 0.98 g/(cm.s) and density 1.34 g.cm^{-3} with batteries into red squares (b). Solution of viscosity 0.2 g/(cm.s) and density 1.28 g.cm^{-3} with a battery into a red square (c).

The high viscosity of the white-clay solution and the fact that all components floated on it led to the idea of availing the decreasing of the viscosity in increments (adding water) to possibly finding a viscosity that makes batteries float and other components sink. By adding water, and constantly testing the solution with pieces of glass, iron, and copper (as can be seen in Figures 4), it was possible to note that in density 1.34 g.cm^{-3} the batteries started to sinking slowly, and all other pieces remained completely floating. In Figure 4c (solution with density 1.28 g.cm^{-3}), one battery completely sank quickly, while other components floated. In the solution of density 1.28 g.cm^{-3}, an extra piece of PCB was inserted in the solution and also completely sank due to its high weight.

It was not possible to separate the components through a solution of white-clay because, considering viscosity as the independent variable and starting from a solution with density lower than 1.8 g.cm^{-}3, the behavior of the components into the solution (tendency to float or quickly sinking) depends on the format and total weight of the piece and not on the relation between volume and mass that made the batteries floating when considering density experiments. Summarizing, since in densities lower than 1.8 g.cm^{-}3 all components tend to sink, the only difference is the velocity it occurs, and heaviest components would sink faster. This can be adapted to visualization through the sedimentation Stokes' law equation for the velocity of sedimentation (Equation 1), in which the velocity basically depends on the radius of the particle (format), weight, and viscosity, also considering that a particle only sediments if its density is lower than the fluid:

V= 2/9 x r2 x g x (dp-df) / n (Equation 1)

where,
V: limit velocity of sedimentation
r: stoke radius of the particle
g: gravitational field strength
dp: particles density
df: medium density
n: dynamic viscosity of the fluid

3.3 Final recycling route

After defining the density separation technique as a possible method to separate the batteries from smartphones, a simple route can be defined for recyclers that aims to apply it (Figure 5). This route is able to substitute a high quantity of man-power and manual work for more automated tasks, including avoiding steps of preparation/organization of the residues as the pyrolysis furnace can accept the smartphones as they are received.

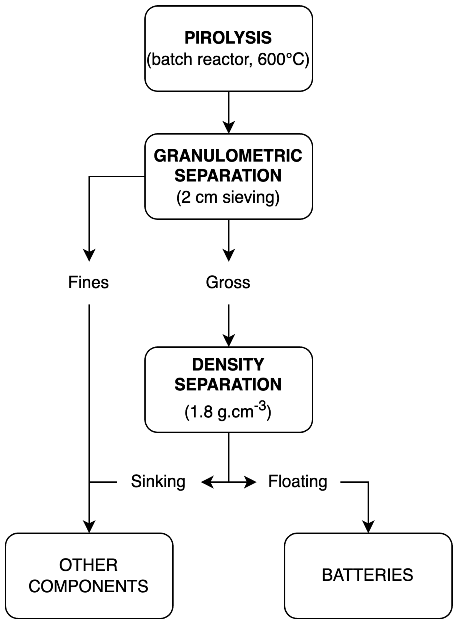

Fig 5. Flowchart of the final recycling route to separate the batteries

Two flows are generated at the end of the route. Firstly, the flow of other components is a rich fraction of valuable and critical metals, including copper, gold, silver, neodymium, and others. Indeed, through processing smartphones in a pyrolysis furnace as the first step, magnets are demagnetized and maintained in the flow of materials, avoiding possible losses to mechanical equipment as crushers, for example. The flow of batteries with 96% of efficacy in number of pieces allows a separated treatment for them, as they have a unique design and elements, such as Li and Co. The main drawback of the density separation step is the remaining of a portion of solution ($ZnCl_2$) on the inserted pieces, and the excess of zinc has to be considered when proposing further methods of hydro or pyro metallurgy to recover target materials. For further studies, solutions of Fe-Si powder and magnetite (commonly utilized in the mining industry) are indicated for testing.

4. CONCLUSIONS

As a proof of concept, the method of density separation was successfully tested for the separation of pyrolyzed batteries from other parts of mobile phones, reaching 96% of efficacy. This method enables processing entire devices into pyrolysis furnaces with the posterior separation of batteries for an adequate treatment for recovering valuable materials. The processing of entire devices from the beginning of the recycling route may facilitate the work of recyclers, avoiding the costly and time-consuming steps of dismantling, and improving profits and valorizing the residue. This method is cheap, practical, and can be utilized by small and medium recyclers.

In terms of products, pyrolysis generates valuable subproducts mainly for energy recovery, and also decreases the fraction of polymers, generating a richer solid product in metals. Another positive point is that, through the processing of entire smartphones, no component/material is wasted, enabling the best use of all parts. The step of density separation provides the recyclers with a separated flow of batteries, in which further special treatment of recycling can be applied (generation of black mass, for example) or simply selling them as a valuable product. The definition of a density (1.8 $g.cm^{-3}$) that allows the separation of batteries represents a novel method in the field of WEEE recycling, with high potential of applicability and profit generation. This method, beyond all, can be tested for other devices such as laptops, tablets, and other small electronics.

5. ACKNOWLEDGEMENTS

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