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Influence of Feedstock Particle Size on the Certain Determination of Chlorine and Bromine in Pyrolysis Oils from Waste Electrical and Electronic Equipment Plastics

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ABSTRACT: Rejected streams emerging from waste sorting and recycling plants are still capable of being valorized by unconventional recycling routes. This is the case of the plastic-rich fraction generated after the treatment of waste electrical and electronic equipment (WEEE). However, the material complexity of this stream supposes a handicap when it comes to obtaining repetitive results in laboratory-scale recycling processes. This work aims to highlight the influence that the pretreatment (mainly particle size reduction) of a real WEEE plastic-rich stream has on the variability of the concentration of halogens (representative pollutants) in the oils obtained from its recycling via pyrolysis. The pretreatment steps were based on the standards of the European Committee for Standardization (ECN) for the analysis of waste samples. Four samples were studied: the WEEE plastics as received; two milled samples (2 and 1 mm particle size) derived from the original one; and a simulated sample composed of virgin polymers. All the samples were treated under the same conditions: 500 °C reaction temperature, 15 °C min^{-1} heating rate, 30 min dwell time, and a 1 L min^{-1} nitrogen purge flow. The oils obtained in, at least, two pyrolysis tests performed on the same sample were deeply characterized, and the results were compared. The oils derived from the "as-received" sample showed an unacceptable relative standard deviation (RSD, ∼42%) in the chlorine concentration. The sample milled to 2 mm reduced the RSD on the concentration of chlorine in the oils down to 8%, while no enhancement in the results was observed for the further milled sample. The other two major pyrolysis fractions were also characterized, showing an overall enhancement in the RSD of the analysis of the main components of the gases, while no improvement in the solids pollutants' characterization was achieved.
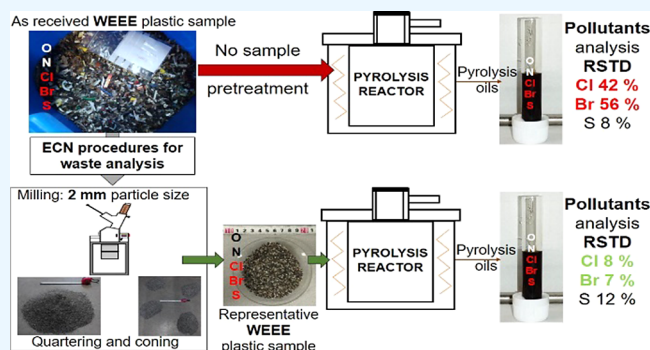
1. INTRODUCTION

The pyrolysis of plastic waste, after many years of research, is becoming a reality at the industrial level. In recent years, pyrolysis technology has been intensively developed and many companies have announced the start-up of plastic waste pyrolysis plants (e.g., Plastic Energy, Pyrum Innovations, Quantafuel, Neoliquid), motivated by the circular economy and waste management policies recently adopted for plastics.[1] In the quest to make plastic a sustainable material, pyrolysis is presented as an opportunity to increase the recycling rates of plastic waste and, at the same time, to contribute to new plastic formulations with higher recycled material content.[2] The way is being opened up by plastic waste from packaging. This kind of plastic is intended to produce a pyrolysis oil that could be coprocessed with the naphtha that feeds the olefins steam cracker, thus being a raw material for the manufacture of ethylene and propylene, which in turn are mainly destined for the production of polyolefins.[3,4] The current development of

pyrolysis technology may serve as an approach to finding a solution for other types of plastic-rich complex waste, which could also produce oil to be employed in industry. Within this large group of complex waste, one of the most relevant, due to its current generation ratio and especially due to its expected increase in the near future, are the mixtures of plastics (and other refused materials) that are generated in the sorting and separation plants of waste electrical and electronic equipment (WEEE plastics).[5,6]
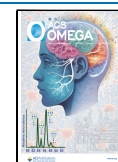
The pyrolysis of WEEE plastics has been studied for many years now.[7,8] Although it produces an oil with some interesting characteristics, it has a very limiting handicap: the high concentrations of chlorine and bromine, resulting from the presence of polyvinyl chloride (PVC) in cables and other pieces and brominated flame-retardants (BFRs) as part of the formulation of plastics used in electronics.[9−11] This issue has also been addressed by the scientific community over the years,[12] which has reported several methods to dehalogenate oils, accomplishing quite successful results in some cases.[13−15] However, there are reasons to believe that the concentration of halogens in pyrolysis oils has a high level of uncertainty. This is a key issue that needs to be studied in more detail because it is a matter of time before the concentration of halogens in pyrolysis oils will have to comply with limit values set in laws or standards. In this situation, addressing concentration values without an uncertainty estimation or with high measurement uncertainty will not be acceptable. Moreover, this is of particular relevance in the case of oils coming from a complex waste. On the one hand, the concentration limits will be probably very low (3 ppm is reported to be the acceptance concentration for chlorine in steam crackers)[4] and, on the other hand, the waste that produces the oil has a high fundamental variability with respect to the halogen content due to its material heterogeneity.[16] In other words, the halogens are only present in some of the particles that constitute the waste, mainly in PVC and its derivative chlorinated polyvinyl chloride (CPVC) and BFR-containing plastics, and their halogen content can be very variable (from 67 wt % for PVC−CPVC to 12.5 wt % or less for BRF containing plastics).[17,18] This means that in the absence of proper pretreatment focused on this issue, an industry treating this kind of waste (or similar) could produce batches of oil with such variability in halogen content that it would not be possible to establish a commercial value for this product. This is because the study of alternatives where these oils can be used is highly dependent on accurate values for the concentration of pollutants, especially halogens.

At the characterization stage, solving the problem of the fundamental variability of the waste is a critical matter that is highly standardized from the sampling stage itself to the preparation of the test portions. Examples of standards addressing how to obtain a representative laboratory sample from waste are the collection of technical reports of the European Committee for Standardization (CEN) 15310 series,[19] the ASTM D5956 standard,[20] or the technical guidance published by the Environmental Protection Agency (EPA) of the United States.[21] Then, the procedure to obtain representative test portions from the laboratory sample is also a matter described in standards like the EN 15002:2015, where a sequence of treatment techniques or operations is proposed: separation of fractions, drying, particle size reduction, homogenization, and subsampling.[22] This standard offers a statistical formula (eq 1 in Section 2.1) to quantify the logical relationship between the particle size of a heterogeneous granular waste and the amount of sample to be used in order to minimize the effect of fundamental variability by obtaining a representative sample.

Following these standards is a common practice in the preparation of samples for waste chemical characterization analysis, such as elemental analysis or proximate analysis. However, these considerations are not normally taken into account when it comes to establishing the pretreatment operations of waste before feeding to an industrial thermal process. Usually, at this step, the issues governing the decision-making concerning pretreatment steps and equipment are heat transfer among particles and the complement of mechanical constraints of the machinery related to bed density and porosity. Therefore, the influence that pretreatment operations may have on the chemical properties of the products when heterogeneous waste is processed is normally ignored.[23,24] The reason could lie in the fact that the status quo of thermal processing of heterogeneous waste at an industrial scale at the moment is incineration, whose product is not material but energetic and therefore is not so sensitive to heterogeneity. However, this is a key issue when secondary raw materials are produced from waste valorization since they must be representative of the waste and the process parameters and variability in the concentration of pollutants must be low, even at low concentrations.

In this article, the pyrolysis of a real sample of WEEE plastics collected from a sorting and separation plant has been carried out at a laboratory scale, in order to study the influence of the pretreatment operations on the uncertainty of the concentration of halogens in the produced pyrolysis oils. The significance of each of the pretreatment operations will be addressed, and some advice will be concluded with a view to industrial implementation. As far as the authors are concerned, there is no publication on the impact of pretreatment operations on the variability of the concentration of halogenated pollutants in pyrolysis oils. In this sense, the innovative character of the paper stands clear, and it addresses one of the important issues in the current industrialization process of pyrolysis of plastic waste.

2. MATERIALS AND METHODS

2.1. Sample Preparation. The field sampling of the real waste was carried out by the operators of the WEEE industrial facility, who sent a 40 kg sample to our laboratory. This sample, from now on the laboratory sample, was what is known as a heterogeneous granular waste, with different materials in size and composition. The laboratory sample, which appeared to be wet, was dried at room temperature until equilibrium moisture was achieved (72 h). Then, it was homogenized with sampling paddles, and 100 g subsamples were obtained by means of the coning and quartering procedure. These subsamples, without any further pretreatment step, were the first feedstock studied in this work for pyrolysis experiments, and they were codified as arW ("as-received" waste). One of these arW subsamples was used to determine the material composition of the waste and to measure the bulk density and the particle size distribution, under the procedures described in the Analytical Techniques section. Another of these arW subsamples was also used for the chemical characterization of the waste (organic elemental analysis and proximate analysis), for which it was ground to a particle size of 2 mm, a common particle size for this kind of analysis.

The second feedstock studied through pyrolysis was obtained by particle size reduction of arW subsamples. In order to know the optimum particle size, the equation for the estimation of the minimum quantity of representative subsamples that is proposed in annex B of the EN 15002:2015 standard was used.[22] The formula shown in eq 1 enables the calculation of the minimum mass (m_s) that allows a sample to be representative as a function of its particle size (D_{95}). Other parameters are also considered in the formula, such as the desired coefficient of variation caused by the
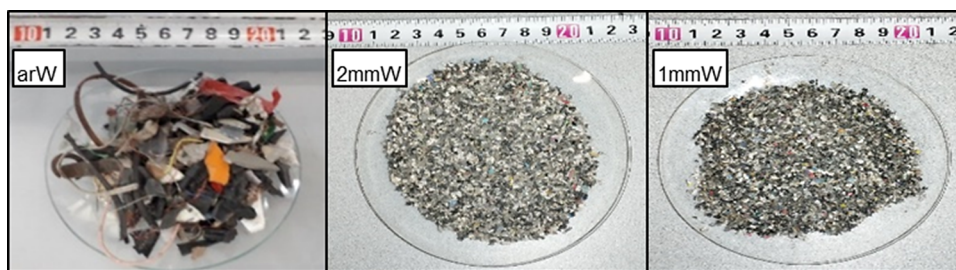
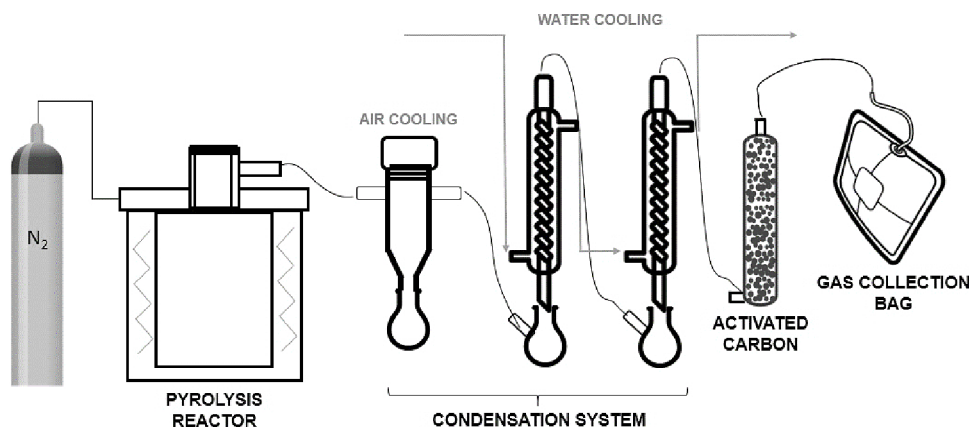**Figure 1.** Visual appearance of the WEEE samples employed in this work.

Figure 2. Pyrolysis plant scheme.

fundamental error (CV) and those related to the characteristics of the waste: density (ρ), particle size distribution corrector parameter (g), fraction of particles with the property of interest (p), and shape factor for the correction of geometric differences between particles (f). However, if the sample quantity to be used is defined (200 g in this case, as the whole experiment consists of two pyrolysis runs of 100 g feed each), the formula can also be used to determine the particle size that this quantity of sample must have in order to be representative. The formula is shown in this way in eq 1. The use of this formula was intended to prove whether the rules for the preparation of test portions for waste analysis could also be used for the pretreatment of waste prior to industrial processing.

$$\text{Particle size(cm)} = \sqrt[3]{\frac{m_s \cdot 6 \cdot \text{CV}^2 \cdot p}{\pi \cdot \rho \cdot f \cdot g \cdot (1 - p)}} \tag{1}$$

The values employed for each parameter contained in eq 1 are the following: m_s = 200 g, CV = 0.1 (typical value recommended in EN 15002 standard), ρ = 0.442 g cm^{-3}, p = 0.001 (typical value recommended in EN 15002 standard when the studied parameter is present in low proportion in the particles of the waste, as it is the case of halogens), f = 1 (for a particle size lower than 5 cm), and g = 0.5 (for values of D_{95}/D_{05} between 2 and 4).

According to eq 1 and using the values shown before, the maximum particle size for representatively processing 200 g of this waste by pyrolysis had to be 2.59 mm, which led to the milling of the sample down to 2 mm. So, this second feedstock, codified as 2 mmW, was a sample obtained from milling down to 2 mm of the arW subsamples. The milling was performed in different steps: first, a 6 mm mesh was used for a primary size reduction, followed by a medium milling step, down to 4 mm,

and finally, the milling to the target particle size of 2 mm. Particle size reduction was carried out in an RETSCH SM 2000 mill. Subsequently, homogenization and a quartering process were also executed before obtaining the test portions of 200 g.

The third feedstock for pyrolysis was obtained through an additional particle size reduction of arW, down to 1 mm, in order to validate the procedure of using eq 1 to determine the particle size reduction before pyrolysis. In other words, to check if the first reduction step was enough to ensure that no enhancement on the uncertainty measurements during the characterization of pollutants occurred for smaller particle sizes. In this case, the milling was carried out in a WANNER mill with a 1 mm mesh and after separating the large metallic components of the sample, in order to preserve the equipment. A total of 130 g of metallic material were removed from a 2000 g sample. The subsequent homogenization and quartering process of the sample followed the same indications as for 2 mmW. This sample was codified as 1 mmW. The appearance of the three real samples used as the pyrolysis feedstock can be seen in Figure 1.

At last, a fourth blank sample composed of virgin materials, containing a known quantity of chlorine, was also used in order to assess the influence of the pyrolysis process itself in the inherent variability of chlorine concentration in the obtained oils. The composition of this sample was established as follows: 47.2 wt % high-impact polystyrene (HIPS), 26.7 wt % acrylonitrile butadiene styrene (ABS), 10.3 wt % polypropylene (PP), 10.3 wt % polyethylene (PE), 3.5 wt % polyvinyl chloride (PVC), and 2 wt % polyethylene terephthalate (PET). The real chlorine concentration in the PVC plastic was analyzed in advance for the control of the chlorine mass entering the pyrolysis process and happened to be 46 wt %. This is 10 points under the stoichiometric quantity of chlorine

in pure PVC resin, probably due to the presence of additives such as heat stabilizers and fillers that are usually added in the manufacturing step to improve the properties of the plastic.[25] All virgin plastics were used in pellets with a particle size of 4 mm. This sample was codified as an SS (simulated sample).

2.2. Pyrolysis Experiments. Pyrolysis experiments were performed in the laboratory-scale installation shown in Figure 2. The installation was composed of (1) a 3.5 L stainless-steel tank reactor, where the pyrolysis process took place in a semicontinuous regime at atmospheric pressure; (2) a two-stage condensation system, comprised of a first air-cooled glass condensation system and a second water-cooled glass condensation system for the recovery of condensable vapors that constituted the pyrolysis oils; (3) an activated carbon column for the cleaning of particles and lighter condensable compounds that may still be present in the gaseous fraction; and (4) gas sampling Tedlar bags, where the remaining gases were collected for their later analysis.

The pyrolysis solid (char) remained in the reactor after the experiments until the temperature decreased to a point where it can be safely recovered.

The operating parameters were the same for all the four samples studied: 100 g of sample fed at room temperature; 500 °C reaction temperature, with 15 °C min^{-1} heating rate; 30 min dwell time at the reaction temperature; and 1 L min^{-1} of nitrogen purge flow. The conditions were determined by previous experience of the authors with similar waste streams.[26−28] With specific regard to the final pyrolysis temperature, the authors' experience indicates that 500 °C is the optimum temperature for the maximization of oil yield with this type of feed. On the one hand, lower temperatures do not ensure the complete decomposition of the plastics present in the mixture. On the other hand, temperatures above 500 °C decrease the production of liquids and increase the generation of gases.[28] Process yields to each fraction are calculated as shown in eqs 2, 3, and 4. In these equations, mPR_f and mPR_i represent the pyrolysis reactor's final and initial mass, respectively, mCS_f and mAC_f, the final mass of the condensation system and the activated carbon column, respectively, and mCS_i and mAC_i the initial mass of both the condensation system and the activated carbon column, respectively. Two experiments were performed under the same operational parameters for each sample. The results of the yields presented in this work comprise the mean value of the two performed pyrolysis tests and their relative standard deviation (RSD).

$$\text{Solid yield(wt \%)} = \frac{(mPR_f - mPR_i)}{\text{WEEE feeding mass}} \times 100 \quad (2)$$

$$\text{Liquid yield(wt \%)}$$
$$= \frac{(mCS_f + mAC_f) - (mCS_i + mAC_i)}{\text{WEEE feeding mass}} \times 100 \quad (3)$$

$$\text{Gas yield(wt \%)} = 100 - \text{Solid yield} - \text{Liquid yield} \quad (4)$$

2.3. Analytical Techniques. The composition of the real sample (arW) was determined via visual analysis based on the experience of the authors, aided by NIR spectroscopy (KUSTA 4004M) and flame tests to determine the nature of some plastics present in the waste. This composition was taken as representative of the three real WEEE samples (arW, 2 mmW, and 1 mmW) used during this work. For the particle size

distribution analysis, a column of 11 different sieves was used (15.00, 12.00, 10.00, 5.00, 3.20, 2.50, 2.00, 1.50, 1.00, 0.50, 0.42 mm wide, respectively). 200 g of the arW sample were poured and after 5 min shaking, the remaining fraction in each sieve was collected and weighted. The bulk density of the real sample was measured by weighting the mass of the sample that a full 100 mL graduated cylinder held. The four samples (arW, 2 mmW, 1 mmW and SS) were characterized through organic elemental analysis (carbon, hydrogen, nitrogen, sulfur, oxygen, chlorine, and bromine) and proximate analysis (moisture, volatile matter, ash, and fixed carbon). Carbon, hydrogen, nitrogen, and sulfur composition (when >0.1 wt %) were measured via the LECO TruSpec CHN and LECO TruSpec S automatic analyzers according to the steps dictated by the EN-ISO 21663:2021 standard. The oxygen content was analyzed in a Eurovector Euro EA Elemental Analyzer. Chlorine, bromine, and sulfur (when <0.1 wt %) were analyzed following the EN 15408:2011 standard, which consists of the combustion of the sample in a calorimetric bomb and the adsorption of the hydrogen halides and sulfur oxides present in the combustion gases in a basic solution in the form of chloride/bromide and sulfates, respectively. This solution was later analyzed by means of ionic chromatography (Dionex ICS 3000). Sulfur was analyzed by this means for 2 and 1 mmW samples. The combustion of the samples was conducted in a LECO AC-500 automatic calorimeter following the EN-ISO 21645:2022. All these analyzed elements, in addition to those included in the "others" section, correspond to the organic part of the sample, while the inorganic elements are included in the ash content determined in the proximate analysis. For the proximate analysis, a LECO TGA-701 was used following the EN-ISO 21660-3:2021 standard for moisture, the EN-ISO 22167:2022 standard for volatile matter, and the EN-ISO 21656:2021 for ash determination. All the analyses were performed at least in triplicate to each sample. The main value of the three analyses, as well as the RSD between them, are presented in this work in the WEEE Sample Composition and Characterization section.

The composition of the pyrolysis oils derived from the four samples was measured by gas chromatography (GC), AGILENT 6890 series equipped with a J&W DB-FFAP capillary column (60 m × 0.320 mm × 0.25 μm), coupled with a mass spectroscopy detector (MS) AGILENT 5973 series. The concentration of compounds was obtained in area % and their identification was subjected to a match quality of more than 85% when comparing the obtained spectra with the one offered by the NIST-08 spectra library. Those components with a lower matching quality were subsumed as "Not identified (n.i.)", while those compounds well identified but with an area percentage lower than 2% were classified as "others". Organic elemental analysis was also performed for pyrolysis oils by the same means as those explained for the raw samples. The higher heating value (HHV) of the pyrolysis oils was determined with the same automatic calorimeter used for the combustion needed for halogen analysis. All of these analyses were performed in triplicate with each oil derived from at least two different pyrolysis experiments held under the same conditions for each sample. The mean value and the RSD of the results are compared and discussed in the Pyrolysis Oil Characterization section. Finally, the ash and water content on the oils was determined according to ASTM D482-19 and ASTM D1744-13, respectively.

The composition of the gases was measured by an Agilent 7890 series gas chromatograph (GC), coupled with a thermal

conductivity detector (TCD) and a flame ionization detector (FID). The quantitative characterization of the gases was performed via calibration of the main compounds usually found in the gaseous stream by a standard mix provided by Air Liquide. The results are given on a dry basis and free of halogenated, nitrogenated, and oxygenated organic substances. HHV was calculated theoretically based on each compound combustion enthalpy, attributing to each compound percentage its own HHV. The elemental composition and the proximate analysis of the solid fraction were determined by the same means as those explained for the raw sample. These analyses were not applicable to the SS, as not enough solid fraction could be retrieved after the pyrolysis process of the simulated sample.

3. RESULTS AND DISCUSSION

3.1. WEEE Sample Composition and Characterization.
The particle size distribution of the laboratory sample is shown in Figure 3. The laboratory sample presented a particle size
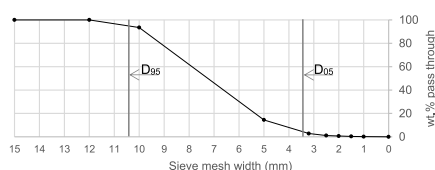

Figure 3. Particle size distribution of the as-received sample (arW).

distribution from 15 mm to dust, with the characteristic diameters D_{95} and D_{05} taking a value of 10.5 and 3.5 mm, respectively. The ratio D_{95}/D_{05} was 3, which indicates a quite broad particle size distribution, i.e., a heterogeneous waste in terms of particle size. On the other hand, the bulk density resulted to be 0.442 g cm^{-3}, close to other values reported by the authors working with similar samples.[29]

The material composition of the real sample is shown in Table 1, and, as stated before, it was considered to be the composition of arW, 2 mmW, and 1 mmW samples. The compositional analysis revealed a predominant polymeric nature of the sample since above 85% of the total weight happened to be plastics. This result was expected, taking into account the origin of the sample and the authors' previous results with samples obtained from the same WEEE treatment plant.[29,30] Styrenic plastics represented the highest percentage, as expected in this kind of stream where technical plastics are present to a great extent.[31] Polyolefins and other thermoplastics were the following materials with more presence in the mixture. It is worth mentioning that the presence of PVC, constituted both by the PVC chips and the PVC-coated metals (cables, 60 wt % on PVC), added 2.9 wt % of the sample. This will be the main agent involved in the release of chlorine during the pyrolysis process[8] and would eventually be distributed across the generated solid, liquid, and gaseous fractions of the pyrolysis. To a lesser extent, materials of different natures were also found in the sample, mainly

nonmagnetic metals and printed circuit boards (PCBs), constituting 3.2 and 2.7 wt % of the total weight, respectively.

Table 2 shows the chemical characterization of the samples, providing the mean value and the RSD of at least three analyses in the case of the original sample and the samples deriving from it. The simulated sample analysis, however, was conducted separately for each polymer composing the mixture and their elemental and ultimate analysis was calculated assigning each polymer result to its percentage in the mixture. The original sample, arW, revealed a C + H concentration above 70 wt %, in accordance with the material composition observed in Table 1, dominated by plastics. However, it was not as high as the values usually obtained with polyolefin-rich samples (≈85 wt %), as some of the predominant polymers in WEEE plastics are ABS, polycarbonate (PC), and their copolymers.[32] These kinds of plastics incorporate other elements such as nitrogen or oxygen, making the C + H sum lower, as can be seen in Table 2. As far as the elements that can give rise to hazardous pollutants and acid gases are concerned (S, Cl, Br), they were logically found in lower concentrations than the main ones. Chlorine was the most predominant, directly coming, as mentioned above, from the presence of PVC in the sample. The presence of sulfur was also related to being part of the composition of some of the polymers and rubbers of the sample, while the bromine content could be attributed to the BFR normally used in WEEE plastics.[8,33]

In general terms, the elemental analysis results of these samples were similar to those reported by other authors who have worked with plastic rejects collected from WEEE treatment plants.[33,34] As regards the comparison between the original sample and the two pretreated samples, no significant differences were found in the elemental analysis, except for bromine. It is worth noting that in the case of bromine, the concentrations measured in the samples with particle size reduction (2 and 1 mmW) were much higher than that measured in the arW sample (5087.5 and 5278.4 ppm, respectively, vs 396.4 ppm). This was the only case in which differences in chemical composition were observed between the different pretreatment procedures. However, as this is an important pollutant, its relevance is remarkable. It should be reiterated that arW was milled down to 2 mm for this characterization, so the only difference among these three samples is that 2 and 1 mmW were homogenized and quartered again after milling, as EN 15002 recommends. This result demonstrated that those elements present only in a certain fraction of the particles of a granular heterogeneous waste could be underestimated if this circumstance is not taken into account in the stages leading to the preparation of the test portions.

Table 2 also shows the results of the proximate analysis of the samples. In this case, no relevant difference was found among them, when in fact it could have been expected that the 1 mmW sample would have a lower ash value than the others since the metallic materials of this sample were separated at source. However, the content of metallic materials in the

Table 1. As-Received WEEE Sample Material Composition (wt %)

polyolefins	styrenic plastics	PVC	PVC + metal	other thermoplastics	rubbers	foams	PCB
13.2	45.0	1.7	2.0	23.2	1.6	0.1	2.7
textile	paper/cardboard	magnetic metals	nonmagnetic metals	petrous	multimaterial	others	fines (Ø < 2 mm)
0.3	0.1	0.0	3.2	0.1	1.5	2.9	2.4

Table 2. WEEE Sample Chemical Characterization

| | Ultimate organic analysis, as-received basis (wt %) | | | | | | | |
| | SS | | arW | | 2 mmW | | 1 mmW | |
	$\overline{x}$	RSD	$\overline{x}$	RSD	$\overline{x}$	RSD	$\overline{x}$	RSD
C	85.5		65.4	3.7	67.1	3.4	67.3	2.9
H	10.5		6.8	4.4	8.4	7.1	7.3	3.6
N	1.2		1.9	10.5	1.2	16.7	1.5	10.8
S (*ppm)	b.d.l.[b]		0.2	50.0	728.8*	14.3	591.1*	19.9
Cl (ppm)	16,450.0		7614.2	9.9	6700.0	4.6	8670.6	6.1
Br (ppm)	b.d.l.[b]		396.4	9.4	5087.5	13.6	5278.4	10.7
O	0.6		7.7	28.6	6.2	1.5	5.3	9.5
others[a]	0.2		4.9		2.4		5.5	
	proximate analysis, as-received basis (wt %)							
	SS		arW		2 mmW		1 mmW	
	$\overline{x}$	RSD	$\overline{x}$	RSD	$\overline{x}$	RSD	$\overline{x}$	RSD
moisture	0.1		0.4	25.0	0.6	22.3	0.6	10.0
volatile matter	98.9		83.2	1.8	83.1	0.9	83.5	2.3
ash	0.3		11.9	11.8	12.8	8.2	11.0	14.1
fixed carbon[a]	0.7		4.5	8.9	3.5	20.5	4.9	7.6

[a]By difference. [b]Bellow detection limit.

sample is low (3.2 wt %, see Table 1), and this result could indicate that the ash content of 1 mmW samples (higher than 10 wt %) was mainly generated by the inorganic fillers that the plastics may contain, rather than to nonorganic materials present in the mixture. In other words, the absence of metals in 1 mmW could have been compensated by the inorganic fillers. Anyway, all the three samples were mainly composed of volatile matter (>83 wt %), which is a very desirable characteristic for pyrolysis processes focused on producing oils and gases. These results also agreed with other proximate analyses published in articles working with similar samples.[30,34]

3.2. Pyrolysis Yields. Figure 4 shows the pyrolysis yields obtained with the four samples (SS, arW, 2 mmW, and 1 mmW). First of all, the behavior of SS will be explained, as it was used as a "blank experiment" to determine the influence of the pyrolysis process on the variability of pollutants in the oils. As can be seen, SS yielded liquids to a great extent (92.0 wt %), followed by gases (5.5 wt %) and solids (2.5 wt %). This

was a somehow expected result since the main plastics in SS, which were HIPS (47.2 wt %) and ABS (27.7 wt %), normally produce very high liquid yields under the employed pyrolysis conditions and, on the other hand, they do not show char-forming tendency.[35] Polyolefins do not generate char either, although their contributions to gases and liquids are usually more balanced. PVC and PET, however, are clearly recognized as char-formers and are probably responsible for the 2.5 wt % of solid yield in these experiments where SS was used.[36] Taking into account that the two samples used in the two experiments carried out with SS were exactly the same and that it is a homogeneous sample, it could be concluded that the deviation observed in the yields between experiments showed the inherent variability of the pyrolysis process, directly related to its experimental nature. As it can be seen in Figure 4, the obtained deviations in this case were very low (RSD of 0.0, 0.7, and 10.9% for the solid, liquid, and gas fractions, respectively), which confirms that the process is reliable for the obtainment of consistent results. In other words, it can be stated that the pyrolysis process itself did not introduce significant uncertainty in the pyrolysis yields.

The three WEEE-derived samples casted similar yields, showing a high tendency to the liquid generation at the reaction temperature, ~70 wt %, which can be explained by the same reasons used for SS, this is, the high quantity of styrenic plastics and polyolefins in the samples. Gas generation was greater than the one observed in the pyrolysis of SS, reaching values of ~10 wt %. Solid generation was also greater than in the case of SS pyrolysis, since in this case, apart from the carbon generated by the plastics, the nondegrading inorganic materials and fillers stayed as part of the solid fractions. A slight reduction in the solid production was observed for 1 mmW (the sample without large metallic pieces), which is not very conclusive, which could have enhanced the production of liquids. The deviation in the solid yield for the two performed pyrolysis tests was lower when the particle size was reduced, casting an RSD of 9.4, 0.5, and 4.3% for arW, 2 mmW, and 1 mmW, respectively. The RSD for liquid and gas yields stayed the same, with values near 3% for the liquids and 20% for the gases, and no effect was observed by the particle size reduction.
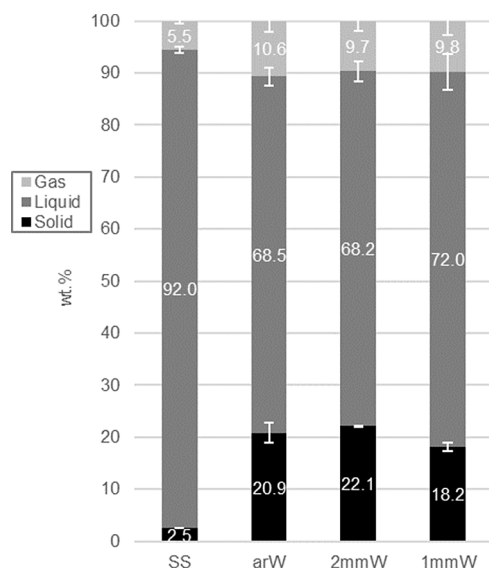

Figure 4. Pyrolysis yields.

Table 3. Pyrolysis Oils Organic Elemental Analysis (wt %), Water Content (wt %), and Ash Content (ppm)

	SS		arW		2 mmW		1 mmW	
element	$\bar{x}$	RSD	$\bar{x}$	RSD	$\bar{x}$	RSD	$\bar{x}$	RSD
C	85.0	1.1	78.4	1.4	78.4	1.8	81.5	1.6
H	9.0	1.3	7.8	3.8	8.5	4.4	9.6	3.4
N	0.8	3.5	2.0	5.0	1.6	9.2	1.3	6.9
S (*ppm)	b.d.l.[b]		0.10	7.5	351.9*	15.1	95.8*	9.3
O	n.d.[a]		4.2	12.2	0.9	8.2	2.2	18.7
Cl (ppm)	4118.6	11.6	5375.1	41.8	3794.4	7.7	4508.6	7.9
Br (ppm)	b.d.l.[b]		849.4	55.7	1944.9	10.4	2706.5	7.2
water	1.2		n.d.[a]		5.8		4.5	
ash (ppm)	0.03		n.d.[a]		0.18		0.01	

[a]Not determined. [b]Bellow detection limit.

Therefore, in this case, it could not be concluded that the different sample pretreatments had an obvious influence on the repeatability of the pyrolysis yields. Another important conclusion can also be drawn from these results, which is that in the range of particle sizes studied (1−10 mm) there did not seem to be important differences in the heat transfer phenomena between the furnace wall and the waste particles as no relevant changes in pyrolysis yields were observed. In other words, heat transfer did not seem to be a limiting phenomenon within this particle size range in the employed experimental installations and under the employed operating conditions. What can be observed is that the deviation of the experiments with the real samples was larger than in the case of the SS sample experiments, which is directly related to the heterogeneity of the real samples. The obtained pyrolysis yields were very similar to those reported by other authors working with similar samples in pyrolysis processes.[34]

3.3. Pyrolysis Oil Characterization. The organic elemental analysis of pyrolysis oils is shown in Table 3. As expected, the sum of C + H ranged from 86 to 92 wt % for real oils and even higher for the oil derived from the simulated sample. This was indicative of their hydrocarbon nature, which is typical of the pyrolysis oils coming from WEEE plastics.[37] The following element in quantity was nitrogen, ABS being its main precursor, as can be proven from the nitrogen content of the oils obtained with the simulated sample, which did not contain any other nitrogenous substance. Then, the pollutants sulfur, chlorine, and bromine were also detected. Sulfur in the oil coming from arW was measured using the elemental S analyzer by LECO, while the sulfur of the two other oils was measured by the combination of sample combustion in the calorimetric bomb and subsequent determination of sulfates in the liquid phase by ion chromatography. This could be the reason the concentrations are so different among them. Specifically, the sulfur content of arW was probably overestimated because the automatic analyzer is designed and calibrated to measure quantities bigger than 0.1 wt %, and the concentration in this case just fell in the lower limit of the calibration. In these circumstances, the precision of the measurement was probably compromised due to the proximity to the lower limit of calibration. In this respect, sulfur measurements in oils from the 2 and 1 mmW samples are considered to be more reliable. Concerning halogens, measured with the same analytical method, they appeared in range concentrations of 3800−5400 ppm for chlorine and 850−2700 ppm for bromine.

The deviation of the mean values of the main elements did not seem to be conditioned by the pretreatment of the sample,

as the values for C, H, and N were consistent for the two executed tests on each sample casting acceptable RSD values. It can be seen that, in the case of sulfur, the deviation of the measurement was higher in the pyrolysis oils of 2 and 1 mmW samples (RSD 12%) compared to that obtained in the oil of sample arW (RSD 8%), which gives the feeling that the result was more uncertain. However, it should be taken into account that the RSD is a relative measure of the deviation and that the mean values measured in the oils of samples 2 and 1 mmW were an order of magnitude lower than that of sample arW. This means that the deviation in absolute values from these mean values, which are very low, is also very small. When looking at the halogens, the situation was radically different. The SS-derived oils cast a deviation in the chlorine concentration of 11.6%, which discards the process as the main generator of the original deviation in the halogen concentration measures. Nevertheless, the RSD for the halogens concentration in arW-derived oils was over 40%, which meant a variance of almost 4000 ppm between the analyses of oils corresponding to different pyrolysis runs under the same conditions (it should be recalled that the chlorine concentration limit value for the acceptance of pyrolysis oils in some industrial processes is 3 ppm). In this case, the influence of the particle size reduction on the sample homogenization had a clear reflection on the deviation of the chlorine concentration in the oils. The RSD was strongly reduced for the milled samples, being 8% for both the 2 and 1 mmW-derived oils, which is a clear improvement when compared with the oils coming from arW. Bromine, the other halogenated pollutant in the oils, experienced the same fate as chlorine concerning deviation of the mean values, and besides, it could also be better characterized in terms of mean values (arW seemed to be underestimated) with the help of the particle size reduction. The results in Table 3 indicate that the approach of calculating the particle size needed for processing a given amount of waste through the recommended formulas for waste characterization is also valid for decreasing the variability of the concentration of contaminants in pyrolysis oils. The water content of the oils, also seen in Table 3, casted values above the initial moisture content of the sample, which indicates that oxygenated plastics release oxygen, promoting secondary reactions that lead to water formation. Finally, the ash concentration in the oils, below 1 ppm in each oil, is negligible, as the values set by legislation for fossil fuels are around 100 ppm. It is worth mentioning that the lower concentration of ash corresponded to the oil derived from the sample to which the metallic fraction was retrieved before the particle size reduction, 1 mmW. In this sense, it can be

Table 4. Composition (Area %) and HHV (MJ kg^{-1}) of the Pyrolysis Oils of This Work and Comparison with Other Research

	area %						
compound classes	SS	arW	2 mmW	1 mmW	Caballero et al.[37]	Stefano et al.[42]	Amodio et al.[43d]
hydrocarbons	91.2	70.2	71.3	78.5	47.5	61.2	30.0
aliphatic hydrocarbons	<2	<2	<2	<2	n.d.[a]	17.7	3.0
aromatic hydrocarbons	91.2	70.2	71.3	78.5	47.5	43.5	27.0
oxygen compounds	n.d.[a]	18.2	18.0	14.2	36.0	10.5	7.5
phenol		11.2	11.1	10.1	21.9	8.5	n.i.a.[c]
phenol derivatives		7.0	6.9	4.1	14.1	n.i.a.[c]	
other oxygen compounds		n.d.[a]	<2	n.d.[a]	n.d.[a]	2.0	
nitrogen compounds	3.7	3.4	3.7	2.9	4.7	25.3	12.0
benzenebutanenitrile	3.7	3.4	3.7	2.9	4.7	8.3[d]	5.0
others	1.0	0.1	1.2	1.8	3.4	n.i.a.[c]	n.i.a.[c]
n.i.[b]	4.1	8.1	5.8	2.6	8.4	3.0	n.i.a.[c]
HHV (MJ kg^{-1})	42.1	36.2	34.2	36.2	34.4	38.7	40.4

[a]Not detected. [b]Not identified. [c]No information is available. [d]Estimated results in wt %.

Table 5. Composition (vol %) and HHV (MJ/Nm^3) of the Pyrolysis Gases

	SS		arW		2 mmW		1 mmW	
compound	$\bar{x}$	RSD	$\bar{x}$	RSD	$\bar{x}$	RSD	$\bar{x}$	RSD
CO$_2$	13.8	5.4	28.8	1.9	39.3	8.3	48.4	1.6
H$_2$	b.d.l.[a]		13.6	22.3	11.2	6.3	12.7	7.2
CO	8.1	1.3	15.7	28.8	10.4	14.1	10.7	3.6
CH$_4$	35.5	5.0	17.0	21.5	18.0	4.1	17.4	14.7
C$_2$H$_4$	17.9	11.1	5.2	33.6	4.9	2.0	3.6	30.8
C$_2$H$_6$	12.2	3.6	6.7	36.2	5.9	7.3	4.5	45.0
C3−C5	12.5		13.0		10.3		2.7	
HHV (MJ/Nm^3)	38.0	1.7	27.3	11.5	23.1	25.1	15.5	6.1

[a]Below detection limit.

considered that the source of inorganic species in the oils is the mechanical drag exerted by the pyrolysis vapors as they leave the reactor.

Particle size reduction could also promote changes in the oil composition and HHV, as the heat transfer among the particles was altered. The compositional analysis for arW-, 2 mmW-, and 1 mmW-derived oils, in Table 4, however, revealed that the nature of the oils was not significantly altered by the reduction in the particle size, which confirms the conclusion obtained concerning heat transfer derived from the pyrolysis yields results. The oils were mainly composed of styrene (over 40% area) and other aromatic compounds such as ethylbenzene, toluene, and α-methylstyrene, the main by-products of the polystyrene thermal depolymerization.[38−40] Phenol and its derivatives also had a great presence in the liquids, as the oxygen originally present in the sample enhances their production. Benzenebutanenitrile, the main nitrogenous organic substance in the oils, is also a common outcome of the ABS pyrolysis, as the styrene and the acrylonitrile, which are part of this copolymer, cleavage and recombine together.[41] The main compounds found in the SS-derived oils also belonged to the aromatic hydrocarbons family, being the major constituents styrene (58 area %) and the other main by-products of the polystyrene thermal decomposition. In contrast to the WEEE sample-derived oils, the low oxygen concentration in the SS prevented the formation of oxygenated compounds in the oils, to the extent that no oxygenated compounds were detected in the GC-MS analysis, which is in accordance with the elemental analysis presented in Table 3. Nitrogenated compounds, in the form of benzenebutanenitrile,

are also present in the SS-derived oils, which confirms the ABS of the original feed as the main precursor of this compound.

Table 4 also shows the composition of oils obtained by the authors and other authors in the pyrolysis of WEEE plastics, where it can be seen that such a composition strongly depends on the nature of the specific WEEE plastic pyrolyzed. For example, Caballero et al.[37] obtained more oxygenated liquids in the pyrolysis of plastics from telephones, while Stefanol et al.[42] and Amodio et al.[43] reported highly nitrogenous liquids in the pyrolysis of external cases of small appliances and mixed plastics with high nitrogen content (mainly composed of PC/ABS). As regards the nature of the hydrocarbons, it appears that in all cases the generation of aromatic hydrocarbons predominates over aliphatic hydrocarbons. As can be seen in Table 4, no halogenated species were detected by GC-MS analysis, so no speciation study of these substances in the oils could be performed. However, the most reported halogenated species in the literature in pyrolysis processes of WEEE plastics are chlorobenzene, 1-chloro-2,3-dihydro-1H-indene, 1-chloroethylbenzene, chloro-acetic acid hexadecyl ester, 8-phenyl-1-octyl chloride, 2-chloropropylbenzene, 2-bromophenol, 2-bromo-4-chlorophenol, 1-bromomethyl-4-methylbenzene, and antimony bromide, due to the presence of antimony as a synergistic element in BFR.[44−46] At last, HHV stayed in similar values for the three WEEE-derived samples (∼36 MJ/kg) and was similar to those obtained by the authors mentioned above, while the lack of oxygenated compounds in the SS-derived oils increased their HHV.

3.4. Pyrolysis Gas Characterization. The composition and HHV of the pyrolysis gases are presented in Table 5. Gases from SS were very rich in hydrocarbons, showing

methane (CH_4, 36.3 vol %) and ethylene (C_2H_4, 18.3 vol %) as the main constituents, followed by carbon dioxide (CO_2, 14.2 vol %), ethane (C_2H_6, 12.5 vol %), and propylene (C_3H_6, 10.6 vol %). Hydrocarbon-rich gases are normally formed in the pyrolysis of plastics, such as PS, PE, and PP, which were present in significant quantities in the SS.[28] On the other hand, the high proportion of CO_2 (and also CO) directly came from the thermal decomposition of PET and the acrylonitrile of ABS.[47] The relatively low RSD values of the SS-derived main gas characterization also allow us to discard the process as the principal generator of the variability in the results. When real samples were pyrolyzed, a predominant tendency for the formation of CO_2 and CO was observed, enabled by the higher quantities of oxygen (and probably oxygenated plastics) in the real sample. Also noteworthy was the generation of hydrogen in the gases of the real samples, which could be attributed to enhanced cracking promoted by the metals present in the sample, which have sometimes been attributed to catalytic functions in pyrolysis processes.[37] Particle size reduction helped to enhance the repeatability of the gaseous stream composition analysis, significantly reducing the RSD cast by the main compounds. In this case, the sample pretreatment had a clear influence on the composition of the gaseous stream, as for a smaller particle size a greater production of CO_2 is observed to the detriment of other compounds as CO and the hydrocarbons in the range from C2 to C5. Finally, the HHV of all of the samples was tightly linked to the CO_2 concentration on the gaseous stream, as its no combustion potential decreases the HHV of the total mix proportionally to its concentration. It is worth mentioning that the HHV of the three waste-derived gaseous streams is close to 40 MJ/Nm³ on a CO_2-free basis. This suggests the potential of these gases to be used as alternative fuels after a CO_2 adsorption process.

3.5. Pyrolysis Solid Characterization. Pyrolysis solids could be collected alongside the inorganic matter present in the feed for all of the original samples and their milled counterparts. However, this was not the case for the SS solids, whose relatively low yield to the solid fraction did not allow the collection of enough solid for its characterization. The studied solid fractions were evaluated by means of elemental and proximate analysis and the results are shown in Table 6. As expected, the ash concentration in the solids was very high and

in good accordance with the ash content shown in the proximate analysis of the three different feeds because all of the inorganic content on the original sample is collected in the solid fraction of pyrolysis. This meant that the concentration of carbon in the solids, although it was the element found in the highest concentration, was lower than that of ash, casting doubt on whether this product can be considered a carbon-like product in this case. With regard to the rest of the elements, the oxygen retention capacity of these pyrolysis solids is of note. Regarding the proximate analysis, the solids showed more fixed carbon than volatile matter, as expected after a pyrolysis process. Particle size reduction also helped in the enhancement of the results in the solids analysis, as it can be observed in Table 6, as for a smaller particle size the RSD of the four main elements analyzed in the elemental analysis was significantly reduced. However, this was not the case for the pollutants characterization, where the main components RSD casted values around 18 and 24% for every sample.

4. CONCLUSIONS

The main conclusion of this work is that the particle size of the sample has a critical role in the variability of some chemical properties of the oils coming from the pyrolysis of plastic-rich waste. These chemical properties are those related to the elements that only appear in some particles constituting a heterogeneous waste. In the case of plastic mixtures coming from WEEE sorting, these elements are mainly halogens, the concentration of which must certainly be determined in the oils before commercialization. ECN procedures for sample analysis (EN 15002:2015) have been found to be adequate to estimate the particle size for pyrolysis processing, i.e., at levels beyond the mere sample preparation for its characterization. In this sense, the ECN standard has helped with the homogenization of the sample and thus in the homogenization of the pollutants that enter the process and subsequently end in the oils.

It has been demonstrated that the deviation in the low-concentration pollutant analysis, key in any industrial application of pyrolysis products, is excessive when this issue is not taken into account. The RSD in the pollutant analysis of two different oils obtained under the same experimental parameters was reduced from 42 to 8%, which can be considered a proper step forward taking into account the original heterogeneity of the sample. The particle size reduction at the tested conditions, in contrast with what was initially thought, did not suppose any significant change in the pyrolysis yields or in the oil nature, as their composition and HHV stayed almost unaltered. Apart from that, the tests carried with the simulated sample have contributed to the discarding of the pyrolysis process itself as responsible for the variability of the pollutant distribution in the pyrolysis oils.

As for the other two major pyrolysis fractions, gas and solid, the pretreatment of the sample did not have such a pronounced effect on their characterization. In the case of the gaseous fraction, while the particle size reduction helped to improve the characterization of the main compounds, it also changed their composition, enabling a higher production of CO_2, and thus, reducing its HHV. As for the solid fraction, the influence of the milling on the main elements analysis and proximate analysis was noticeable, achieving the reduction of an RSD that was already acceptable in the first place. However, no enhancement in the deviation of the pollutant characterization was obtained.

Table 6. Pyrolysis Solid Ultimate and Proximate Analysis

element	arW $\bar{x}$	arW RSD	2 mmW $\bar{x}$	2 mmW RSD	1 mmW $\bar{x}$	1 mmW RSD
pyrolysis solids organic elemental analysis (wt %)						
C	36.8	6.5	36.4	1.4	38.9	5.7
H	1.0	7.2	1.6	7.3	1.4	8.8
N	1.4	11.1	1.0	6.0	1.1	5.6
O	1.4	8.3	3.3	0.6	3.9	22.6
S (ppm*)	0.12	38.6	899.7*	20.2	807.0*	12.4
Cl (ppm)	11,163.7	24.2	7279.1	19.3	9302.4	23.9
Br (ppm)	3702.9	25.3	2752.9	18.4	4853.2	19.8
others[a]	3.1		1.3		1.3	
pyrolysis solids proximate analysis (wt %)						
moisture	4.4	28.1	1.7	24.2	2.1	15.9
volatile matter	10.2	8.2	9.4	5.1	12.5	1.6
ash	50.3	4.1	53.6	5.8	49.8	2.2
fixed carbon[a]	35.1	1.2	35.3	4.0	35.6	2.0

[a]By difference.

From the results obtained in this work, it can be suspected that the batches of oil produced at the industrial level may contain highly variable concentrations of halogens, which may compromise the commercial contracts of these plants. This issue is especially critical, keeping in mind the low-concentration limits for some pollutants in plastic pyrolysis oils (some ppm). In this sense, the authors recommend paying attention to minimizing as much as possible the effect of the fundamental variability of mixed plastic waste streams through homogenization and, mainly, particle size reduction techniques. Finally, the authors believe that this issue should be taken into account when designing future industrial plastic pyrolysis processes, insofar as it affects the grinding and waste conveying stages and, of course, the heat transfer phenomena.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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