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Research Paper

Enabling the recycling of metals from the shredder light fraction derived from waste of electrical and electronic equipment via continuous pyrolysis process

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ABSTRACT

The surge in Waste Electrical and Electronic Equipment (WEEE) generation, reaching 53.6 million metric tons (Mt) in 2019, demands efficient recycling solutions. This study focuses on the Shredder Light Fraction (SLF), a material stream derived from the mechanical pre-processing of WEEE, which is considered “municipal waste”. SLF constitutes 4.2% of the output material and is rich in metals like copper, tin, lead, zinc, silver, and gold.

Pyrolysis treatment was applied to SLF, enabling recyclability. Both batch and continuous setups were employed for materials flow analysis and technical evaluation of the resource potential. The research evaluates the impact of pyrolysis technology on solid fraction metal content and pyrolysis gas/oil energy potential. Scaling up the process addressed material heterogeneity and increased the reliability of the obtained results.

An innovative pyrometallurgical extraction approach was suggested, to recover valuable metals in SLF which otherwise could be lost via energy recovery methods. The resulting solid product after pyrolysis showed enriched concentrations of copper, zinc, lead, and precious metals with concentrations acceptable for industrial use. Additionally, it displayed reduced mass and diminished hazardous constituents.

The non-condensable gas, rich in hydrogen, carbon monoxide, and methane, exhibited potential as an alternative energy source or reducing agent in the metallurgical sector.

This research advances metal recycling from SLF, offering valuable insights for environmental impact mitigation as waste was transformed into a valuable by-product for potential use in the copper industry.

1. Introduction

Waste from Electrical and Electronic Equipment (WEEE) has become one of the fastest-growing waste streams, reaching 53.6 million metric tons (Mt) worldwide in 2019. The total generation of WEEE has increased by 9.2 Mt since 2014 and is projected to reach 74.7 Mt by 2030 due to an annual increase in Electrical and Electronic Equipment (EEE) consumption of 2.5 Mt (Forti, 2020). Therefore, an efficient and sustainable solution for WEEE recycling is necessary. WEEE recycling involves the collection, pre-processing, and recovery of metals (Vanegas et al. 2017). After collection, WEEE is sent to pre-treatment facilities where toxic substances like PCB and mercury-containing components are removed. Manual separation of metallic parts follows to avoid unnecessary shredding, and then they are transferred to appropriate recycling facilities (Bigum et al. 2012; Bilitewski and Härdtle 2013; Fujita et al. 2014). The unsorted material is crushed to promote individual component liberation (Chagnes 2016). Once sufficient liberation is achieved, the crushed waste stream is sorted based on physical properties like magnetic, conductivity, and density into its main constituents and various fractions, including steel or Fe-fraction, copper fraction, aluminium, plastics, etc.(Bilitewski and Härdtle 2013; UNEP 2013).

However, challenges persist in effectively liberating and separating valuable elements that may be bound to lower-value materials, leading to metal losses and increased waste generation (UNEP 2013; C. Meskers et al. 2009). A significant example of such problematic waste is shredder residue (SR), also known as “light fraction” or “fluff.” SR is produced as a residue of density separators, such as air classifiers or cyclones, and is characterized by its low density and diverse composition (Vijayan et al., 2022; Veit, 2015). SR typically contains light metals, paper, cardboard, foam, textiles, wires, wood, metals, glass, and various types of plastics, making material recovery a challenging task (Vijayan et al. 2022a; Jiri

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Hyks et al. 2014).

After being banned from landfills, for example, in Germany in 2007 (Holzer 2007; Michael Brunn 2017), SR from the automotive sector (ASR) has been studied at academic and industrial levels to develop strategies to handle such complex material stream properly. Some of these methods are based on energy recovery in a fluidized bed, rotary kiln, cement kiln, or on thermochemical processing in a pyrolysis or gasification plant (Jiri Hyks et al. 2014; Rotheut et al. 2015; Schulte et al. 2023). The main reason is due to the considerable intrinsic heat of SR (LHV 18830 kJ/kg). However, the main problem with this method is the poor recovery rate of the valuable metals, which cannot be adequately separated and are lost after treatment. In addition, the presence of heavy metals limits their use as energy substitutes in the cement industry because of environmental constraints (Jiri Hyks et al. 2014).

The SR from WEEE pre-treatment is known as shredder light fraction (SLF), comprising approximately 4.2 % of output materials with a high concentration of primary metals such as copper, tin, lead, zinc, silver, and gold (Ueberschaar et al. 2017). The resource potential found in SLF and the added cost of disposal drive pre-processing companies to find more efficient strategies to handle SLFs. It is worth noting that a direct use of this sort of material in common metallurgical processing for metal extraction, could lead to different challenges, such as, handling of halogens present in flame retardants, heterogeneous composition and complex morphology for feeding into metallurgical aggregates (Jacob Wood et al. 2011; Reuter and Matusewicz 2011).

Pyrolysis, or cracking, is an irreversible thermochemical process that leads to decomposition of organic matter at elevated temperatures (300–900 °C) in the absence of oxygen. During this process, complex polymer structures break down into smaller intermediate products, such as oil, gas, and char/solid (Vijayan et al. 2022a; Zuo et al. 2011; Alex Luyima 2013). Compared to energy recovery methods like incineration, pyrolysis avoids metal oxidation and promotes the concentration of weak metal oxides in the solid product, beneficial for downstream metallurgical recycling of metal-containing scraps (Diaz et al. 2015; Gabriele 2019). In addition, the production of high-quality pyrolysis gas, which is usually rich in hydrogen, methane, carbon monoxide, and other hydrocarbons (Nunes et al. 2017; Ciuta et al. 2017), could be beneficial for metallurgical applications in reduction processes or as a greener energy source.

Pyrolysis of different fractions from the commercial WEEE categories, such as printed circuit boards (Zhu et al. 2023; Liu et al. 2023), solar panels (Wang and Shen 2022; Trivedi et al. 2023), and others (Schulte et al. 2023; Charitopoulou et al. 2022), has also been explored. In addition, as an alternative to direct energy recovery, the use of pyrolysis as a pre-treatment for SR has already been investigated for automotive shredder residue (ASR) (Vijayan et al. 2022a; Day et al. 1996; Vijayan et al. 2022b; Manente et al. 2022). However, no information about pyrolysis of SLF from WEEE has been documented.

In this context, SLF remains categorized as "municipal waste" or "general waste" (Mikalsen et al. 2021), overlooking its essential resource potential in terms of metal content and pousing a relevant risk of hazards associated with landfills or storage facilities (Mikalsen et al. 2021).

To implement pyrolysis technology as a solution to transform SLF from waste into a recyclable product, it is essential to consider the significant influence of process parameters on pyrolysis products. Parameters studied in pyrolysis include chemical composition, types of organics or polymers, process temperature, heating rate, residence time, reactor type, pressure, and particle size. Current state-of-the-art results indicate that operating pyrolysis at high heating rates in continuous operation, with low residence time and enhanced catalytic conditions, improves the quality of pyrolysis gas. This leads to increased generation of key stable short molecules, such as hydrogen, carbon monoxide, and methane (Scheirs and Kaminsky 2006; Basu 2010; Ali et al. 2014; Acomb et al. 2013). Moreover, improved cracking performance reduces the generation of oils, which primarily consist of long-chain hydrocarbons like naphthenes, aromatics, paraffin, and olefins (Epple et al. 2009; Luda 2012).

In summary, in contrast to most of the fractions derived from WEEE, SLF is still considered as "waste". Therefore, metals presented in this fraction are lost due to incorrect treatment methods, mainly focused on energy recovery through incineration. Moreover, SLF is rejected from the metallurgical sector due to its inherent characteristics like density, morphology, and the expected excess of heat if used directly in pyrometallurgical extraction methods. It is worth noting that no studies have been reported on SLF from WEEE prioritizing the resource potential based on metal content and suggesting an effective strategy to recover these metals.

In this context, this research strives to transform SLF waste into a recyclable material via continuous pyrolysis and evaluate the outcomes from a metallurgical perspective. This inquiry is significant because this waste originates from WEEE, one of the most crucial waste stream containing vital resources for modern life (Shittu et al. 2021). This approach fosters a relevant discussion regarding the production of high-quality byproducts as an alternative means to reintegrate resources from Shredder Light Fraction (SLF) derived from WEEE back into the value chain. Additionally, the study scrutinizes the quality and composition of pyrolysis gases and oils.

This study evaluated the pyrolysis technology using the previously mentioned "best parameters", including continuous operation, high heating rate, low residence time, and increased scale to overcome the heterogeneity challenge. The investigation involved a comprehensive analysis of the treated material using both batch-wise and continuous setups. The batch-wise trials were conducted to assess the pyrolysis products and principles applied to the studied material in a laboratory environment, while the continuous operation provided insights into a closer industrial setting.

In this framework, comparing the technology on batch and continuous is only done for academic reasons and not to generate technological competition, as both setups offer different insights from the process based on the parameters used. The aim is to gain a comprehensive understanding of the pyrolysis process applied to SLF in two different setups and its potential for resource recovery.

2. Material and methods

2.1. Laboratory-scale batch pyrolysis

The setup used for lab-scale batch pyrolysis is illustrated in Fig. 1 (A). It comprises a tubular reactor with a volume of 19 L, placed inside a resistance heating furnace. The experimental procedure involved loading the reactor with 2 kg of SLF and purging it with argon to eliminate atmospheric oxygen. Throughout the experiment, argon was continuously supplied into the reactor at a rate of 10 L/min. The reactor was then gradually heated to 650 °C with a heating rate of 2.5 °C/min, and held at this temperature for a dwell time of 90 min.

The gas produced during the pyrolysis process was directed through a heated hose to prevent premature condensation and clogging. It was then passed through a water-cooled condenser and a wet scrubber. The non-condensable gas that exited the system was subsequently burned out. Additionally, part of the produced gas was pumped into an online FTIR analyzer at a rate of 2.2 L/min for further analysis and characterization.

The mass balance of the products in this experimental setup was determined through direct gravimetric measurement of the solid product, gravimetric measurement of the condensed matter, and the remaining portion considered as volatile matter, with the total mass of the input material being 100 wt% of the distributed products. The separation of the pyrolysis oil from the water solution collected in the condenser was performed using a decantation procedure.

Analysis of pyrolysis oils was conducted following the norms DIN 38407–2 (GC–MS-Screening), DIN EN 14582 (Bromine and Chlorine),

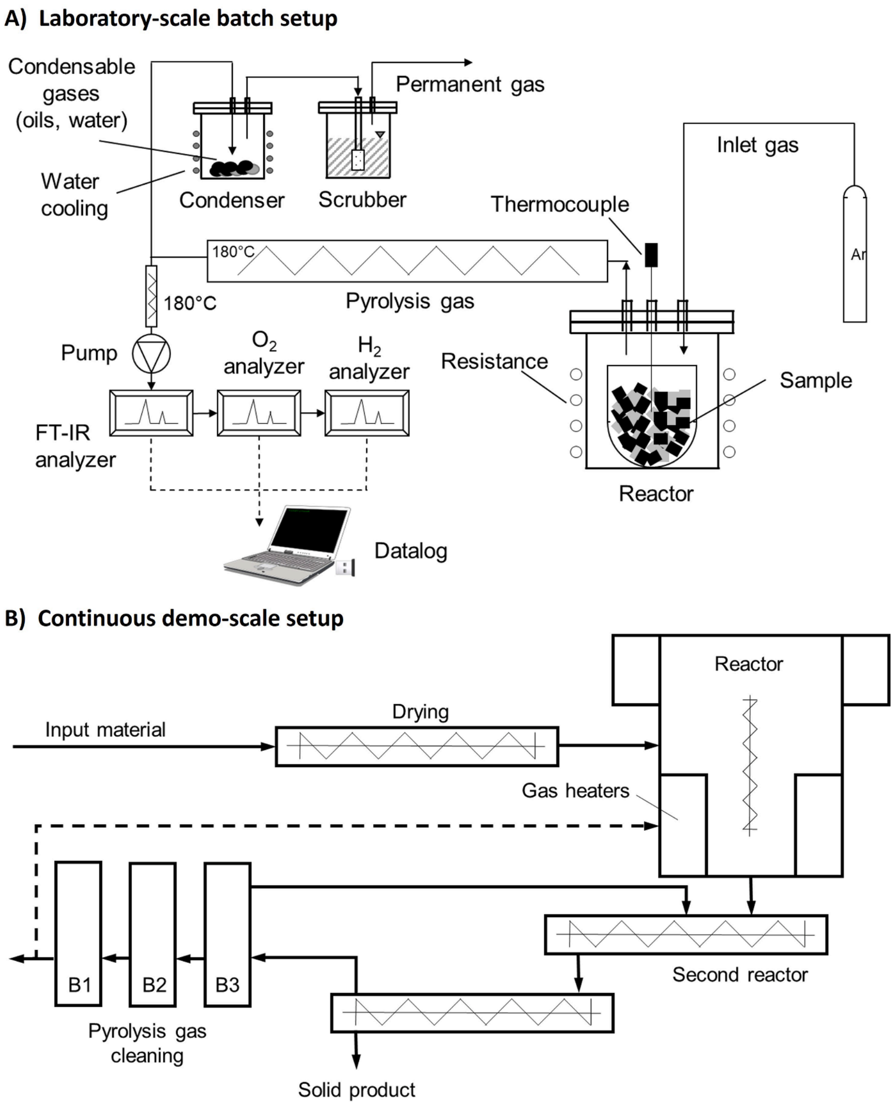

Fig. 1. A) Schematics of the setup used for the laboratory-scale batch pyrolysis, B) Schematic of the pilot plant used for the continuous demo-scale pyrolysis.

DIN 51732 (carbon), DIN 51900–1 (Calorific value), DIN 51732 (hydrogen and nitrogen), and E DIN 51777 (water content using the Karl Fischer principle). The water collected in the wet scrubber was also analyzed for the same selected elements (bromine, chlorine, carbon, hydrogen, nitrogen, and calorific value) as measured for the pyrolysis oil, following the same norms. Additionally, samples of the permanent gas after scrubbers were collected for chemical analysis (DIN 51872).

The FTIR analyzer utilized in these experiments was the Gasmet DX4000 spectrometer, capable of measuring H_2O, CO_2, CO, NO, NO_2, N_2O, SO_2, NH_3, CH_4, HCl, HF, and various volatile organic compounds. Gas samples were collected using a portable sampling system every 20 s, then transferred to the measuring cell and heated to 180 °C to prevent condensation of the produced gases.

In addition to the Gasmet DX4000, a PMA 10 paramagnetic O_2 analyzer and an LFE Conthos 3E thermal conductivity H_2 analyzer were also employed to detect O_2 and H_2 in vol %.

2.2. *Demo-scale continuous pyrolysis*

Demo-scale pyrolysis was conducted at Kunststoff- und Umwelttechnik GmbH in Forst, Germany, using a continuous pilot plant, as depicted in Fig. 1 (B). The process involved charging the material into an endless screw at a rate of 2 kg/min and pre-drying it in an oven to remove moisture before feeding it into the pyrolysis reactor.

Inside the reactor, the pre-dried SLF was continuously heated using a gas burner in the jacketed chamber. The reactor temperature could be controlled within the range of 400 to 850 °C. Although the exact final temperature and heat distribution inside the reactor was challenging to establish due to the reactor's construction and inhomogeneous material composition, the system was set up and monitored to maintain temperatures of at least 600 °C and a maximum of 800 °C during the continuous process.

To ensure continuous decomposition, an endless screw recirculated the treated SLF within the reactor, constantly moving the material towards the top. Once the pyrolyzed SLF reached the desired particle size smaller than 5 mm, it was transferred to a second reactor where pyrolysis gas was injected back after being cleaned. This additional step promote further decomposition and cracking of long-chain hydrocarbons from the pyrolysis gas.

The produced gas underwent cleaning through a sequence of three wet scrubbers (B3-B1 on Fig. 2 (B), which also collected condensable gases (oils and water) as they were being quenched. The scrubbers had a pump system that allowed the recirculation of water and condensed matter to produce homogeneous samples for characterization. The

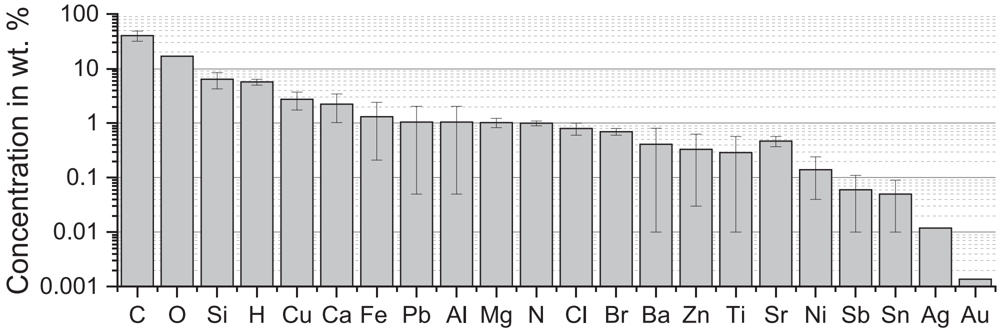

Fig. 2. Chemical composition of studied Shredder Light Fraction (SLF) from WEEE.

permanent gas was subsequently burned outside the plant.

In the demo-scale experiment, 250 kg of SLF was used, and the duration of the trial was approximately 3 h. During the trial, the solid product was collected every hour for further analysis, while pyrolysis oil and water samples were collected from each scrubber every 60 min. Due to the demo plant setup, online analysis of the off-gas was not possible. Instead, gas spectrometric analysis was conducted on three gas samples taken every 60 min. To collect these samples, a gas collecting tube was positioned after the scrubber and before the burner and flushed only with permanent pyrolysis gas to capture the gas sample. During sampling, a flame was ignited at the end of the gas collecting tube to ensure gas flow and prevent any oxygen from entering. After 1 min, the bottles containing the gas samples were sealed and removed from the apparatus for analysis.

The mass balance determination process for the continuous system was similar to that used in lab-scale batch experiments, but it also accounted for the wet scrubber plant used for pyrolysis gas cleaning. The total weight of each scrubber unit was measured before and after the experiment to calculate the mass balance of condensed water and oils. Additionally, the oil and water collected from the three scrubbers were sent for analysis following the same preparation as the lab-scale batch procedure.

2.3. Physical preparation of solid materials for chemical analysis

The input material (SLF- Fig. 3 (A)) underwent cryogenic milling to prevent overheating during the milling process and enhance the brittleness of both organic and metallic components. Two different analytical methods were applied to this milled material: X-ray fluorescence (XRF) screening (DIN 51001) and Inductively coupled plasma optical emission spectrometry (ICP-OES) using brom-methanol digestion (ISO 5416). The last one enabled the discrimination between metallic and non-metallic fractions in the milled material, providing information on the elemental composition.

To determine the calorific value, carbon, hydrogen, nitrogen, and oxygen content, the respective norms DIN 51900–1, DIN EN ISO 15350, DIN 51732, DIN EN ISO 15351, and DIN EN 10276–2 were followed. The same norms used for the SLF sample were followed to determine the calorific value, carbon, hydrogen, nitrogen, and oxygen content in the pyrolyzed material. These analytical methods and characterizations help in understanding the composition and properties of materials before and after undergoing the pyrolysis process.

The solid products obtained from both the lab-scale batch and demo-scale continuous pyrolysis were prepared for chemical analysis. To begin, the samples were pulverized using a Fritsch Pulverisette 6 planetary ball mill and then separated into three fractions with particle sizes of < 90 μm and 90–200 μm using a Retsch AS200 sifting machine.

For the metallic parts of each fraction with sizes > 200 μm, the analysis was conducted using inductively coupled plasma-atomic emission spectrometry (ICP-AES) after dissolution in aqua regia. This analytical method is well-suited for detecting elements in low concentrations or even trace elements (in parts per million).

For the non-metallic fractions (<90 μm and 90–200 μm), X-ray fluorescence spectrometry (XRF) was used as the primary characterization method. The analysis was performed using a PANalytical WDXRF spectrometer Axios with the Pro-trace program mode, which is specifically designed for trace element analysis (in the lower ppm range) of slags, flue dust, ores, and minerals. Halogens (Cl and Br) were determined through XRF analysis following the DIN 51001 standard.

2.4. Methodology for net calorific energy determination from pyrolysis products

The following formulas (1–5) were used to determine the distribution of the net calorific energy among the pyrolysis products for both batch and continuous pyrolysis.

$$E_{p.product,a}[\%] = \frac{LHV_{P.Product}, a^{*}m_{P.product,a}}{LHV_{SLF}{}^{*}m_{SLF}} \tag{1}$$

$$E_{p.Losses}[MJ] = LHV_{SLF}{}^{*}m_{SLF} - \sum\nolimits_{i=1}^{p} LHV_{P.Product,i}{}^{*}m_{P.product,i} \tag{2}$$

$$LHV_{P.Gas}\left[\frac{kJ}{kg}\right] = \sum\nolimits_{j=1}^{q} LHV_{component,j}{}^{*}X_{component,j} \tag{3}$$

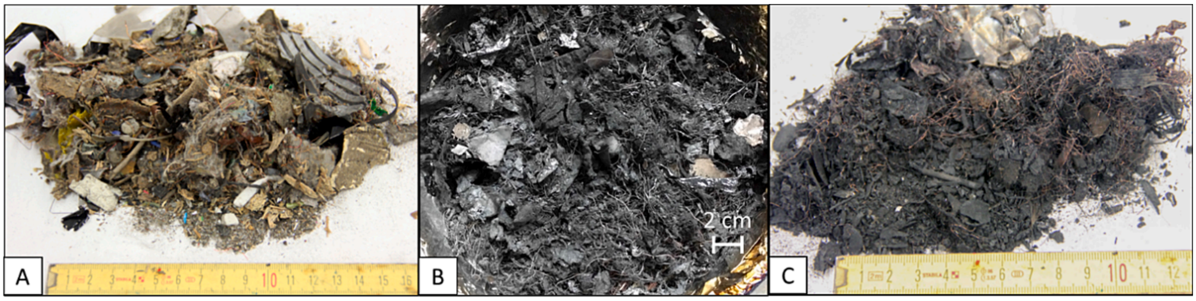

Fig. 3. Visual comparison of SLF before pyrolysis (A), after lab-scale batch pyrolysis (B) and after demo-scale continuous pyrolysis (C).

$$X_{component,j} = \frac{m_{component,j}}{\sum_{k=1}^{q} m_{component,k}} \tag{4}$$

$$m_{component,j}[kg] = \varnothing_{component,j} {}^{*} \rho_{component,j} \tag{5}$$

In this case, ∅ represents the volume in m^3 of gas component *j* per 1 m^3 of pyrolysis gas. ρ indicates the density in kg/m^3 at normal conditions of that component, m the resulting mass of a component *j* in kg, *q* the number of detected components, *X* the mass fraction of a component j, LHV the low heating calorific value in kJ/kg according to the defined denotation, $E_{p.product,a}$ represents the resulting net calorific energy distributed in a specific pyrolyzed product “a”, which can be pyrolysis gas, condensed oil and water, pyrolyzed solid product. In addition, $LHV_{SLF}{}^{*}m_{SLF}$ represents the net calorific energy of the studied SLF, and $E_{p.Losses}$ represents the difference between the net calorific energy in the input material and all products combined. Notably, the mass balance and net calorific energy distribution were modelled as 1000 kg of SLF using the collected results from the batch and continuous pyrolysis.

The total volume per component of gas produced during laboratory-scale pyrolysis can be calculated by integrating the time-concentration records from FTIR, obtaining the total volumes in NL, as shown in equation (6).

$$\mathbf{V} = \frac{1}{d}\sum_{i=0}^{n} \dot{V}(\mathrm{ti}+1-\mathrm{ti})\,(\mathrm{ci}+1+\mathrm{ci})\,/\,2 \tag{6}$$

Determination of the heat value of pyrolysis gas for the laboratory experiments, presented in Table 2 (section 3.4), has been determined using the chemical composition of individual components and normalization of the FTIR data from the Batch system. The normalization was performed by isolating their concentration from condensable substances based on the total volume produced and assuming the volume of gas generated during pyrolysis is negligible compared to the amount of argon gas flowing as a carrier medium.

3. Results and discussion

3.1. Shredder light fraction from WEEE recycling

Based on optical observation, SLF is a heterogeneous material primarily consisting of dust, soft rubble, biological material (small wooden pieces), natural or synthetic fibers (small ropes), and thin plastic sheets. The metal content in this type is very low and mainly comprises very fine copper wires and some electronic components.

Fig. 2 presents the detailed chemical composition of the main elements found in the SLF, including metallic, ceramic, and organic fractions. Carbon is the dominant element, constituting approximately 40 wt % of the composition and contributing to its significant lower heating value (LHV) of 18,830 ± 3419.7 kJ/kg. Copper is another significant element in the SLF, found in concentrations of 2.74 ± 1 wt%, and it is a primary target element along with tin and precious metals, as they are mainly present in metallic form. Other elements such as Si, Ca, and Al are present in important concentrations, primarily in oxide form, characteristic of the fiberglass contained in printed circuit boards as reinforcement material.

3.2. Material transformation through pyrolysis

The visual examination of SLF before and after pyrolysis, seen in Fig. 3 (B-C), shows clear signs of organic material decomposition. Metallic materials, like copper wires, are also visible, with no major differences between the two pyrolysis setups.

The initial SLF is characterized by an extremely low bulk density of 0.215 kg/L. However, this density increases to approximately 0.396 ± 0.027 kg/L after pyrolysis. This change can be attributed to the removal of volatile organic matter during pyrolysis, leading to a higher concentration of metals.

During pyrolysis, the input material is transformed into three distinct products: pyrolysis gas (P.Gas), pyrolysis oil and water (P.Oil), and a solid product containing metals, oxides, and pyrolysis coke (PSLF). Fig. 4 (A), shows the mass balances for batch and continuous pyrolysis. Continuous pyrolysis exhibited higher organic degradation, resulting in approximately 7 wt% less solid and oil products, and an 11.3 wt% increase in permanent gas.

The SLF has significant intrinsic heat due to its diverse organic content. Fig. 4 (B) displays the distribution of net calorific energy among the pyrolysis products for both batch and continuous pyrolysis. It is important to note that this balance is intended to show how the intrinsic energy found in SLF is transferred to the products, and not the overall energy balance of the process, as the required energy for the pyrolysis was not taken into account.

The results showed a notable increase of 6 % in the energy distribution gathered in the permanent gas after the pyrolysis process during continuous operation. In contrast, the energy concentrated in P.Oil and PSLF decreased by 11 % and 5 %, respectively. This decrease in net energy correlated with a significant reduction in mass production.

The energy loss in both setups can be attributed to the various scission and recombination mechanisms that occur during pyrolysis. These reactions liberate and consume a portion of the calorific energy initially present in the input material. Consequently, a lower total net heating value after pyrolysis is expected, primarily due to reforming reactions and oxidation of components by free radicals, such as hydroxyl, leading to the formation of components with neutral net heating values, such as water and CO_2. This effect is particularly noticeable during continuous pyrolysis, which exhibited a more pronounced degradation effect, resulting in decreased oil formation and increased permanent gas production.

3.3. Degradation of organics in SLF

Fig. 5 displays concentrations of the main gas compounds (a-j) and temperature values during both batch and continuous pyrolysis, as well as additional minor compounds during batch setup (k). The formation of hydrogen, carbon monoxide, and hydrocarbons was primarily influenced by process temperature. During batch trials, the initial compound formed was water vapor, produced during the drying stage at around 100 °C and later due to oxidative reactions during organics degradation. The most significant H_2O formation occurred at 480–500 °C (Fig. 5 (k)).

In batch pyrolysis, primary formation of CO, CO_2, acetic acid, and cresols (p- and m-groups) took place between 220 °C and 400 °C before hydrogen formation and again later during the hydrogen peak. Between 500 and 550 °C, heavier hydrocarbons like propane (C_3H_8) and propane (C_3H_6) were observed. Ethane was initially detected during batch pyrolysis at around 450 °C, with higher concentrations again after reaching 600 °C. Additionally, hydrogen and methane formation occurred simultaneously at 400 °C, with H_2 reaching a higher concentration after methane decreased. A hydrogen peak was achieved after reaching approximately 600 °C, and then its concentration gradually decreased until the holding time was complete.

The continuous pyrolysis process exhibited improved degradation, leading to higher concentrations of shorter molecules like H_2 and CH_4. This enhancement can be attributed to two main factors. Firstly, the faster heating rate and higher temperature in continuous pyrolysis promote the production of shorter molecules, facilitated by catalytic conditions resulting from the presence of metals and oxide (Diaz et al. 2018a; Bahadir et al. 2001). Various mechanisms, such as the degradation of ethane (Diaz et al. 2018a), methanation reactions (Basu 2010), and shift reactions (Basu 2010; Kurzweil 2013). Additionally, catalytic reactions like water- aluminum reaction, steam reforming (equation (7)), and dry reforming reactions (equation (8)) aid in the cracking process at relatively lower temperatures, thanks to the presence of metals like aluminum and nickel (Basu, 2010; Diaz et al., 2018b).

Secondly, the recirculation of pyrolyzed gas in the reactor promotes

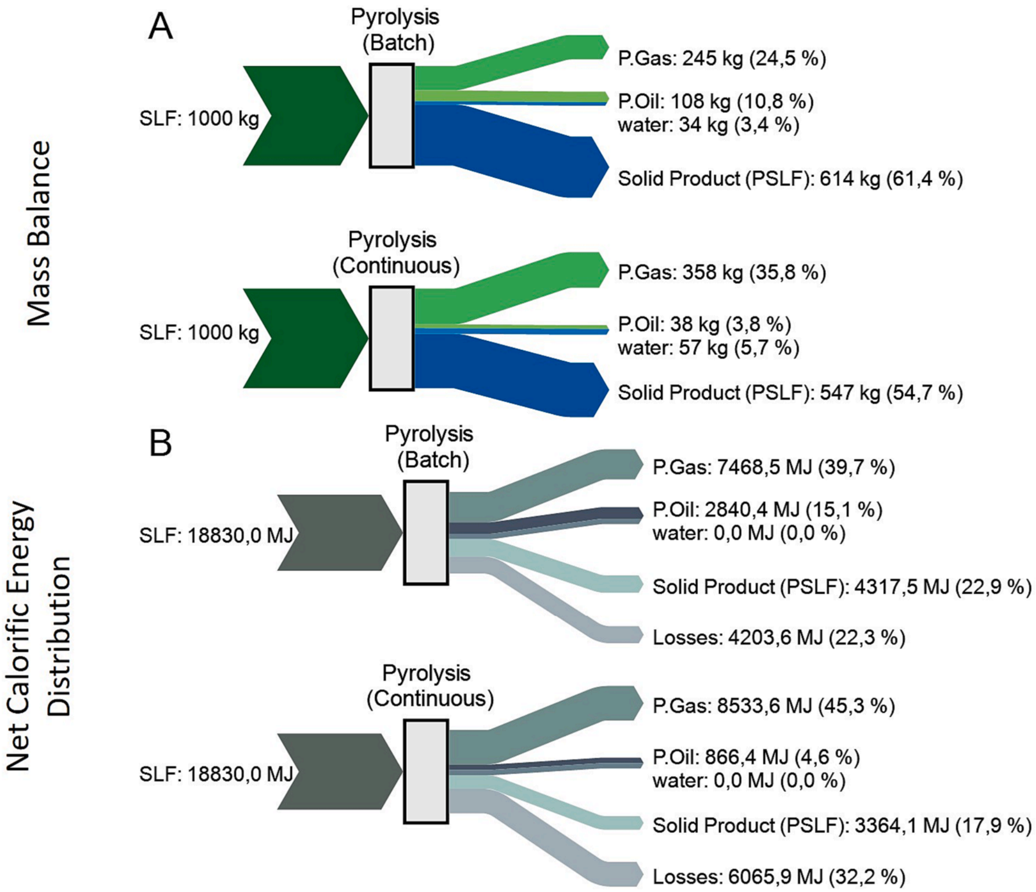

Fig. 4. Mass balance (A) and distribution of net calorific energy in the products (B) after laboratory-scale batch and demo-scale continuous pyrolysis of SLF.

secondary cracking reactions of long-chain hydrocarbons through steam reforming or methanization reactions, resulting in increased CH_4 and H_2 generation, thereby improving the overall quality and composition of the pyrolysis gas.

Catalytic steam reforming reaction (Basu 2010):

$$C_nH_m + nH_2O \rightarrow \left(n + \frac{m}{2}\right)H_2 + nCO \tag{7}$$

Catalytic carbon dioxide (or dry) reforming reaction (Basu 2010):

$$C_nH_m + nCO_2 \rightarrow \left(\frac{m}{2}\right)H_2 + 2nCO \tag{8}$$

3.4. *Permanent gas as an energy carrier*

Both batch and continuous pyrolysis provided valuable insights into the degradation of SLF. In continuous, it exhibited a notable increase in high-quality combustible gases, including CH_4, H_2, CO, ethylene, and ethane, with a calorific value of 23.8 MJ/kg (see Table 2). However, it had a slightly lower net heating calorific value, partly due to the presence of butane in the batch pyrolysis gas. The findings indicate the favorable mechanisms in continuous pyrolysis for producing short-molecule gases, while the batch process predominantly generated heavy hydrocarbons like butane and propane, indicating a need for improved control to avoid recombination and precipitation in oils.

After continuous pyrolysis, most of the energy in SLF was concentrated in the permanent gas (80.4 %) and PSLF, representing a significant improvement. The permanent gas finds versatile applications, serving as an alternative to fossil fuels in industry, powering the pyrolysis process, and acting as a reducing agent in metallurgy to reduce the carbon footprint.

3.5. *Condensable product gas as an energy carrier*

The characterization of condensed products (water and oils) provides insights into pyrolysis behavior.

Table 1 displays elemental compositions of condensed water and pyrolysis oil from batch and continuous setup. The pyrolysis oil in continuous processing has a lower heating value (LHV) of 22.8 MJ/kg, compared to 26.3 MJ/kg for the batch trial. This LHV aligns with higher hydrogen and hydrocarbon contents in the continuous pyrolysis gas and its higher proportion in the mass balance of the experiment. The LHV values of pyrolysis oils are comparable to those of petroleum fuel (30 to 50 MJ/kg), highlighting the potential of pyrolysis oil as a fuel source (Chagnes 2016; Scheirs and Kaminsky 2006; Luda 2012).

GC/MS analysis of the pyrolysis oil revealed that it primarily consists of three main constituents: paraffins, naphthalenes, and aromatics. In the batch pyrolysis, the oil showed 75 vol% aromatic hydrocarbons, 13 vol% naphthalene, and 12 vol% paraffin and alkenes. In contrast, oils from continuous pyrolysis showed a negligible amount of paraffins/alkenes, an increased concentration of naphthenes (~33 vol%), and a significant amount of aromatic hydrocarbons. A more detailed description of the chemical species found in the pyrolysis oil from both laboratory- and demo-scale trials can be found in the supplementary material, annexed to this paper.

Hydrocarbon liquid fuels typically consist of paraffins, naphthenes, and aromatics, each with a different hydrogen/carbon (H/C) index configuration, which assesses their quality and performance characteristics. A low H/C index leads to a lower smoke point for paraffin, while the opposite holds true for the aromatic series. Conversely, a high H/C index suggests better-cracking performance, high feed conversion, and a high yield of light olefins. Heavy oils with a lower H/C index exhibit poor secondary cracking performance, resulting in higher coke

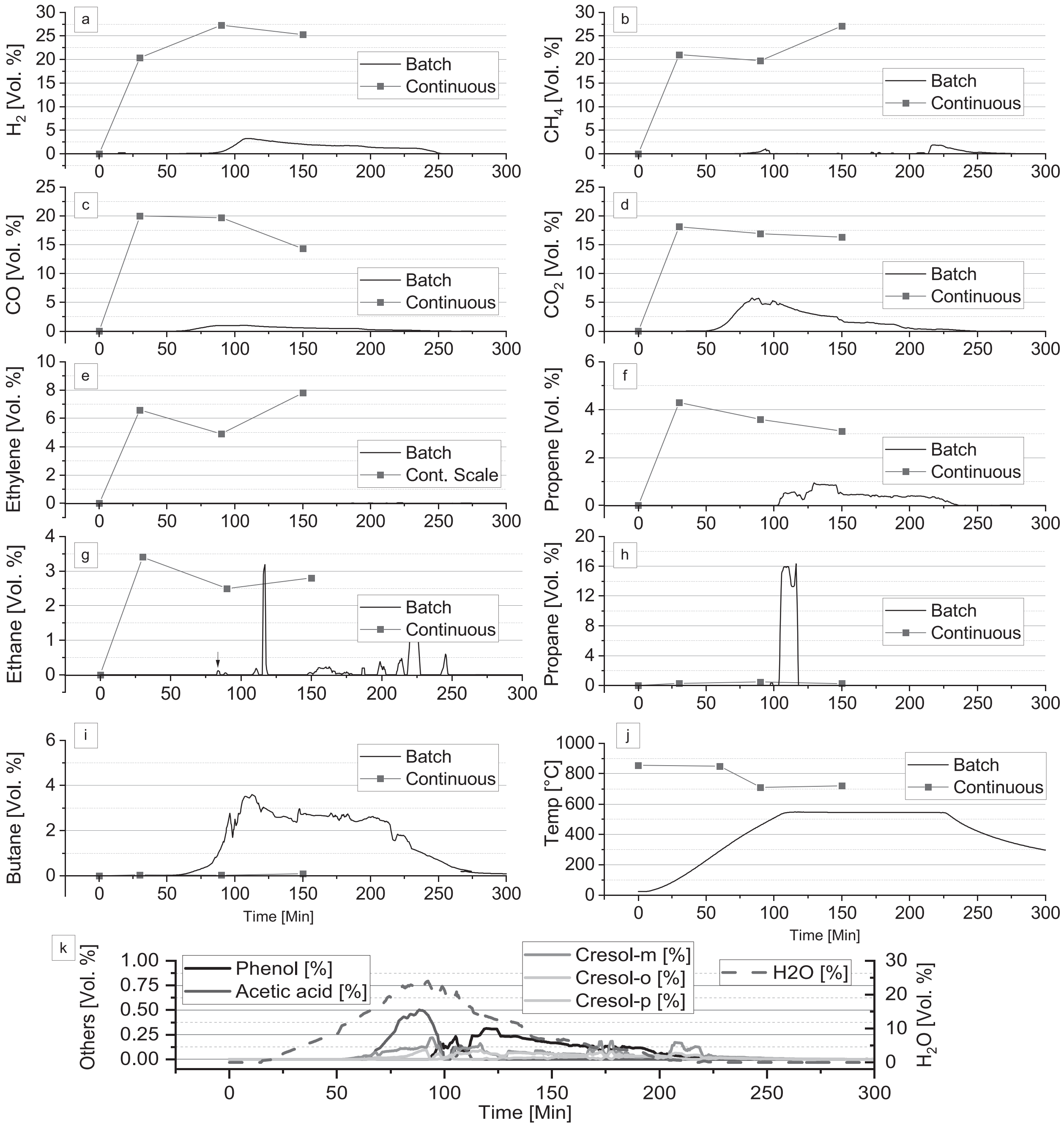

Fig. 5. Concentration of (a-j) main gas compounds, (h) temperature values registered during pyrolysis in batch and continuous of SLF, (k) additional gas compounds measured during batch pyrolysis.

formation (Yue et al. 2016).

The resulting H/C index from the pyrolysis oil Table 1, ranges from 1.66 to 2.80, with lower values in continuous pyrolysis compared to the batch setup. L. Yue (Yue et al. 2016) explained that H/C is inversely proportional to the total content of aromatics and naphthalenes, aligning with the GC/MS analysis (higher in continuous pyrolysis oil). These compound groups play a crucial role in coke production during cracking reactions. Consequently, despite significantly reduced oil production in continuous pyrolysis, this oil is expected to generate increased coke deposits if used as fuel compared to batch-produced oil. A high coke deposit signifies poor fuel properties, leading to risks like high thermal resistance, fuel pressure drops, and blocked fuel passages (Yue et al. 2016).

During the pyrolysis process, halogens (Br and Cl), metals, and some oxides, such as antimony oxide, a common substitute for halogenated flame retardants, can be found in all three products. However, pyrolysis parameters can influence the efficiency of their collection and separation into specific products. Based on the results in Table 1, elemental bromine and chlorine can be concentrated in the oil and water phases produced during the pyrolysis of SLF. In Table 1, there is a difference in the concentration of Br and Cl identified in the condensable products when comparing batch and continuous processes. The higher concentration of halogens observed in the continuous process can likely be attributed to three primary factors. Firstly, the heterogeneity of the material plays a role. Secondly, there is a reduction in the production of condensable matter, while the quantity of halogens in the input material remains relatively constant. Thirdly, the inefficiency in the condenser used in the batch pyrolysis may lead to premature condensation within

Table 1
Composition of pyrolysis oil and condensed water during treatment of SLF.

Element	Water (Batch)	Water (Continuous)	Oil (batch)	Oil (Continuous)
	Wt%	Wt%	Wt%	Wt%
Carbon	0.22 ± 0	1.48 ± 0.5	43.33 ± 3.8	52.6 ± 11.8
Hydrogen	10.6 ± 0.3	10.65 ± 0.5	10.04 ± 0.5	7.27 ± 0
Nitrogen	0	0.86 ± 0.7	2.18 ± 0.1	1.65 ± 1
Bromine	0.01	1.54	0.03	<LOD
Chlorine	0.02	1.21	0.11	2.97
Oxygen*	Balance	Balance	Balance	Balance
H/C Index			2.78	1.66
LHV (MJ/kg)	–	–	26.3 ± 1.9	22.8 ± 8.7

[*] defined as the balance in the composition.

the piping system. The scope of this research did not provide the necessary data to identify the most likely cause, therefore, future investigations should be carried out to better understand these phenomena.

The presence of halogens (Br, Cl) in the oils poses a challenge, necessitating safe removal before any potential utilization. The decrease in oil production observed in continuous pyrolysis holds promise from both economic and environmental perspectives. It indicates a reduction in the costly handling required for halogen removal and an improvement in cracking performance. Further advancements in cracking techniques, such as catalysts and recirculation methods, can minimize the production of pyrolysis oils and enhance process efficiency.

3.6. Pyrolysis solid product and the recycling potential

The initial chemical compositions of the SLF and PSLF produced in batch and continuous pyrolysis are shown in Fig. 6 (A). Fig. 6 (B) illustrates the upgrading effect experienced by the material, resulting from the removal of volatile matter, leading to a higher concentration of some elements and the removal of others. The upgrading effect was calculated using the following equation:

$$Upgradingeffect[\%] = \frac{m_{element,PSLF} - m_{element,SLF}}{m_{element,SLF}} x100\% \tag{9}$$

The analysis indicates that most elements in the metallic and oxide forms experienced an increase in concentration for both pyrolysis setups. These elements include Si, Ca, Cu, Mg, Na, Ti, Co, Sb, P, and precious metals. On the other hand, other elements like Pb, Ba, Sr, Ni, Zr, and Sn experienced an upgrading effect in concentration only during continuous operation. Notably, volatile elements such as C, N, and H experienced a significant reduction in concentration after thermal treatment. The detailed chemical composition of the solid pyrolysis products (batch and continuous scales) and the original composition of the SLF are listed in the supplementary material, annexed to this paper.

The results show that the heterogeneity of the input material, represented by a large mathematical deviation in the data before and after pyrolysis in both setups, strongly influenced the calculated upgrading effect. Elements with higher concentrations in the input material exhibited the most significant deviation in the reported results. It should be noted that while continuous pyrolysis led to an increased degradation of organics, the upgrading effect in elements such as Cu, Na, and Zn was not directly proportional to the organic removal during pyrolysis. This disparity could be attributed to heterogeneity in the material. In the case of volatile elements, besides to the heterogeneity factor, also could be expected an enhanced volatilization of specific elements like halogens.

Throughout the process, approximately 50 % of the weight was removed, primarily due to the elimination of approximately 50 wt% of organic carbon, which is the primary element in the input material. Organic carbon is present often with halogens in WEEE in plastics, textiles, wood, PCBs, and other materials. Even if these elements do not show a significant decrease in concentration in the solid product, removing half of the organics means eliminating a large amount of halogen (approximately 45.5 wt% Cl and 73.4 wt% Br removal during batch pyrolysis) from the input material. However, continuous pyrolysis resulted in more halogens in the pyrolyzed SLF than in the input material. This observation can only be explained by the extreme heterogeneity of the analyzed input sample, suggesting a higher concentration of halogens in the input material than that of the analyzed sample before treatment. Further research on the characterization of halogens present in SLF should be conducted in the future, as they pose a significant challenge for metallurgical extraction when SLF is considered an alternative resource to primary materials.

Fig. 6 also indicates oxygen concentration in PSLF in both setups. For this element, an increase in the percentage after pyrolysis in the solid product can also be observed, which can be explained by the fact that oxygen is mainly present in stable metal oxides that do not undergo any transformation during pyrolysis.

Table 2
General composition of pyrolysis gas and corresponding gravimetric and volumetric net heating value during batch and continuous pyrolysis of SLF.

		Volume distribution		Weight distribution		Gravimetric Net Heating Value		Volumetric Net Heating Value	
		Vol%	σ	Wt. %	σ	Energy value kJ/kg	σ	kJ/m^3	σ
Continuous Pyrolysis	H_2	24.3 %	2.9 %	2.5 %	0.4 %	2972.8	445.0	2493.2	297.0
	CH_4	22.6 %	3.2 %	17.1 %	2.7 %	8531.4	1354.9	7674.1	1083.7
	CO	18.0 %	2.6 %	23.6 %	3.1 %	2382.5	316.3	2166.3	315.2
	CO_2	17.1 %	0.7 %	35.5 %	0.6 %	0.0	0.0	0.0	0.0
	Ethylene (C_2H_4)	6.4 %	1.2 %	9.1 %	1.7 %	4311.6	816.2	3667.4	678.2
	Propene (C_3H_8)	3.7 %	0.5 %	7.2 %	0.7 %	3297.5	337.5	2979.6	399.9
	Ethane (C_2H_6)	2.9 %	0.4 %	4.1 %	0.4 %	1956.6	185.8	1761.2	227.2
	Propane (C_3H_8)	0.3 %	0.1 %	0.7 %	0.2 %	329.8	109.3	294.5	91.9
	Butane (C_4H_{10})	0.1 %	0.0 %	0.2 %	0.1 %	96.7	33.3	81.3	26.1
	Total					**23878.9**	**642.4**	**21117.6**	**531.0**
Batch Pyrolysis	H_2	20.8 %	2.2 %	1.3 %	0.2 %	1530.9	270.9	2126.2	228.0
	CH_4	8.6 %	4.8 %	4.1 %	2.5 %	2027.4	1233.2	2919.8	1639.5
	CO	6.5 %	0.0 %	5.2 %	0.4 %	522.4	40.8	787.0	5.6
	CO_2	25.6 %	2.3 %	31.8 %	0.6 %	0.0	0.0	0.0	0.0
	Ethylene (C_2H_4)	0.0 %	0.0 %	0.0 %	0.0 %	5.2	5.2	8.0	7.9
	Propene (C_3H_8)	4.2 %	0.4 %	5.0 %	0.8 %	2309.3	353.7	3433.2	285.0
	Ethane (C_2H_6)	2.6 %	1.1 %	2.3 %	1.1 %	1085.1	519.4	1569.5	662.2
	Propane (C_3H_8)	6.2 %	6.2 %	7.4 %	7.4 %	3431.4	3431.4	5507.3	5507.3
	Butane (C_4H_{10})	25.4 %	0.0 %	42.9 %	3.0 %	19945.1	1400.8	28189.1	23.6
	Total					**30856.9**	**1337.3**	**44540.1**	**1538.7**

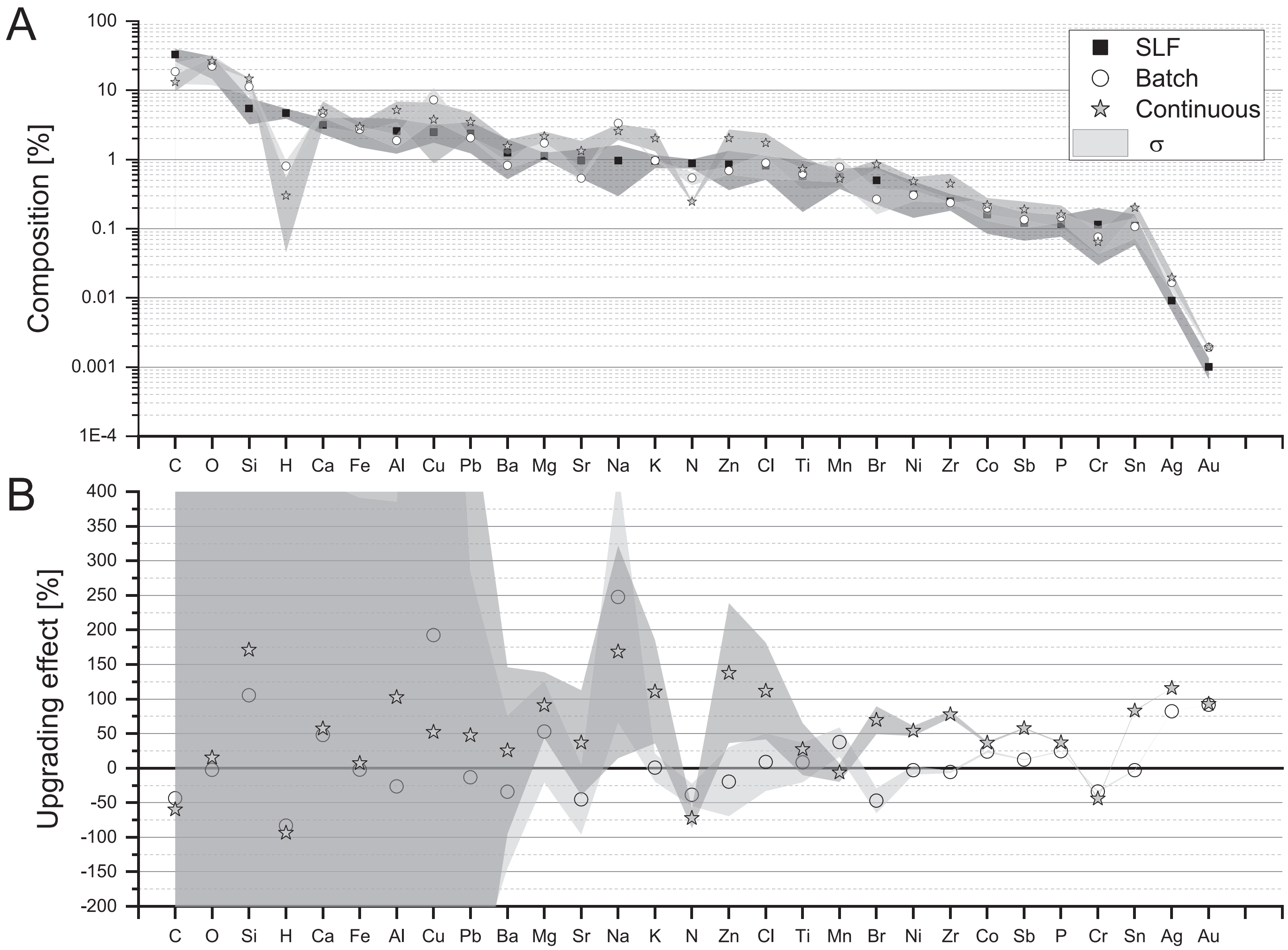

Fig. 6. A) Composition of SLF, PSLF from Continuous and Batch pyrolysis trials, B) Upgrading effect per element in the solid product after pyrolysis using the Batch and the Continuous trials.

In the case of carbon, it can be seen a significant amount being volatilized during pyrolysis. However, the solid product still retains a considerable amount of intrinsic heat in the form of carbon (approximately 17 wt%).

Regarding the net heating value, the PSLF indicated 7037.5 kJ/kg for the batch setup and 6150 kJ/kg for the continuous setup. This suggests that even after pyrolysis, the solid product retains substantial energy content, which could be advantageous for further energy utilization or resource recovery purposes. The slight difference between the two setups can be attributed to the increased degradation rate in continuous pyrolysis, thanks to slightly higher temperatures, faster heating rates, and increased surface area achieved through material recirculation within the reactor. The recirculation, aided by a backward-moving screw, promotes mixing and partial crushing of the material.

In addition to the chemical composition, it noticeable that the solid material becomes highly brittle after pyrolysis, which could facilitate the mechanical separation of unwanted metals like iron and aluminum, if required for further use in the e.g. copper industry.

3.6.1. *Integration of PSLF into the metallurgical value chain*

The recycling of Shredder Light Fraction (SLF) poses challenges due to its physical properties, chemical composition, and high heterogeneity (Jiri Hyks et al. 2014). As a result, there is currently no established recycling method for this waste material.

However, pyrolysis treatment offers synergistic benefits by enhancing metal concentrations while reducing intrinsic heat. This makes it a promising option for integration into the metallurgical industry, especially for valuable metal extraction. In this subchapter, a technical assessment from a metallurgical perspective is conducted to evaluate opportunities and potential challenges for integrating pyrolyzed SLF into the metallurgical sector.

PSLF holds significant potential as a secondary raw material within the copper industry due to its high concentration of copper-related (Cu, Pb, and Zn) and precious metals. By effectively incorporating these valuable metals into the value chain, the circular economy of raw materials can be supported. The utilization of pyrolysis to SLF offers several anticipated advantages. Firstly, there is the potential for a substantial reduction in volatile matter by up to 50 wt%. Additionally, PSLF exhibits an upgrading effect on targeted elements and oxides (such as Si, Al, Ca, Cu, Pb, Fe) that are valuable for the copper sector. Furthermore, the process enables the significant removal of corrosive materials to the melting unit such as halogen elements (Br, Cl).

The concentration of copper in PSLF is comparatively lower than the average concentration found in WEEE streams accepted by the copper recycling industry, which typically ranges between 10 wt% and 20 wt% (Chagnes 2016). However, it is noteworthy that the copper concentration in PSLF is approximately 12.5 times higher than the minimum requirement for economically viable extraction from primary sources, which typically range in concentration from 0.3 wt% to 1.7 wt% (Schlesinger et al. 2022). Additionally, other metals present in PSLF, such as nickel, zinc, lead, and tin, can be successfully separated and extracted as valuable by-products through the copper recycling route.

Various global processes, including those implemented by Umicore (Belgium), Outotec (Finland), Boliden Rönnskär (Sweden), and Aurubis (Germany), have reported the extraction of these metals at different process stages. For instance, zinc, lead, and tin are primarily collected in the flue dust during copper smelting and copper blister conversion, while nickel is typically recovered as crude Ni-sulfate in copper slimes during the copper electrolysis (Chagnes 2016; Khaliq et al. 2014).

The presence of silver (195 ppm) and gold (19.24 ppm) in PSLF indicate a significant resource potential for extraction, with concentrations 2.7 times higher for silver (72 ppm of Ag) (Swinkels et al. 2021)) and 962 times higher for gold (0.02 ppm of Au) (Adams, 2016) compared to major commercial ores used for primary extraction of these precious metals. Similarly, PSLF contains precious metals at concentrations similar to the average WEEE scraps, ranging from 20 to 30 ppm for gold and 200–3000 ppm for silver (Chagnes 2016; Khaliq et al. 2014; Zhang et al. 2017).

Recovering precious metals from PSLF not only offers economic advantages but also addresses environmental concerns by reintroducing these valuable resources into the raw material value chain, alleviating pressure on natural resources. Primary production of gold, for example, involves significant waste disposal, pollution, and water usage (Gorain and Lakshmanan 2019). In contrast, gold and silver present in PSLF can be easily accessed and recovered by metallurgical Cu-recycling plants. Precious metals initially accumulate in the copper phase after smelting, are separated as anode slimes, and then refined through precious metal electrolysis (Chen et al. 2015).

The presence of precious metals in SLF derived from WEEE highlights the significance of not treating it as waste and incinerating it for energy recovery. Instead, their concentrations through pyrolysis reach acceptable ranges for the recycling industry. Precious metals are one of the main products of WEEE scrap recycling, emphasizing the importance of achieving high efficiencies (>95 %) using modern processes (Hagelüken and Goldmann 2022) (Trivedi et al. 2023). The findings demonstrate that both batch and continuous technologies enable efficient recovery in later metallurgical extraction, particularly for upgrading precious metals and copper. However, the research stance did not assess whether the effect on later recovery varies between the technologies. Observations are primarily based on mass transfer in the process. Notably, only in continuous processing, the benefits of process control and energy efficiency contribute to the sustainability of the process. This is attributed to lower energy consumption and effective utilization of resources such as Pyrolysis gases as energy source within the process itself.

PSLF contains significant concentrations of elements such as calcium, silicon, manganese, and aluminium, which are either present as oxides in the input material or undergo rapid oxidation during metallurgical treatment due to their high thermochemical oxygen affinity at the operating temperatures of 1050–1200 °C (Matusewicz and Baldock 2000; Maurell-Lopez 2016). These elements are predominantly collected in the slag phase during copper smelting. Notably, silicon (∼15 wt% from PSLF) requires careful monitoring during the melting processes as it leads to the formation of highly viscous slags. SiO_2 is considered a “network former” with strong bonding forces that tend to solidify, and only higher temperatures can maintain the viscosity of the liquid slag under optimum conditions (Shamsuddin 2021). To prevent the need for excessively high process temperatures, fluxes such as CaO and MgO, also present in PSLF, are employed (Matusewicz and Baldock 2000; Maurell-Lopez 2016).

Despite the significance of these documented oxides in PSLF, it is important to note that the SiO_2-CaO-Al_2O_3 system is a standard slag system in nonferrous metallurgy (Shamsuddin 2016), and their presence does not pose additional challenges to the ordinary control operations of pyrometallurgical WEEE recycling processes. Furthermore, some of the oxides present in PSLF, such as SiO_2, serve as required additives during the blister copper conversion step. Moreover, the produced slags can be considered part of the circular economy as, after appropriate processing, they can be utilized as feedstock in the construction industry (Kovacs et al. 2017).

3.6.2. *Integration of PSLF as fuel or reducing agent*

Pyrolytic carbon is generated from intermediate tars during the pyrolysis process (Diaz et al. 2018a; Diaz et al. 2018b). The PSLF contains significant amount of pyrolytic carbon, which could serve as a carbon source in copper metallurgy as energy carrier or reducing agent. Previous studies explored using high-organic-content materials, like WEEE plastics, as an alternative energy source for copper recycling (TSL at Umicore), but off-gas limitations were observed due to large amount of off-gas during combustion, particularly with materials high in volatile matter and halogen concentrations (Brusselaers et al. 2006). To overcome this, autothermic smelting in a TBRC was investigated, using organic-containing metal waste as an energy source (Maurell-Lopez 2016). In both industrial plants, PSLF could be used as energy carrier considering the significant volatile matter removal, still considerable heat value and presence of relevant target elements.

Similarly, the carbon present in PSLF could serve as an alternative reducing agent to conventional fossil sources. Promising results have been reported from similar research that utilized pyrolyzed materials from agriculture in metallurgical processing (Griessacher et al. 2012; Sommerfeld and Friedrich 2021). Notably, the use of pyrolytic carbon from waste materials represents a “carbon-neutral” value from an environmental perspective (Griessacher et al. 2012), which would positively impact the CO_2 footprint of the copper production sector.

In this context, it is essential to determine the CO_2 footprint of the pyrolysis process to establish the environmental benefits of utilizing PSLF as fuel or reducing agent under broader boundary conditions. Therefore, based on the accumulated experience, the potential of PSLF in the metallurgical sector appears plausible and warrants further investigation.

4. Conclusion

This study introduced pyrolysis as a transformative method for converting Shredder Light Fraction (SLF) into a recyclable material. Both batch and continuous setups were evaluated. With approximately 50 % of the mass removed, the resulting solid product exhibited enriched concentrations of key metals, including copper, zinc, lead, and precious metals, while hazardous constituents such us Cl and Br were reduced up to 45 wt% and 73 wt%, respectively.

The batch setup provided precise insights into the organic degradation process, while the continuous setup demonstrated scalability and feasibility. Pyrolyzed SLF containing pyrolytic carbon holds promise as a carbon–neutral reducing agent in the copper industry, reducing environmental impact of metallurgical processes. Additionally, the effective recovery of copper and precious metals from SLF constitutes a crucial achievement, as these metals would be lost otherwise, further exacerbating the strain on natural resources. In this context, it could be concluded that SLF can be successfully transformed into a material with potential applications in the metallurgical industry.

Pyrolysis oil, a potential alternative energy carrier, warrants further exploration, though potential coke deposits may impact its suitability as a fuel source. Non-condensable gas, rich in hydrogen and methane, which concentrated almost 45 % of the available net calorific value from SLF, holds promise for various applications and as a reducing agent in metallurgy, requiring additional research for optimal production.

Further investigations are necessary to understand combustion kinetics, reduction performance, the effect of pyrolysis in the recovery of precious metals, and the presence of impurities and slag builders in the solid product for effective pyrometallurgical use in the recycling of copper-containing materials. Additionally, comprehensive environmental impact assessments of pyrolysis and its product utilization in the copper industry require future study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2023.11.001.

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