



# Treball Final de Grau

**Valorization of bromine-containing waste printed circuit boards and biowastes through co-pyrolysis process for fuel production**

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*The waste of plenty is the resource of scarcity.*

Thomas Love Peacock

En primer lloc voldria agrair de tot cor a l'Alberto per la seva confiança en mi, i en el meu projecte. Per tots els cops de mà que m'ha donat al llarg del semestre, i per tot el temps que ha dedicat per a fer possible que avui aquest treball sigui una realitat.

També voldria agrair l'ajuda que he rebut al llarg del grau, per part d'absolutament tots els professors i professores. Cadascú aportant el seu granet de sorra. Sense ells aquest treball no hagués estat possible.

Per últim, el meu agraïment incondicional als meus pares, Marissa i David-Joan, al meu germà Arnau, a la meva germana Júlia. A tota la meva família, i també a tots els meus amics. Perquè encara que ells no ho sàpiguen, l'aprenentatge que en trec d'ells, dia rere dia, és de valor incalculable. Només puc agrair l'ajuda incondicional que, directa o indirectament, m'han proporcionat. No només per a la realització d'aquest treball. També al llarg de tota la meva etapa universitària.

Moltíssimes gràcies a la meva família.

Moltíssimes gràcies als meus amics.

Moltíssimes gràcies a tots els professors del grau.

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## SUMMARY

The present study investigates the co-pyrolysis process of waste printed circuit boards (WPCBs) and biowastes as a sustainable solution for managing e-waste, focusing on the challenges posed by brominated flame retardants. The study aims to maximize fuel recovery and manage bromine content effectively.

The study initiates with an overview of the growing issue of electronic waste due to industrialization and technological advancements. It highlights the complex composition of WPCBs, which contain valuable materials and hazardous brominated compounds that require careful treatment.

The core of the project focuses on co-pyrolysis, a process where WPCBs and biomass are thermally decomposed together. This method enhances the yield of liquid and gas products, directing bromine to the solid phase and resulting in bromine-free liquid fuels.

Based on the comprehensive information compiled, the study outlines a preliminary design for implementing the co-pyrolysis process. This includes considerations for reactor selection, temperature control, residence time, and product collection strategies, all aimed at optimizing the process for efficient fuel recovery and effective bromine management.

The project concludes by summarizing the benefits of co-pyrolysis for WPCBs and biomass, proposing further research into scaling the process and optimizing bromine recovery. This work contributes to advancing sustainable waste management practices and resource recovery from e-waste.

**Keywords:** WPCB, BFR, e-waste, co-pyrolysis, auger reactor, biowastes, fuel production, bromine recovery, sustainable valorization, circular economy.



## RESUM

En aquest estudi, s'analitza el procés de copiròlisis de residus de plaques PCB (*printed circuit boards*) i bioresidus com a una potencial solució sostenible per a la gestió de residus electrònics, centrant-se en els reptes plantejats per la presència, a les plaques PCB, de retardants de flama bromats. L'objectiu de l'estudi és proposar un procés per a maximitzar per una banda l'obtenció de combustibles i per altra banda la correcta gestió dels compostos bromats.

L'estudi comença amb un anàlisi generalitzat sobre el problema creixent dels residus electrònics, a causa de la industrialització i els avenços tecnològics. Es destaca la complexa composició de les plaques PCB, les quals contenen materials valuosos però també compostos bromats perillosos que requereixen d'un tractament curós.

El nucli del projecte es centra en el procés de copiròlisis, un procés en que els residus de plaques PCB i els bioresidus es descomposen tèrmicament de manera conjunta. Aquest mètode incrementa la producció de productes líquids i gasosos, fent migrar els compostos bromats al producte sòlid, resultant en un combustible líquid i gasós lliure de brom.

Basant-se en la informació recopilada, l'estudi proposa un disseny preliminar per implementar el procés de copiròlisis. Aquest inclou consideracions per a la selecció del reactor, el control de la temperatura, el temps de residència, així com estratègies per a la recollida del producte.

L'estudi conclou resumint els beneficis del procés de copiròlisis proposat, plantejant també possibles línies d'investigació per a escalar el procés i optimitzar la bona gestió del brom. Aquest treball contribueix en avançar en la línia de processos de gestió de residus sostenibles, centrant-se en la recuperació de recursos de residus complexes com ho són els residus electrònics.

**Paraules clau:** WPCB, retardants de flama bromats, residus electrònics, copiròlisis, reactor auger, bioresidus, producció de combustibles, recuperació de brom, valorització sostenible, economia circular.



## SUSTAINABLE DEVELOPMENT GOALS

The present study explores innovative solutions for managing electronic waste (e-waste), focusing on the co-pyrolysis of waste printed circuit boards (WPCBs) and biomass. The goal is to enhance the recovery of valuable fuel products and manage bromine content effectively, contributing to several Sustainable Development Goals (SDGs) established by the United Nations. This section reflects on how the project aligns with the SDGs and its potential impact.

Planet: The project significantly impacts environmental sustainability, directly addressing issues related to waste management and pollution. It contributes to reducing environmental pollution and promoting the recycling and reuse of valuable materials. This aligns with SDG 12 (Responsible Consumption and Production) and SDG 13 (Climate Action), as the project promotes sustainable waste management practices and helps mitigate the environmental impacts associated with traditional e-waste disposal methods.

### SDG 12: Responsible Consumption and Production

Target 12.5: By 2030, substantially reduce waste generation through prevention, reduction, recycling, and reuse.

Indicator: The project contributes to reducing e-waste by transforming WPCBs and biomass into valuable fuel products, promoting resource efficiency and the circular economy.

### SDG 13: Climate Action

Target 13.2: Integrate climate change measures into national policies, strategies, and planning.

Indicator: By reducing reliance on harmful disposal methods like landfilling and incineration, and by producing cleaner energy sources, the project supports efforts to combat climate change and reduce greenhouse gas emissions.

**Prosperity:** The project promotes economic growth by exploring innovative technologies that can convert waste into valuable resources. The co-pyrolysis process not only addresses waste management but also supports the creation of sustainable energy sources. This aligns with SDG 9 (Industry, Innovation, and Infrastructure), which focuses on building resilient infrastructure and promoting sustainable industrialization and innovation.

### **SDG 9: Industry, Innovation, and Infrastructure**

Target 9.4: By 2030, upgrade infrastructure and retrofit industries to make them sustainable, with increased resource-use efficiency and greater adoption of clean and environmentally sound technologies and industrial processes, with all countries taking action in accordance with their respective capabilities.

Indicator: The project represents technological innovation in waste management, enhancing the sustainability and efficiency of industrial processes through co-pyrolysis.

**People:** While the primary focus is on environmental and economic benefits, the project indirectly contributes to public health and community well-being by reducing the hazardous impacts of e-waste. By developing safer methods for treating WPCBs, the project helps minimize the exposure of communities to toxic brominated compounds. This supports SDG 3 (Good Health and Well-being), which aims to ensure healthy lives and promote well-being for all, at all ages.

### **SDG 3: Good Health and Well-being**

Target 3.9: By 2030, substantially reduce the number of deaths and illnesses from hazardous chemicals and air, water, and soil pollution and contamination.

Indicator: By preventing the release of toxic brominated compounds into the environment, the project contributes to reducing health risks associated with e-waste pollution.

This project highlights the crucial role of innovative engineering solutions in advancing sustainable development. By addressing the challenges of e-waste management and promoting resource recovery, the project supports several SDGs and demonstrates the potential for academic research to drive significant societal and environmental progress.

# 1. INTRODUCTION

The rapid pace of industrialization and technological innovation, coupled with a growing global population and significant improvements in quality of life, have undoubtedly brought numerous benefits to society. Advances in technology have revolutionized industries, enhanced communication, and improved healthcare, contributing to a higher standard of living for many people around the world. However, these advancements have also led to substantial challenges, particularly in the waste generation and environmental pollution domain. As the volume of industrial and technological output increases, so does the amount of waste produced, leading to significant environmental and public health concerns.

Chemical engineers play a crucial role in addressing these challenges by developing and implementing processes that minimize the negative impacts of waste and pollution. Through innovative solutions and sustainable practices, chemical engineers are at the forefront of efforts to mitigate the adverse effects of industrial activities and technological advancements on the environment.

One pressing example of these challenges is the issue of electronic waste. Despite the omnipresence of electronic devices in modern life, the problems associated with their disposal and recycling are often overlooked. E-waste comprises a complex mixture of materials, some of which are hazardous and can pose serious environmental and health risks if not properly managed. Current disposal methods for e-waste, such as landfilling and incineration, are not only unsustainable but also contribute to pollution and resource consumption. However, many components of e-waste, including valuable metals but also other materials, can be recovered and valorized through appropriate recycling processes.

To propose a realistic and effective solution for the management of e-waste, it is essential first to understand the current state of the problem. This involves analyzing the generation, composition, and current disposal practices of e-waste. With a comprehensive understanding of the issue, it becomes possible to explore and evaluate the available technologies that can be employed to mitigate the problem. One such promising technology is the co-pyrolysis of waste

printed circuit boards (WPCBs) and biomass, which offers a sustainable approach to valorize WPCBs and produce bromine-free liquid fuel.

In this project, the intricacies of the co-pyrolysis process will be delved into, examining its potential to address the challenges posed by WPCBs. By investigating the synergistic effects of co-pyrolysis and analyzing the resulting products, this study aims to contribute to the development of innovative and sustainable solutions for e-waste management. Through this research, the importance of chemical engineering in creating processes that not only mitigate environmental impacts but also enhance resource recovery and sustainability is highlighted.

## 2. OBJECTIVES

This project is focused on addressing the environmental and resource challenges posed by waste printed circuit boards (WPCBs) through the design of a co-pyrolysis process.

To achieve this the following objectives are defined:

- The analysis of current global rates of electronic waste generation focused on waste printed circuit boards, aiming to understand the scale of the problem and its potential impact on the environment.
- Research into the composition of printed circuit boards, with a particular emphasis on the presence and effects of brominated flame retardants (BFRs), to evaluate the environmental and human health impacts associated with these compounds.
- Review of existing methods for treating WPCBs residues to identify areas for improvement and assess their environmental effects.
- Exploration of co-pyrolysis processes involving biomass for the treatment of WPCBs, assessing the potential of co-pyrolysis for recovering bromine and simultaneously producing high-quality fuel.
- Pre-design of a co-pyrolysis process for the efficient recovery of bromine and high-quality fuel from WPCBs, optimizing process parameters to maximize bromine recovery and fuel quality while minimizing environmental impact.

These objectives aim to provide a comprehensive understanding of the challenges posed by WPCBs and to develop an effective and sustainable solution for their treatment and resource recovery.



### 3. METHODOLOGY

This project, as a comprehensive bibliographic study, involved a systematic approach to gathering, evaluating, and synthesizing relevant literature on the electronic waste problem, the printed circuit boards, the pyrolysis process approach of waste printed circuit boards, and the co-pyrolysis process approach of waste printed circuit boards and biomass. The research methodology was designed to ensure a thorough exploration of the topic, leveraging a wide range of academic sources and search techniques.

The first step in the research process was the identification of key terms and concepts central to the study. Critical keywords such as BFR, WPCB, Pyrolysis, Co-pyrolysis, Auger Reactor, Biomass Wastes, E-waste, and Waste Electrical and Electronic Equipment were identified. These keywords formed the foundation for targeted searches across various academic databases, guiding the direction of the literature review.

An initial broad search was conducted using these keywords to locate articles that provided comprehensive overviews of the relevant topics. This search was primarily carried out through reputable academic databases, including ACS Publications, ScienceDirect, and Scopus. The criteria for selecting articles included their relevance to the primary research focus, their recentness to ensure incorporation of the latest research developments, and their credibility and impact, favoring high-impact journals.

Following the initial search, a snowballing technique was employed to expand the literature base. This involved examining the references and citations within the initially identified articles to uncover additional significant studies. This method was particularly effective in identifying innovative, more specific works and important research developments that were not captured in the initial keyword search.

As the research progressed, more focused searches were conducted to address specific gaps in the understanding of the topic. These searches used combinations of the key terms to locate articles that provided detailed insights into particular aspects, such as the role of biomass in the co-pyrolysis process or the mechanisms involved in bromine removal during pyrolysis.

Throughout the research process, the databases ACS Publications, ScienceDirect, and Scopus were consistently used to find and access peer-reviewed articles. These platforms were chosen for their extensive coverage of scientific and engineering disciplines, ensuring access to a broad range of high-quality and relevant literature.

The final phase of the methodology involved extracting critical information from the selected articles and synthesizing it into a coherent narrative.

This structured approach ensured that the study was grounded in robust, credible, and up-to-date research, providing a solid foundation for the analysis and conclusions presented in the project. By systematically exploring and synthesizing the available literature, the study offers a comprehensive understanding of the co-pyrolysis process and its implications for managing waste printed circuit boards and biomass.

## 4. UNDERSTANDING THE IMPACT OF BROMINATED FLAME RETARDANTS

In an increasingly technology-dependent global society, the reliance on Electric and Electronic Equipment (EEE) such as mobile phones, computers, vehicles and household appliances amongst others in our day-to-day activities has become undeniable. This dependence, along with increased purchasing capacity of consumers, continuous advancements of the technology, and shorter lifespan of EEE products, are significant factors contributing to the growing volume of EEE waste (WEEE) generation, also known as e-waste [1].

In 2019, the global generation of e-waste reached approximately 53.6 Mt, equivalent to 7.3 kg per capita. By 2030, it is projected to surpass 74 Mt, indicating an alarming average annual increase of 2 Mt. By 2050, e-waste generation worldwide is expected to be more than four times the current rate [2][3].

In 2019, only 17.4% of total e-waste generated was formally documented as properly collected or recycled. The rest of it is managed outside the official collection system or shipped to developing countries [2].

As shown below, Figure 1 offers a comprehensive overview of the generated electronic waste (e-waste) across various continents and the proportion of this waste that is relatively adequately collected and managed. This visual data highlights the significant volumes of e-waste produced globally and underscores the critical gaps in effective collection and recycling systems.

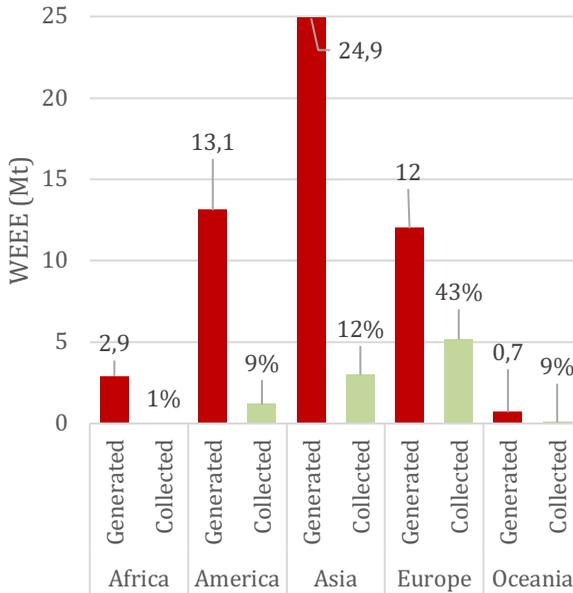


Figure 1. Generation and collection rates of WEEE by continent in 2019

## 4.1. PRINTED CIRCUIT BOARDS

Printed Circuit Boards (PCBs) serve as the backbone of the entirety of modern EEE, playing a fundamental role in enabling both mechanical and electrical connection and communication between electronic components. They consist of conductive pathways, tracks, or signal traces etched onto a non-conductive substrate [10]. PCBs constitute 1-10 wt.% of the total mass of the electric appliances [4]. This number is even higher in some kinds of EEE such as TV's, computers and phones [14].

In recent years, there has been an annual average increase of 8.7% in the global waste PCB (WPCB) output. Southeast Asia and mainland China have experienced even higher average growth rates, with rates of 10.8% and 14.4%, respectively [13]. This trend is expected to persist, driven by the ongoing large-scale production of electronic products, resulting in significant e-waste generation.

In 2018, WPCBs resin generation (containing brominated flame retardants) was 391.39 thousand tons, projected to exceed 568.27 thousand tons by 2035 [6].

WPCBs are the most challenging and valuable component to treat and recycle within e-waste. Despite comprising only 1-10 wt.% of the total weight of e-waste, WPCBs contribute significantly to pollution and environmental and human risk due to the presence of toxic substances such as heavy metals, brominated flame retardants, and organic polymers [28].

PCBs depict a highly complex composition, consisting of a heterogeneous mix and interconnection of metals, polymers, and ceramics within a single material. As a consequence, waste PCB (WPCB) is one of the most complex types of waste [11]. Depending on the EEE source, PCB structure is different [10]. Even so, on average, a typical WPCB is formed by approximately 35 wt% metals (including Cu, Fe, Sn, Zn, Al, Pb, Ni, Au, Ag and Pd), 25-30 wt% polymer (mainly phenoxy resin, polyvinyl acetate and vinyl chloride containing brominated flame retardants), and 35 wt% refractory oxides (glass fiber and ceramic primarily composed of SiO<sub>2</sub>, CaO and Al<sub>2</sub>O<sub>3</sub>) [5][12], as seen in Figure 2.

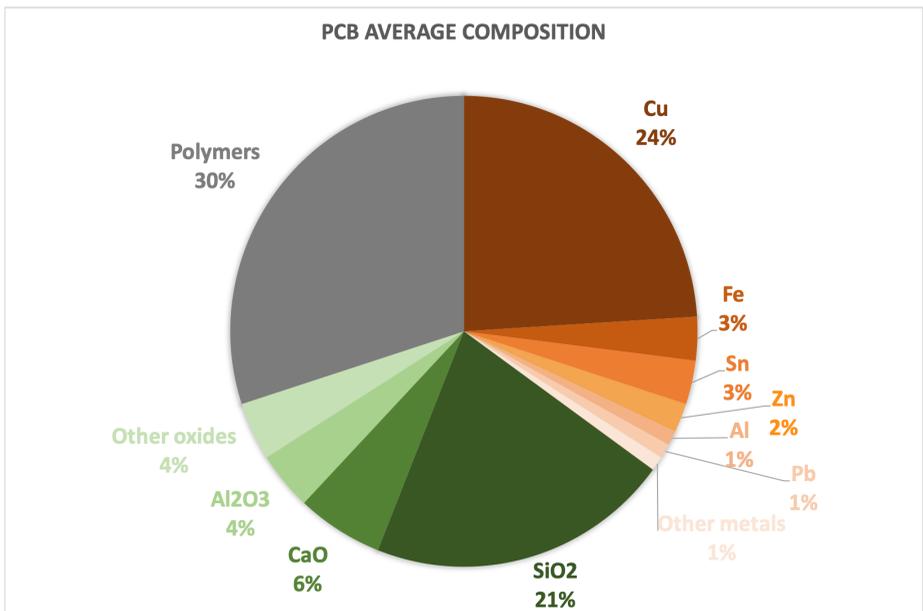


Figure 2. Printed Circuit Board average composition

WPCBs contain a large amount of attractive resources, such as metals, but also hazardous pollutants such as brominated flame retardants (BFRs) to a large extent [7].

## 4.2. BROMINATED FLAME RETARDANTS

BFRs are a major class of organohalogen compounds widely used in various industries due to their high efficiency and low cost. Over 75 different BFRs are commercially available. These compounds are utilized as additive or reactive components in various polymers such as foam, high-impact polystyrene, and epoxy resins, which are then incorporated into commercial EEE products, but also textiles and furniture foam [8]. BFRs are added to PCBs by manufacturers to help products meet flammability standards [9].

BFRs reduce material flammability through a multi-faceted mechanism. When heated, BFRs decompose to release bromine atoms or radicals, which react with hydrogen and hydroxyl radicals to interrupt the combustion chain reactions. Additionally, BFRs promote the formation of a protective char layer on the material's surface, insulating it from heat and oxygen. The end products of these reactions, such as hydrogen bromide (HBr), further quench flames by cooling the flame zone and inhibiting further free radical reactions [9].

The global brominated flame retardant industry is of significant economic importance, with a market size valued at USD 13.75 billion in 2023. It is expected that the market revenue will reach USD 17.85 billion by 2030. BFRs play an essential role in various industries, with more than 30% of produced BFRs being used in the manufacturing of Electric and Electronic Equipment [15].

However, and because of the high usage rate of these compounds in a variety of everyday objects and materials, BFRs are omnipresent environmental pollutants with the potential to bioaccumulate and cause adverse effects in living organisms [16]. Brominated pollutants, including BFRs, can interfere with thyroid hormones, and induce hepatotoxicity, immunotoxicity, neurotoxicity, diabetes, and (potentially) carcinogenicity [17][18][19]. Human exposure to brominated pollutants, particularly in e-waste dismantling areas, has been associated with serious health risks, as evidenced by high concentrations of these compounds in hair, blood, breast milk, and umbilical cord blood of residents in these areas [20].

Concerns about the safety of these compounds have led to strict bans of certain BFRs, such as pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE) in California, USA, and decabromodiphenyl ether (deca-BDE) in Europe and USA [21]. To replace these

banned BFRs, the denominated 'novel BFRs' have been introduced to the market, including decabromodiphenyl ethane (DBDPE), bis(2,4,6-tribromophenoxy) ethane (BTBPE), and tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE) [21]. However, recent studies have revealed the occurrence of novel BFRs in different environmental matrices, including air [22], dust [23], sewage sludge [24], sediments [25], and human serum [26]. These compounds have even been found in the Arctic, indicating a huge potential for long-range atmospheric transport [27], just as the restricted and banned traditional BFRs. Novel BFRs have demonstrated bioaccumulation potential and adverse effects, similar to those of restricted and banned BFRs, thus raising concerns about their environmental and human health impacts.

The treatment of WPCBs poses significant environmental challenges. Currently, the primary methods for disposing of the non-metallic components of WPCBs (after valuable metals recovery) involve landfilling and incineration [29]. However, these methods present serious environmental risks.

Landfilling leads to the accumulation of large quantities of non-metallic WPCBs [29], resulting in several global problems. It occupies valuable land resources, contributing to land wastage [29]. The non-metallic materials in WPCBs degrade very slowly, negatively impacting soil air permeability, storage capacity, and microbial balance, thus causing soil deterioration [29]. The inorganic metals, heavy metal ions, and toxic substances (such as BFRs) used in the fillers and coloring agents of non-metallic WPCB materials can leach into groundwater, negatively impacting water quality and plant growth [30]. Furthermore, the synthetic materials used in non-metallic WPCB components are derived from non-renewable petroleum resources, making landfill treatment a wasteful use of resources [30].

Incineration is another method used for disposing of non-metallic WPCB materials. While it allows for the recovery of some heat energy through burning, it still poses significant environmental hazards. High temperatures during incineration can cause thermal cracking of polymers, releasing toxic gases and harmful pollutants such as polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs), derived from BFRs, into the environment [31]. Highly dangerous metals such as lead and arsenic, can vaporize into the atmosphere, further contributing to environmental pollution [32].

Traditional disposal methods, such as landfilling and open burning (incineration), have resulted in severe environmental problems and represent a wasteful use of resources [28]. Toxic

brominated flame retardants leaching from landfills and WPCB stockpiles, not only cause environmental damage but also lead to economic losses [30]. Therefore, it is imperative to dispose of WPCBs in a safe manner, with debromination and fuel recovery as key processes. In this context, pyrolysis-based strategies stand out as potential solutions.

## 5. PYROLYSIS AS AN ALTERNATIVE PROCESS FOR TREATING WASTE PRINTED CIRCUIT BOARDS

The ideal method of recycling e-waste is one that recovers valuable resources while minimizing environmental hazards and ensuring sustainability. Pyrolysis is a thermochemical decomposition process that occurs at elevated temperatures (300-1200°C) in the absence of oxygen (inert environment). It involves the simultaneous change of chemical composition and physical phase, resulting in the irreversible breakdown of organic materials [33]. In the context of waste treatment, pyrolysis stands as a process that can be used for treating a variety of wastes that have complex nature, including printed circuit boards [34]. Pyrolysis stands out as a promising technology for the treatment of waste printed circuit boards, owing to several advantages including rapid reaction kinetics, reduced emissions in an oxygen-deficient environment, heavy metal immobilization, high efficiency, and compact structure [50]. It helps reduce drastically air contaminants such as dioxins, dibenzofurans, and polybrominated diphenyl ethers (PBDEs) [35], from both BFRs and polymer materials in PCBs, compared to incineration methods commonly used in e-waste treatment.

Pyrolysis yields liquid (oil), gaseous, and solid products (wax and char) in varying proportions, which can be adjusted by controlling variables such as residence time, temperature, and heating rate [36]. It enables the conversion of low-energy-density waste materials into high-energy-density fuels and facilitates the recovery of valuable and toxic compounds such as brominated compounds [35]. Moreover, pyrolysis offers several advantages over other thermochemical treatment techniques, including greater energy recovery, reduced pollutant emissions, lower land requirements, and the production of more flexible and higher-quality products.

### 5.1. OVERVIEW OF PYROLYSIS REACTOR TYPES

The choice of reactor type significantly impacts the pyrolysis process and the final product outcomes. Various types of pyrolysis reactors have been developed to enhance process efficiency. These reactors are classified based on their heat transfer and mixing methods.

Common pyrolysis reactor types include fixed bed reactors, batch reactors, microwave reactors, and auger reactors. A comparison of the main advantages and disadvantages of pyrolysis reactor types is displayed in Table 1.

### 5.1.1. Batch reactor

The batch reactor, being the simplest type of reactor used in chemical processes, is not ideally suited for fast pyrolysis due to several limitations. While batch reactors offer high conversion rates, they require batch feeding, which complicates the scaling up of production. Furthermore, the separation of coke produced during the reaction poses challenges [41].

### 5.1.2. Fixed-bed reactor

The fixed-bed reactor is widely utilized in the pyrolysis process due to its simple structure, low operational complexity, and capability to accommodate larger sample sizes [45]. This reactor type is commonly employed in various pyrolysis applications, offering the advantage of recovering pyrolysis products efficiently [44]. Its versatility makes it suitable for large-scale processes, making it a preferred choice for pyrolysis operations [45].

### 5.1.3. Microwave pyrolyzer

Microwave pyrolysis offers several advantages over conventional pyrolysis methods, primarily due to its unique heating mechanism. Unlike conventional pyrolysis, microwave pyrolysis rapidly and evenly heats the sample from the inside out. This method does not require specific sizes of raw materials, leading to significant reduction in energy consumption compared to conventional techniques [45]. In the case of WPCBs, which contain metals, microwave exposure induces a discharge that elevates local temperatures, facilitating rapid pyrolysis. Research has shown that microwave pyrolysis of WPCB samples results in higher weight loss compared to conventional heating methods [46]. However, the high cost of equipment requirements and high electric power consumption associated with microwave pyrolysis may limit its scalability and increase manufacturing costs.

#### 5.1.4. Auger reactor

Auger reactors represent a promising pyrolysis technology known for their versatility in converting various feedstocks. Widely used in biomass and waste pyrolysis, these reactors employ a solid-phase heat carrier to facilitate reactions. The feedstock, along with the heat carrier, is conveyed into the reactor using a rotary screw, allowing for treatment of feedstocks with different sizes and compositions. Both enhanced mixing of the feed particles and improved heat transfer between the reactor wall and feed particles are key advantages of this process. However, auger reactors may experience issues such as mechanical wear, clogging, and challenges in heat transfer during large-scale pyrolysis operations [47].

Table 1. Pyrolysis reactor types comparison.

| Reactor type      | Advantages                                | Disadvantages                                       |
|-------------------|---|---|
| Batch reactor     | High conversion rate                      | No continuous operation                             |
|                   | Simple maintenance                        | Qualified labour cost                               |
|                   |   | Challenging scalability                             |
|                   |   | No uniform product from batch to batch              |
| Fixed-bed reactor | High conversion rate                      | Low temperature control                             |
|                   | Low labour cost                           | Channeling  |
|                   | Continuous operation                      |   |
| Microwave reactor | Rapid and even heating of the sample      | Difficulty mass flow control                        |
|                   | Low energy consumption                    | Electricity supplied from external sources required |
|                   | Non-uniform feedstock                     |   |
| Auger reactor     | Low cost                                  | Mechanical wear                                     |
|                   | Allow for feedstocks with different sizes | Clogging  |

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Increased mixing of the feed particles      Heat transfer

Improved heat transfer between the reactor wall and feed particles      Difficut scalability

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## 5.2. PYROLISIS REACTION MECHANISM

During the pyrolysis process of WPCBs, the material is heated to temperatures over 400°C in an inert environment. Under these conditions, the feedstock undergoes thermal decomposition, facilitated by heat transferred from the surrounding gas to the feedstock particles [50]. This decomposition results in the release of pyrolytic vapor, while non-vaporized residue remains as char. A portion of the pyrolytic vapor can condense, forming a complex mixture of chemical species with a wide range of molar masses and boiling points [50]. Meanwhile, non-condensable volatiles, such as CO, CO<sub>2</sub>, H<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbons, remain in the gas phase [50]. The physical processes and chemical reactions occurring during pyrolysis are highly complex and dependent on various operational parameters, such as temperature, heating rate, pyrolysis reactor type, and feedstock characteristics.

Pyrolysis of waste feedstock typically involves primary and secondary pyrolysis stages, as shown in Figure 3. In the primary stage, which occurs at temperatures below 500°C, pyrolytic vapor is evolved from the feedstock, and char is formed [50][51]. This stage is characterized by shrinkage and fragmentation of the feed particles [51]. The secondary pyrolysis stage, occurring at temperatures above 500°C, involves successive or simultaneous secondary reactions such as cracking, dehydrogenation, and polymerization [50][51]. These reactions lead to the formation of condensable species different from those produced during primary pyrolysis. Both primary and secondary pyrolysis processes occur simultaneously within the bulk gas and/or inside pores of the feed particles [50]. Factors such as temperature, pyrolysis medium, feedstock particle size,

feedstock loading, and residence time have an effect on the secondary stage in the pyrolysis process.

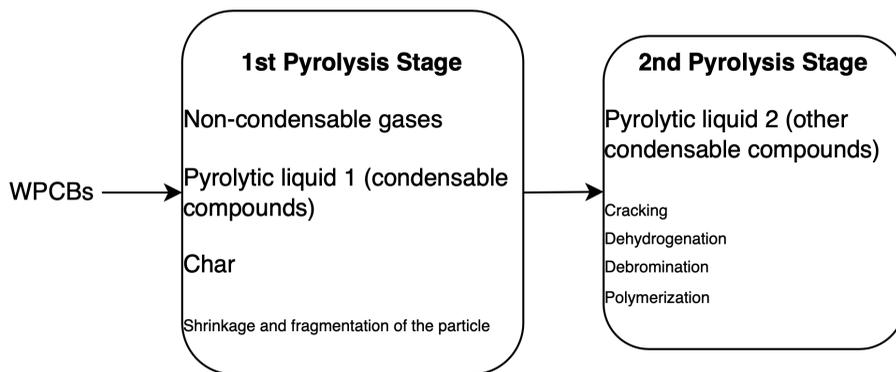


Figure 3. Two stages of the pyrolysis process of WPCBs [50]

### 5.3. PYROLYSIS PRODUCTS FROM WPCBS

In the pyrolysis process applied to WPCBs, the focus is to maximize the yield of liquid phase products, as those are the most valuable for fuel production. Additionally, it is crucial to optimize the recovery of bromine, ensuring its effective removal from the liquid phase and subsequent capture in the solid phase, thereby minimizing its environmental impact and enhancing the sustainability of the process. Pyrolysis of polymers typically generates a large rate of wax-like products, which have limited commercial applications. Furthermore, the high melt viscosity of polymer waste can lead to operational challenges, as the materials may agglomerate in the reactor, potentially blocking the flow channels [48]. Therefore, optimizing the pyrolysis conditions to maximize liquid yield is essential for efficient fuel production and bromine recovery from WPCBs.

During the pyrolysis process of WPCBs, the presence of metallic components usually results in a high amount of solid residue, ranging from 50 wt.% to 75 wt.%, and a lower yield of gas and liquid products [49]. However, if the feedstock primarily consists of the non-metallic parts of WPCBs, after removing the metals in a feedstock pretreatment process, the process predominantly produces pyrolysis oil, with yields between 40% and 70% [49]. Removing metals from WPCBs before pyrolysis significantly boosts the production of valuable liquid oil.

Various studies have focused on exploring the pyrolysis of WPCBs to recover valuable resources. One fundamental aspect investigated in these studies is the product yield obtained from the pyrolysis process. Researchers have focused on optimizing pyrolysis conditions to maximize the production of liquid-phase products. In the present study, a comparative analysis of different studies, essential to identify and optimize the operational conditions, has been conducted, as shown in Table 2.

Table 2. Yield product of WPCBs pyrolysis process under various operational conditions

| Operational conditions |                                     |                |                 |                             |                          |                            |      |
|------------------------|-------------------------------------|----------------|-----------------|-----------------------------|--------------------------|----------------------------|------|
| Temperature<br>(°C)    | Temperature<br>increase<br>(°C/min) | Atmosphere     | Reactor<br>type | Liquid<br>product<br>(wt.%) | Gas<br>product<br>(wt.%) | Solid<br>product<br>(wt.%) | Ref. |
| 300                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 5.21                        | 9.85                     | 84.94                      | [37] |
| 300                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 0.26                        | 0.49                     | 99.25                      | [38] |
| 350                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 7.96                        | 10.17                    | 81.87                      | [38] |
| 350                    | 10                                  | N <sub>2</sub> | Auger           | 17.34 <sup>a</sup>          | 11.03 <sup>a</sup>       | 69.56 <sup>a</sup>         | [47] |
| 400                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 6.9                         | 13.56                    | 80.9                       | [37] |
| 450                    | 10                                  | N <sub>2</sub> | Auger           | 21.18 <sup>a</sup>          | 18.34 <sup>a</sup>       | 59.77 <sup>a</sup>         | [47] |
| 500                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 9.06                        | 12.93                    | 78                         | [37] |
| 500                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 25.2 <sup>a</sup>           | 4.6 <sup>a</sup>         | 70.2 <sup>a</sup>          | [39] |
| 500                    | 15                                  | N <sub>2</sub> | Batch           | 16.2                        | 7.3                      | 76.5                       | [41] |
| 500                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 50.1 <sup>a</sup>           | 3.6 <sup>a</sup>         | 25.2 <sup>a</sup>          | [40] |
| 550                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 14.63                       | 12.6                     | 72.77                      | [38] |
| 550                    | 10                                  | N <sub>2</sub> | Auger           | 22.66 <sup>a</sup>          | 22.24 <sup>a</sup>       | 56.58 <sup>a</sup>         | [47] |
| 600                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 9.13                        | 13.18                    | 77.69                      | [37] |
| 600                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 52 <sup>a</sup>             | ---                      | ---                        | [40] |
| 650                    | 10                                  | N <sub>2</sub> | Auger           | 20.31 <sup>a</sup>          | 25.91 <sup>a</sup>       | 53.57 <sup>a</sup>         | [47] |
| 700                    | 10                                  | N <sub>2</sub> | Fixed-bed       | 8.87                        | 13.9                     | 77.23                      | [37] |
| 700                    | unknown <sup>b</sup>                | N <sub>2</sub> | Fixed-bed       | 11.89                       | 8.35                     | 79.75                      | [42] |

|     |    |                |           |                    |                    |                    |      |
|-----|----|----------------|-----------|--------------------|--------------------|--------------------|------|
| 700 | 10 | N <sub>2</sub> | Fixed-bed | 34.5 <sup>a</sup>  | ---                | ---                | [40] |
| 750 | 10 | N <sub>2</sub> | Auger     | 18.25 <sup>a</sup> | 29.07 <sup>a</sup> | 52.78 <sup>a</sup> | [47] |

(a) Just the non-metallic fraction of the printed circuit board was analyzed

(b) Microwave heating

In the subsequent sections, the yields of these products are discussed in detail, providing insights into their significance and the factors influencing their production during the pyrolysis process. These discussions aim to highlight the key observations and trends from the studies, offering a comprehensive understanding of the product distribution in WPCBs pyrolysis reactions.

### 5.3.1. Liquid product

Pyrolysis of WPCBs generates a complex mixture of organic compounds in the resulting pyrolysis oil. The components typically include phenolic compounds, aromatic hydrocarbons, furan derivatives, other oxygen-containing compounds, bromine compounds, nitrogen-containing compounds, and benzene phosphate derivatives.

Regarding the studied pyrolysis process in Table 2, the yield of pyrolysis oil initially increases and then decreases with increasing temperature conditions. Larger WPCB particle sizes tend to result in incomplete decomposition of organic matter, leading to a reduction in the yield of pyrolysis liquid product. Temperature is the main factor influencing the composition of pyrolysis oils. Higher temperatures promote the dehydroxylation and cyclization of phenolic compounds, leading to the formation of aromatic compounds. As a result, phenol and methylphenol remain the major components in the pyrolysis oil.

Despite its potential as a fuel source, pyrolysis oil from WPCBs has low higher heating value and yield, and it contains brominated compounds, which limit its commercial application. To address these challenges, pretreatment techniques such as debromination, separation, purification, and drying are necessary to decrease the bromine content.

### 5.3.2. Gas product

The pyrolysis gases generated from waste printed circuit boards primarily consist of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, HBr, and various volatile organic compounds. The composition of these gases varies

enormously, as shown in Table 3. The feedstock composition and pyrolysis conditions significantly influence the gas phase composition.

Higher temperatures and longer residence times generally lead to increased production of pyrolysis gas. Elevated temperatures promote the formation of H<sub>2</sub>, CH<sub>4</sub>, and CO, while inhibiting the production of CO<sub>2</sub>. This inhibition occurs because high temperatures favor reactions that convert CO<sub>2</sub> into CO, such as the Boudouard reaction and the water-gas shift reaction, resulting in more CO and less CO<sub>2</sub> in the gas mixture.

Although the pyrolysis gas product has limited economic and application value, it can be utilized as an energy source during the pyrolysis process or in synthesizing materials such as carbon nanotubes. However, it is essential to note that pyrolysis gas contains brominated compounds, urging a purification process before utilization.

Table 3. Composition range of various compounds in gas product of WPCBs pyrolysis products [38]

| Compound        | Composition range (vol.%) |
|-----------------|---------------------------|
| H <sub>2</sub>  | 5.1 – 45                  |
| CO              | 0.4 – 32.1                |
| CH <sub>4</sub> | 1.2 – 32.1                |
| CO <sub>2</sub> | 1.8 – 50.4                |

### 5.3.3. Solid product

Increasing temperatures result in an increased content of aromatic compounds and carbonaceous matter in the pyrolysis solid products. Generally, high temperatures are favorable for bromine migration to the gas phase, significantly reducing the bromine contents in the pyrolysis solids. Moreover, the metal elements of WPCB are enriched in the solid residue through the pyrolysis process, which improves the efficiency of metal recovery in the subsequent treatment process. The main metal in the pyrolysis solids is copper, followed by tin and lead from the solder [41].

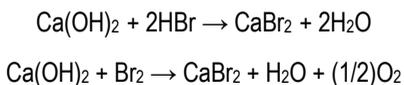
## 5.4. DEBROMINATION OF THE PYROLYSIS PRODUCTS

A significant challenge in the pyrolysis of WPCBs is the presence of brominated species in the resulting pyrolytic products, coming from the brominated flame retardants present in the printed circuit boards' polymers.

To effectively utilize the pyrolytic gas and liquid as fuels and chemical resources, it is imperative to remove, and subsequently recover, the brominated compounds. While scrubbing systems can be employed to eliminate inorganic bromine from the gas stream, it is quite difficult to achieve satisfactory results because some organic bromine such as methyl bromide and ethyl bromide cannot react with alkali solutions [50][52]. Therefore, it is generally preferred to minimize or avoid pre-treatment and post-treatment of the products [50].

Several methods for debromination of pyrolytic products without pre-treatment and/or post-treatment have been explored. The addition of specific reagents and substances, such as calcium-based compounds and biomass, during the pyrolysis process has shown promising results [50] and has the advantages of easy operation and simple equipment, unlike the pre-treatment and/or post-treatment processes [56]. The efficiency of debromination is influenced by various factors, including additive loading or the pyrolysis operation temperature [50].

Calcium-based additives, such as calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and calcium carbonate ( $\text{CaCO}_3$ ), play a fundamental role in bromine removal. These compounds react with brominated species during pyrolysis to form stable, non-volatile bromine-containing compounds, effectively preventing their release into the gas or liquid products [50]. For instance, calcium hydroxide reacts with hydrogen bromide (HBr) and bromine gas ( $\text{Br}_2$ ) to form calcium bromide ( $\text{CaBr}_2$ ), as shown in the following reactions:



Similarly, calcium carbonate reacts with hydrogen bromide (HBr) to form calcium bromide ( $\text{CaBr}_2$ ) and carbon dioxide ( $\text{CO}_2$ ):



These reactions help to fix bromine in the solid form, reducing its presence in the gas phase and converting it into a stable solid residue ( $\text{CaBr}_2$ ) that remains in the char [50]. This method is advantageous as it prevents the emission of toxic brominated compounds into the environment.

However, biomass additives can also play a significant role in the co-pyrolysis process. Biomass, composed mainly of cellulose, hemicellulose, and lignin, contributes to debromination through several mechanisms. The high hydrogen content in biomass acts as a hydrogen donor during pyrolysis, facilitating the formation of hydrogen bromide (HBr) from brominated species [54]. The resulting HBr can then react with other additives, such as calcium-based compounds, to form stable bromine salts [50] .

Moreover, the char produced from biomass during pyrolysis has a porous structure and a high surface area, which can adsorb brominated compounds, immobilizing them within the char matrix and reducing their release in the gas phase [54]. Biomass can also aid in the reduction of organic bromides to inorganic forms like HBr and Br<sub>2</sub>, which are easier to capture and neutralize using additives [54].

The efficiency of debromination through these methods depends on optimizing various parameters, such as the type and amount of additive used, the pyrolysis temperature, and the residence time. Therefore, effective additives play a crucial role in WPCB pyrolysis by reducing the activation energy of the reaction, fixing bromides, and enhancing the quality of both pyrolysis oil and gas. Controlling the migration of bromides using additives during the pyrolysis process is essential to improve product quality and minimize secondary contamination.

Optimizing bromine removal efficiency involves matching different elements present in polymers, biomass, catalysts, and circuit boards. This facilitates the reorganization of these elements, leading to more efficient bromine removal and enhanced overall process efficiency. A promising approach to further improve the pyrolysis of WPCBs and debromination of its products is through co-pyrolysis, where additional materials such as biomass are introduced. This modification can offer significant advantages over traditional pyrolysis, enhancing product yield and quality while improving the overall sustainability of the process.

## 6. CO-PYROLYSIS OF WPCBS

Co-pyrolysis is a pyrolysis process which involves the simultaneous thermal decomposition of two or more substances. During co-pyrolysis, the synergistic effect between the volatiles of different materials enhances the overall pyrolysis process and influences the properties of the resulting products [52].

Therefore, the addition of various materials can induce different reactions and changes, offering greater possibilities for product optimization.

In this study, the co-pyrolysis of WPCBs with biomass additives is comprehensively analyzed. Biomass is selected due to its abundant availability and renewable nature, often generated as a byproduct from agricultural and forestry sectors. Chemically, biomass consists of three main components: cellulose, hemicellulose, and lignin. While current valorization technologies predominantly focus on cellulose, hemicellulose and lignin remain largely underexploited. The integration of biomass in the co-pyrolysis process with WPCBs leverages the inherent synergistic interactions between these materials, thereby optimizing the conversion efficiency and product yield.

This approach facilitates the valorization of all biomass fractions, including the often-neglected hemicellulose and lignin, enhancing the overall resource efficiency. Moreover, the co-pyrolysis process offers a dual advantage: it not only improves the treatment and recovery of valuable products from WPCBs but also converts biomass residues into valuable outputs, supporting a more sustainable waste management strategy.

### 6.1. CO-PYROLYSIS WITH BIOMASS ADDITIVES

Co-pyrolysis of waste printed circuit boards (WPCBs) with biomass additives is a thermal treatment approach aimed at enhancing the efficiency and sustainability of WPCB treatment. This process involves the simultaneous thermal decomposition of WPCBs and biomass materials, such as wood chips or agricultural residues, in a controlled environment.

One of the key advantages of this technology lies in the properties of biomass additives. Biomass typically possesses a significantly higher H/C molar ratio compared to WPCBs, indicating a relatively high hydrogen content. During co-pyrolysis, this hydrogen-rich biomass serves as a hydrogen donor to the WPCBs, facilitating the decomposition of complex organic compounds present in the circuit boards [54].

Moreover, water is a major component in biomass pyrolysis, which plays a crucial role in promoting further cracking of tar produced from WPCBs. This hydrolysis reaction leads to the generation of additional volatile compounds, thereby increasing the overall yield of pyrolysis liquid product (oil) [54].

Owing to the synergistic effects of biomass additives, co-pyrolysis of WPCBs and biomass materials can be considered a technology of interest for WPCB recycling, offering higher efficiency, increased product yields, and reduced environmental impact compared to traditional pyrolysis methods.

### 6.1.1. Product yield and composition

In the present study, data from different scholars investigating the co-pyrolysis of biomass and WPCBs, has been compiled and analyzed, focusing on the yields of gas, liquid, and solid products, as shown in Table 4.

This comparative analysis aims to provide insights into the potential of the process as a sustainable WPCB treatment method and highlight trends in product formation under different process conditions.

Table 4. Yield product of WPCBs and biomass co-pyrolysis process under various operational conditions

| WPCB/polymer Pyrolysis process |                    |                      | WPCB + Biomass Co-pyrolysis process |       |                  |                       |                    |                      |      |
|--------------------------------|--------------------|----------------------|-------------------------------------|-------|------------------|-----------------------|--------------------|----------------------|------|
| Liquid product (wt.%)          | Gas product (wt.%) | Solid product (wt.%) | Biomass type / analyzed material    | Ratio | Temperature (°C) | Liquid product (wt.%) | Gas product (wt.%) | Solid product (wt.%) | Ref. |
| 18                             | 25                 | 57                   | Rice husk / WPCB <sup>a</sup>       | 1:1   | 800              | 20.2                  | 30.8               | 49                   | [53] |

|      |    |      |                                       |     |     |      |      |      |      |
|------|----|------|---------------------------------------|-----|-----|------|------|------|------|
| 18   | 25 | 57   | Rice husk / WPCB <sup>a</sup>         | 2:1 | 800 | 20.4 | 41.6 | 38   | [53] |
| 35   | 5  | 60   | MWL <sup>b</sup> / PE                 | 1:2 | 650 | 45.7 | 7    | 47.3 | [48] |
| 35   | 5  | 60   | MWL <sup>b</sup> / PE                 | 2:1 | 650 | 40.5 | 10.8 | 48.7 | [48] |
| 50.7 | 5  | 44.3 | MWL <sup>b</sup> / PP                 | 1:2 | 650 | 63   | 8.1  | 28.9 | [48] |
| 50.7 | 5  | 44.3 | MWL <sup>b</sup> / PP                 | 2:1 | 650 | 47   | 10.5 | 42.5 | [48] |
| -    | -  | -    | Undefined biomass / WEEE <sup>c</sup> | 1:1 | 400 | 48.5 | 9.8  | 41.7 | [54] |
| -    | -  | -    | Undefined biomass / WEEE <sup>c</sup> | 1:1 | 450 | 55.4 | 15   | 29.6 | [54] |
| -    | -  | -    | Undefined biomass / WEEE <sup>c</sup> | 1:1 | 500 | 62.3 | 16.8 | 20.9 | [54] |
| -    | -  | -    | Undefined biomass / WEEE <sup>c</sup> | 1:1 | 550 | 58.8 | 21.1 | 20.1 | [54] |
| -    | -  | -    | Undefined biomass / WEEE <sup>c</sup> | 1:1 | 600 | 55.1 | 30.6 | 14.3 | [54] |

(a) Non-metallic fraction

(b) Milled Wood Lignin

(c) Waste Electric and Electronic Equipment

Compared with the pyrolysis process of waste printed circuit boards, the co-pyrolysis with biomass approach consistently yields lower quantities of solid products while exhibiting increases yields of both gas and liquid (oil) products across all of the data analyzed. This highlights the potential of this process as an effective method for maximizing the recovery of high-end products.

Furthermore, the data compiled indicates a direct correlation between process temperature and product distribution during the process. With increasing temperatures, there is a noticeable enhancement in gas products production accompanied by a decrease in solid product yield. The liquid product initially experiences an increase in yield as temperature rises, followed by a subsequent decline. Therefore, the importance of optimizing the process conditions to achieve the desired product yields and overall process efficiency is remarked.

### 6.1.2. Brominated compounds behaviour

Through biomass co-pyrolysis, bromine compounds from brominated flame retardants present in WPCBs can be efficiently enriched into the char (solid) phase, significantly reducing the emission of toxic bromine species like polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). At relatively higher pyrolysis temperatures, organic bromine compounds, undergo conversion into inorganic bromine compounds such as HBr, Br<sub>2</sub>, and small molecular bromine species like TBBPA.

As shown in Figure 3, in a recent study [53], it was observed that during pyrolysis process of WPCBs, a substantial portion of bromine (51.5%) was released into the liquid phase, and 19.7% was emitted into the gas phase, thereby affecting fuel quality and potentially contributing to air pollution. Approximately 28.8% of bromine stabilized in the solid phase was attributed to interactions between bromine compounds and metals present in the char.

However, through the co-pyrolysis process of biomass and WPCBs, significant bromine enrichment in the char phase was demonstrated, surpassing 66.2%, producing a significant high-quality fuel in the liquid and gas phase. This observation suggests that minerals, particularly alkali metals present in biomass, play a crucial role in enhancing bromine stabilization during the co-pyrolysis process.

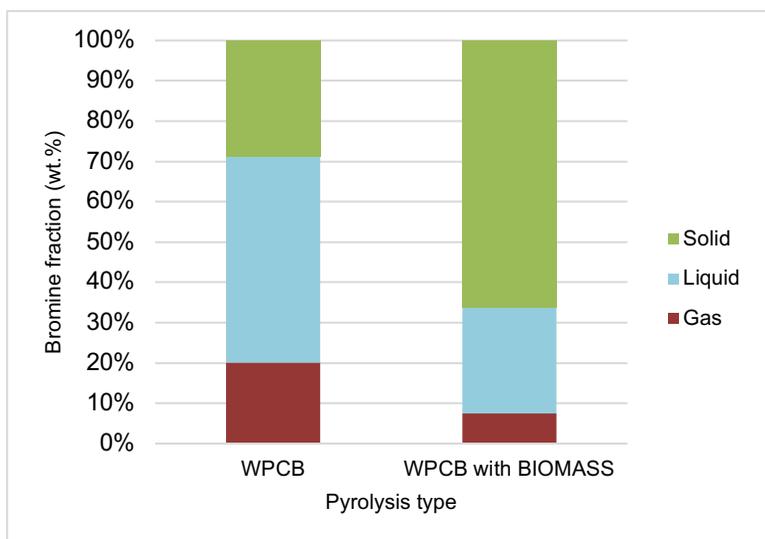


Figure 4. Bromine presence in each pyrolysis product type (solid, liquid, and gas) [53]

Moreover, it's worth noting that bromine migration in each pyrolysis product depends heavily on the temperature conditions of the process [54]. At lower pyrolysis temperatures, the majority of bromine compounds from feedstock WPCBs concentrate in the liquid product. However, as the temperature increases, the percentage of bromine in the pyrolysis oil steadily decreases, while the percentage of bromine in the solid product exhibits a continuous rise, as shown in Table 5.

Table 5. Bromine distribution in each pyrolysis product depending on temperature conditions [54]

| Temperature (°C) | Bromine distribution by pyrolysis product (wt.%) |     |       |
|------------------|--|-----|-------|
|                  | Liquid   | Gas | Solid |
| 400              | 75   | 7   | 18    |
| 450              | 65   | 7.3 | 27.7  |
| 500              | 58   | 7.5 | 34.5  |
| 550              | 50   | 7.8 | 42.2  |
| 600              | 41   | 8.1 | 50.9  |

In the co-pyrolysis process of WPCBs with biomass, several key outcomes have been observed. This process notably enhances the yield of liquid and gas products while reducing the solid residue. Importantly, it effectively facilitates the migration of bromine from the WPCBs to the solid phase, resulting in gas and liquid fuel products that are virtually bromine-free. This is advantageous because it prevents the release of toxic bromine compounds into the atmosphere, which is a significant environmental and human health benefit. However, it is important to notice that the issue of bromine contamination is not completely resolved, as the bromine compounds are now concentrated in the solid residue rather than being eliminated.

To further address the bromine issue, a promising approach could involve optimizing the co-pyrolysis conditions to maximize the production of inorganic bromine compounds ( $\text{Br}_2$  and  $\text{HBr}$ ). These compounds, could be recovered as more valuable and less hazardous forms of bromine. This recovery would not only prevent the environmental and human health risks associated with bromine in the solid phase but also enable the reuse of bromine in industrial applications.

Given the promising results of co-pyrolysis with biomass in terms of both enhancing fuel production and managing bromine, the following section presents a preliminary design of the co-pyrolysis process. This pre-design will explore the practical implementation of this co-pyrolysis method, focusing on optimizing conditions for efficient bromine management and maximizing the valorization of both WPCBs and biomass.

## **7. DETAILED DESCRIPTION OF THE CO-PYROLYSIS PROCESS OF WPCBs AND BIOMASS**

Co-pyrolysis of waste printed circuit boards with biomass stands out as a promising method for valorizing both the e-waste and the biomass waste into valuable products, such as fuels. Through a comprehensive analysis of the process, it has demonstrated significant advantages, including enhanced product yields, improved bromine removal, and lower environmental impact.

In this section, a detailed description of the design of the co-pyrolysis process involving WPCBs and biomass is presented. The proposed conceptual framework outlines the design and operational parameters essential for optimizing the performance and efficiency of the co-pyrolysis reactor.

### **7.1. PROCESS FLOW DIAGRAM**

This co-pyrolysis process is a relatively simple yet effective method. The process flow diagram is shown in Figure 5.

Firstly, the feedstock undergoes meticulous preparation to ensure optimal processing efficiency. For WPCBs, this includes manual sorting, followed by mechanical shredding, magnetic separation, eddy current separation and, density separation, as described in Section 7.2. In parallel, biomass waste is shredded into small particles to facilitate its integration into the co-pyrolysis process.

The prepared feedstocks are introduced into the co-pyrolysis reactor, through the hopper feeder and the feeding system, where the co-pyrolysis reaction takes place under controlled conditions, in absence of oxygen, yielding solid char and ash products, liquid products (oil), and gaseous byproducts.

The final step of the process involves the product collection system. The solid product is separated through gravitational means and collected in dedicated containers for further handling.

The remaining products, including condensable and non-condensable vapors, are guided through a series of heat exchangers to facilitate efficient cooling. The condensed vapors are then collected in containers for tar extraction, while the non-condensable gases are partially re-used as fuels for the process heat requirements.

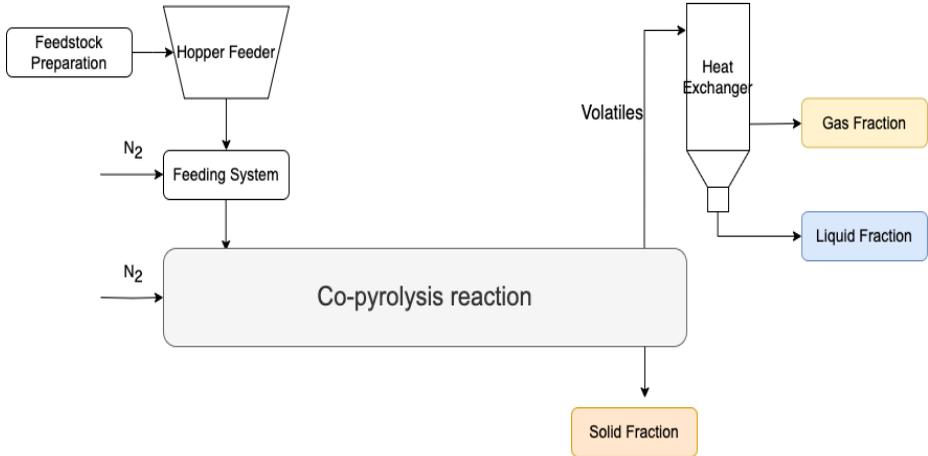


Figure 5. Co-pyrolysis process block diagram

## 7.2. FEEDSTOCK SELECTION AND PREPARATION

The selection of appropriate feedstock is a critical aspect of the co-pyrolysis process. The feedstock comprises two primary components: the waste printed circuit boards (WPCBs) fraction and the biomass waste fraction, also known as biowaste.

The WPCB fraction utilized in the process comes from various source and completely different types of electrical and electronic equipment (EEE), resulting in a complex and heterogeneous feedstock composition. Firstly, the WEEE undergoes manual sorting procedures to eliminate components containing hazardous substances such as batteries, oil, toner, lead, and asbestos [57]. This meticulous sorting ensures that only the most suitable and contaminant-free materials proceed to subsequent processing stages [57].

Following manual sorting, the WEEE is subjected to mechanical shredding to achieve a particle size of approximately 1mm – 6mm, and therefore facilitate downstream processing [57]. Subsequent stages involve magnetic separation and eddy current separation, which effectively segregate ferrous and nonferrous metals for recycling purposes [57]. Further refinement is

achieved through density separation techniques, resulting in the separation of the light fraction comprising recyclable plastics, primarily thermoplastics set aside for recycling, from the high-density brominated plastics fraction [57].

The high-density brominated plastics fraction, representing a mixture of hard unsorted plastics, constitutes the fundamental component of the feedstock for the co-pyrolysis process. This fraction serves as a valuable source of brominated compounds and fuel recovery.

In contrast, the biomass waste component of the feedstock can encompass a wide range of shredded waste materials, characterized by their small particle size. This flexibility in biomass selection allows for the incorporation of various organic materials into the co-pyrolysis process, contributing to the overall efficiency and sustainability of the system [57].

These two distinct feedstock fractions, namely the high-density brominated plastics fraction from WPCBs and the shredded biowaste, are combined and loaded into the reactor feeder for subsequent co-pyrolysis processing.

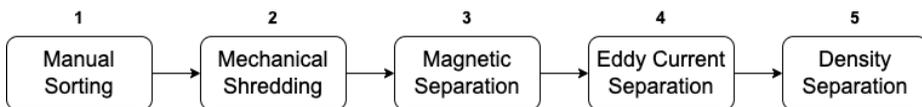


Figure 6. Feedstock WEEE fraction preparation process

For the present study, a medium-scale plant is targeted, chosen to balance between demonstrating commercial feasibility and managing operational conditions.

### 7.3. REACTOR SELECTION

The selection of an appropriate reactor plays a pivotal role in determining the process efficiency, product quality, and overall feasibility. For the co-pyrolysis of WPCBs and biomass, the auger reactor emerges as an effective choice [57], boosted by its distinctive features and proven track record in analogous applications.

Auger continuous reactors are widely used for pyrolysis applications, especially for converting biomass and diverse organic fractions into bio-oil and bio-char [57]. What distinguishes the auger reactor from other pyrolysis reactor types is its versatility in controlling critical process parameters such as residence time and temperature [58]. This flexibility lends itself well to accommodating

materials of varying size and composition, essential when dealing with the heterogeneous nature of WEEE and biowastes.

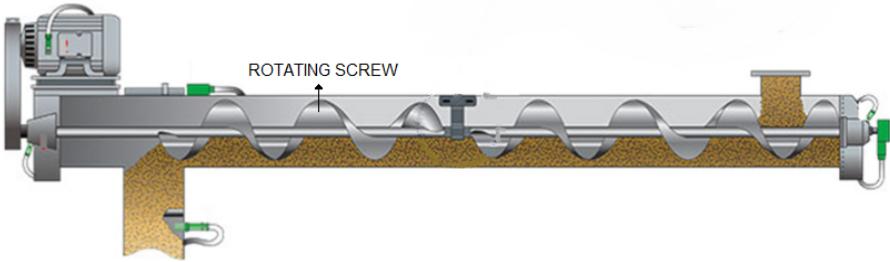


Figure 7. Auger reactor scheme [58]

Furthermore, auger reactors excel in enhancing particle mixing and facilitating heat transfer, thereby ensuring optimal interaction between the heated reactor walls and the fed material [57]. This attribute assumes central importance in the thermochemical treatment of WPCBs, characterized by its inherent heterogeneity. Under its design, the auger reactor overcomes challenges associated with conveying heat for the pyrolysis of biomass or wastes, thereby offering a robust solution for efficient and reliable processing.

Their relatively simple design, coupled with their ability to address heat transfer challenges, positions them favorably for its application in the biomass and WPCBs co-pyrolysis process.

Table 6. Auger pyrolysis reactor main advantages and disadvantages

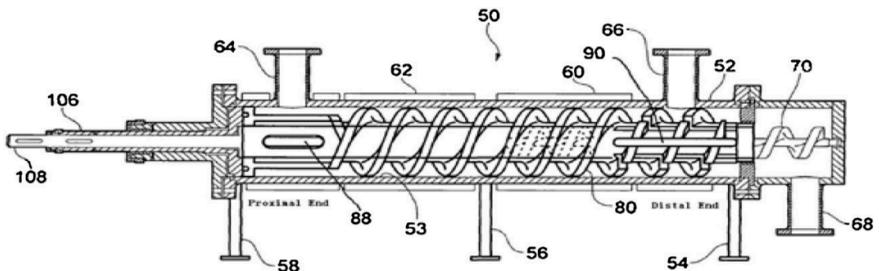
| <b>Auger pyrolysis reactor</b>                          |   |
|---|---|
| <b>Advantages</b>                                       | <b>Disadvantages</b>                                |
| Excellent control of mass flow rate and particle mixing | Poor mixing in the radial direction                 |
| Excellent control of residence time                     | Plugging risk                                       |
| Facilitates optimum heat transfer                       | Potential heat transfer difficulties at large scale |
| Low energy consumption                                  |   |
| Versatility   |   |

- Simple design, operation and maintenance
- Flexibility to operate under different conditions

### 7.3.1. Operating Principles of the Auger Reactor

Auger reactors operate on the principle of transporting solid materials through a rotating screw within an enclosed shell, as shown in Figure 6.

In the context of pyrolysis, auger reactors serve a dual purpose. Not only do they transport the feedstock into the reaction vessel, but they also facilitate the removal of residual solid fractions. Additionally, well-designed auger reactors enhance particle mixing and heat transfer between solid heat carriers and reactants [57]. This feature ensures efficient thermal processing by promoting uniform exposure of feedstock particles to thermal conditions.



106 External Screw Shaft, 108 Internal Screw Shaft, 64 Feed Inlet Pipe, 62,60,52,50 Electrical Heating Bands, 58,56,54 Supports, 88 External Screw Slot, 90 External Screw Slot, 80 External Screw, 70 Internal Screw, 68 Solid Drop Out Pipe, 66 Gas Outlet Pipe

Figure 8. Auger pyrolyzer operational basis [61]

The operation of an auger reactor involves feeding the feedstock into the reactor and conveying it via the rotation of an endless screw. To initiate the pyrolysis process, the reactor's wall is heated to temperatures above the desired pyrolysis temperature [62]. The rotating screw aids in mixing the feedstock particles, improving contact with the heated wall and promoting pyrolysis reactions [57].

Control over residence times for solids and gases within the reactor is achieved by adjusting the auger speed and inert gas flow rate, typically N<sub>2</sub>, respectively [58].

It's worth noting that auger reactors can also be configured as twin-screw reactors, featuring two intermeshing screws within a reactor [58], as shown in Figure 8. This configuration promotes superior mixing effectiveness between the feedstock and granular solids acting as heat carrier media [58]. Compared to single-auger configurations, twin-screw reactors offer improved heat transfer rates and more complete feedstock devolatilization [58]. Consequently, twin-screw reactors are capable of achieving fast pyrolysis conditions and higher liquid yields, making them an attractive option for this process [58].

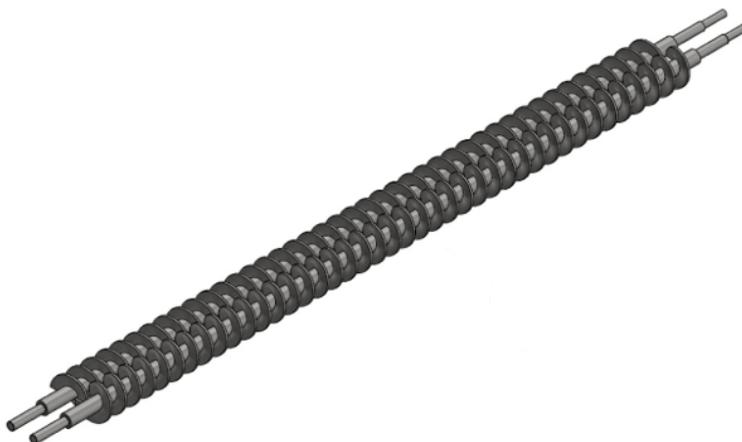


Figure 9. Twin screw configuration [58]

### 7.3.2. Operating Conditions

In the co-pyrolysis process of WPCBs and biomass, the ideal conditions are fast pyrolysis conditions, characterized by moderate temperatures between 400 – 600 °C and short residence times. These conditions facilitate the desired liquid product formation, comprising both organic compounds and water, with potential yields of up to 75 wt.% [58]. High temperatures and prolonged residence times, promote secondary reactions, leading to increased yields of solid and non-condensable gases at the expense of liquid products.

The key operational variables in the co-pyrolysis process in an auger reactor are the screw rotating frequency, temperature, and heating rate, emerging as fundamental factors to be controlled, shaping the outcome of the pyrolysis process and pyrolysis products obtained [59].

### 7.3.2.1. Rotating Frequency

The rotating frequency serves as a critical operating parameter, influencing the residence time of particles within the reactor and consequently impacting the mixing efficiency of the process [59]. As the screw speed increases, particles are transported more rapidly through the reactor, resulting in shorter residence times.

The influence of rotational speed on mixing is not solely determined by this parameter alone but is also influenced by other factors such as the load factor of the reactor and cohesive/adhesive forces between the biowaste and WPCBs non-metallic fraction particles [59].

Furthermore, studies on twin screw conveyors have revealed distinct flow patterns and higher mixing efficiency compared to single screw conveyors [63].

In the context of the studied co-pyrolysis process of biomass and WPCBs, high rotating frequencies of the screw are necessary to enhance particle movement and mixing within the reactor, to ensure uniform heat distribution and contact between the feedstock and the reactor wall.

### 7.3.2.2. Temperature

In the operation of the auger reactor pyrolyzer, a process based on the thermal decomposition of the organic materials, temperature undoubtedly plays a fundamental role in determining both the product yield and composition [59]. The interaction between temperature and vapor residence time significantly influences the pyrolysis process, with different temperature regimes favoring specific product outcomes [59].

Moderate temperatures, around 400 - 600 °C, coupled with shorter vapor residence times are optimal for maximizing liquid yield [64]. Operating within this temperature range facilitates the volatilization of biomass and organic compounds from the polymer-based WPCBs while minimizing secondary reactions, leading to a higher yield of bio-oil, the desired product in the co-pyrolysis process of WPCBs and biomass [64].

### 7.3.2.3. Heating Rate

The heat rate also plays a crucial role in determining the product yield and composition, particularly concerning liquid yield optimization [59]. High heating rates and short vapor residence times are key factors in maximizing the production of liquid products [59].

Achieving high heating rates is facilitated by the addition of solid heat carriers such as sand, steel shots, silicon carbide, or ceramic pellets, and ensuring effective mixing of the heat carrier with the biomass [58]. This is often accomplished by operating at relatively high rotating frequencies, which enhance the convective heat transfer between the heat carrier and the biomass feedstock [58]. By rapidly heating the feedstock, high heating rates promote efficient volatilization and vaporization, leading to increased liquid yield [59].

### 7.3.3. Design Features

#### 7.3.3.1. Feedstock Feeding System

The feeding system of the auger reactor is composed of two primary components: the feeding hopper and the feeding screw, as shown in Figure 9.

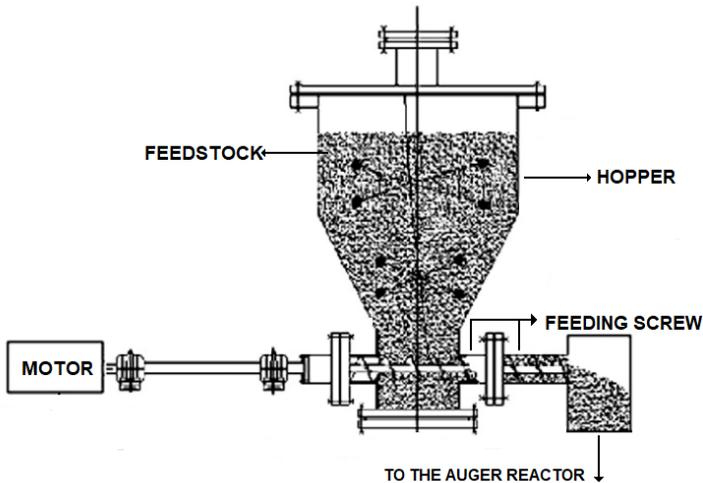


Figure 10. Hopper and screw feeding system [60]

The feeding hopper serves as the reservoir tank for the raw feedstock mixture, allowing for its controlled loading into the reactor system. It is designed to accommodate heterogeneous feedstock and it ensures a consistent supply of material to the reactor [60].

The feeding screw, located at the bottom of the hopper, is responsible for conveying the feedstock into the auger reactor at a controlled rate [60]. Through precise rotation, the feeding screw regulates the feedstock's flow into the reactor, facilitating uniform mixing and distribution of the feedstock within the pyrolysis zone [60].

### 7.3.3.2. Residence Time Control

The residence time refers to the duration that solid feedstock, and also gases, remain in the auger reactor.

Solid feedstock is primarily controlled by the rotation frequency of the auger reactor screw. Higher rotation frequencies lead to shorter residence times, while lower rotation frequencies extend the residence time accordingly [58].

The control of gas residence times is achieved through the regulation of inert gas flowrate [58], typically  $N_2$ .

### 7.3.3.3. Heating Mechanism

In the auger reactor, precise temperature control is achieved through both indirect and direct methods, as shown in Figure 7.

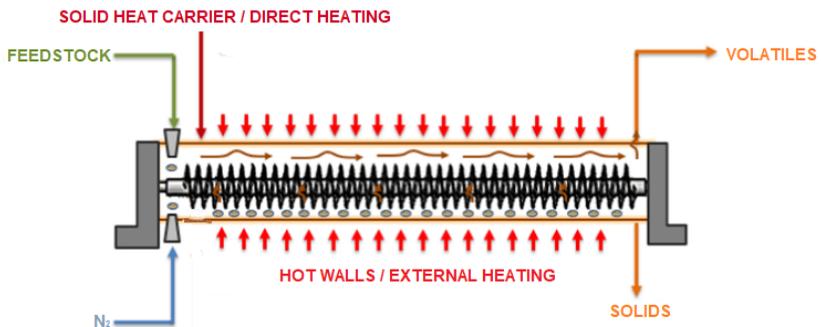


Figure 11. Auger pyrolyzer heating system [58]

Indirect heating involves transferring heat through the reactor walls, often using electrical resistances or burning the uncondensable gas pyrolysis product released during the process [58]. Direct heating, on the other hand, utilizes heat inert solid carriers like sand or ceramic balls [58]. These carriers facilitate fast pyrolysis by transferring heat directly to the feedstock, thereby enhancing reaction rates.

Various studies have investigated the enthalpy for pyrolysis of different biomass and e-waste materials using auger reactors as pyrolyzers. The energy required for pyrolysis can vary significantly depending on operating conditions, with values ranging from 0.8 to 3.5 MJ/kg [65]. Achieving autothermal pyrolysis, where the energy produced from the pyrolysis process maintains the reactor at the desired temperature, offers significant advantages in terms of reactor simplicity, cost, and scalability [58].

While indirect heating methods are more common in intermediate and slow pyrolysis, direct heating through heat carrier materials provides excellent conditions for fast pyrolysis [58]. In particular, inert solid heat carriers offer efficient heat transfer and have been shown to influence both pyrolysis product yield and reactor performance [58].

## 7.4. PRODUCT COLLECTION SYSTEM

As stated in Section 5.3. pyrolysis processes yield three types of products: solid products, liquid products, and gas products. Although the present study is focused on the oil recovery and

its corresponding debromination, each of these product types has distinct applications, making its proper collection system a fundamental consideration for its subsequent use.

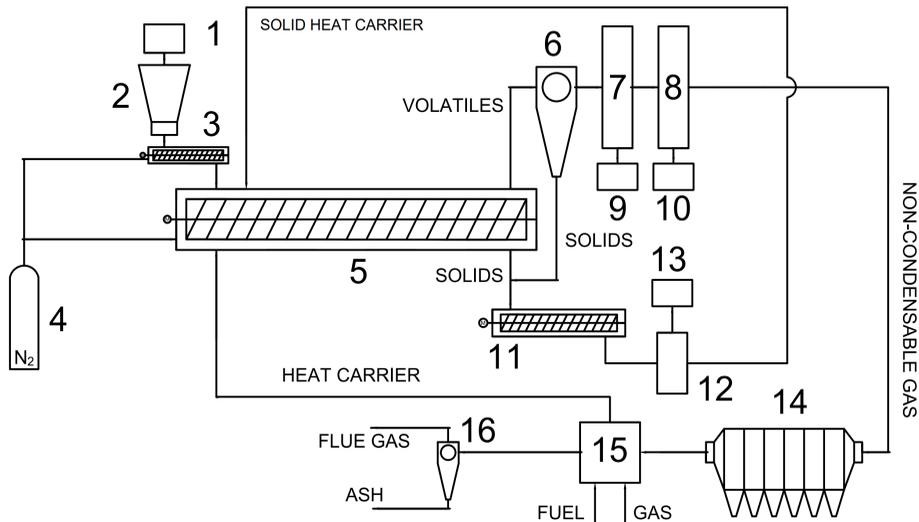


Figure 12. Co-pyrolysis process scheme and collection system proposed

Depending on the feedstock, and therefore the composition of the gas and solid products, and the interest applications for those products, various gas and solid treatment processes are suggested in multiple related articles. Given this variability, a suitable gas and solid treatment approach for the process of the co-pyrolysis of WPCBs and biomass is suggested in the present study.

Figure 11 shows a schematic representation of the co-pyrolysis process designed in the present study, with its corresponding collection systems detailed below. Where: 1 Feedstock pretreatment; 2 Feeding hopper; 3 Feeding Screw; 4 Nitrogen source; 5 Auger Reactor Pyrolyzer; 6-16 Cyclone; 7 Shell and tube water cooled condenser; 8 Shell and tube ethanol cooled condenser; 9-10 Oil collectors; 11 Cooling Screw; 12 Solid separator; 13 Solid collector; 14 Electrostatic Precipitator; 15 Combustor.

### 7.4.1. Solid Product Collection System

The solid fraction is composed of the feedstock solid and the solid heat carriers. These two fractions must be separated. Initially, the solid is separated by gravitational means from the auger

reactor, simplifying its collection process. As the pyrolysis reactions progress within the reactor, the solid products are formed and accumulate. Once the pyrolyzed feedstock, simultaneously with solid heat carriers, reach the end of the auger reactor, the two fractions fall down under the influence of gravity forces into a designated cooling screw (11), which enhances cooling rates and high mixing, to ensure the stability of the biochar fraction in the solid product and prevent spontaneous ignition upon contact with air. By this separation process approach, the solid fraction can be efficiently collected without the need for additional equipment or more complex mechanisms. After cooling, the solid fractions are separated (12) and collected (13) or reused (solid heat carriers), and are then ready for further applications/treatment.

#### **7.4.2. Gaseous and Liquid Products Collection System**

In the pyrolysis product collection system of auger reactors, gaseous products generated during the pyrolysis process must be efficiently managed to recover both liquid and gaseous high-energy-density products. A suitable gas treatment approach for the treatment of the co-pyrolysis of WPCBs and biomass is suggested in the present study.

The gas product, along with any particulate matter, swept out of the reactor by an inert gas stream, typically a N<sub>2</sub> stream, must go through an initial purification process where solid particles are separated from the gas stream. For this matter, the utilization of a cyclone (6) is proposed, ensuring efficient separation of char particles larger than 10 μm.

Subsequently, the gas product goes through a quenching process in two shell and tube steel condensers set up in a series configuration. The first condenser (7), employing water at 20°C as a cooling agent, efficiently lowers the temperature of the gas stream, initiating the condensation process. As the gas cools further, the second condenser (8), utilizing ethanol at -20°C as a cooling agent, complements the process by providing additional cooling capacity, thereby facilitating the effective condensation of pyrolysis oil. With this gas product cooling process, the liquid/oil product is efficiently obtained and collected (9-10), ensuring high-quality output and maximizing the overall yield of valuable high-energy-density liquid products.

The remaining non-condensable gases are further treated in an electrostatic precipitator (14) to remove aerosols and high molecular weight molecules, ensuring the purification of the gas stream. These non-condensable gases retain a relatively high calorific value, making them valuable as a potential energy source, suitable to be combusted (15) in the same process system,

partially providing the heat required for the pyrolysis process in the auger reactor. Nevertheless, an additional external fuel source is necessary to supplement this heat generation.



## 8. PRE-DESIGN OF THE CO-PYROLYSIS PROCESS OF WPCBs AND BIOMASS

Catalonia, with its advanced economy and significant technological footprint, faces a growing challenge in managing e-waste. With a population of approximately 8 million people as of 2024, generating substantial amounts of e-waste annually, innovative and sustainable waste management solutions are fundamental.

This section presents a pre-design for a co-pyrolysis process aimed to address the e-waste management needs of Catalonia. By leveraging biomass as a co-feedstock, this approach not only enhances the valorization of WPCBs but also aligns with the region's sustainability goals.

All data used in this pre-design is sourced from established scientific articles and reputable publications.

### 8.1. FEEDSTOCK FLOW RATE DETERMINATION

To design an effective co-pyrolysis reactor that addresses the specific e-waste generation in Catalonia, it is essential to determine the feedstock flow rate based on regional data.

Catalonia, with a population of approximately 8 million people, generates significant amounts of electronic waste. As of 2022, Spain's average e-waste generation was approximately 8.5 kg per capita per year. Applying this figure to Catalonia, the region produces approximately 68,000 tons of e-waste annually (8 million people \* 8.5 kg/person).

However, WPCBs constitute a smaller fraction of total e-waste. On average, WPCBs account for about 5% of the total weight of electronic and electrical equipment. This translates to approximately 3,400 tonnes of WPCBs generated annually in Catalonia.

To design a co-pyrolysis process that effectively valorizes these WPCBs along with biomass, we propose a balanced feedstock flow. The reactor will process a mixture of WPCBs and biomass within a 1:1 ratio. To determine the feed rate in kg/h:

- Annual WPCB generation: 3,400 tonnes.
- Daily WPCB generation (assuming 365 operational days per year):  $\frac{3400 \text{ tons}}{365 \text{ days}} = 9.32 \frac{\text{tons}}{\text{day}}$

$$- \text{ Hourly WPCB generation (assuming 24-hour operation): } \frac{9.32 \text{ tons}}{24 \text{ h}} = 388 \frac{\text{kg}}{\text{h}}$$

Since the reactor will process WPCBs and biomass at a 1:1 ratio, the combined feedstock flow rate will be:

$$- \text{ Total feedstock flow rate} = \text{WPCBs flow rate} + \text{Biomass flow rate} = 388 \text{ kg/h (WPCBs)} + 388 \text{ kg/h (biomass)} = 776 \text{ kg/h.}$$

Given this calculation, the proposed feedstock flow rate for the co-pyrolysis reactor is 776 kg/h. This rate is chosen to effectively process the average annual WPCB generation in Catalonia, ensuring that the reactor can handle the region's e-waste efficiently while also leveraging biomass for improved process outcomes.

This feed rate aligns with the capacity of a medium-scale reactor, ensuring that the system is designed to manage the thermal and mechanical demands of such throughput.

## 8.2. REACTOR VOLUME AND RESIDENCE TIME CALCULATION

For the co-pyrolysis process, a residence time of 1 minute and 15 seconds (75 seconds) has been chosen. This short residence time, consistent with those reported in other studies on fast pyrolysis processes, aims to maximize the yield of liquid products while minimizing the formation of char and non-condensable gases.

To determine the required volume of the reactor, the following calculations are performed:

Convert the feedstock flow rate to kg/s:

$$- \text{ Total flow rate: } (776 \text{ kg/h}) / (3600 \text{ s/h}) = 0.2156 \text{ kg/s}$$

Calculate the volume flow rate for each feedstock:

$$- \text{ Biomass: } (388 \text{ kg/h}) / (3600 \text{ s/h}) = 0.1078 \text{ kg/s}$$

$$- \text{ WPCBs: } (388 \text{ kg/h}) / (3600 \text{ s/h}) = 0.1078 \text{ kg/s}$$

Convert mass flow rates to volume flow rates using densities:

$$- \text{ Biomass density: } 0.35 \frac{\text{g}}{\text{cm}^3} = 350 \frac{\text{kg}}{\text{m}^3}$$

$$- \text{ WPCBs density: } 1.85 \frac{\text{g}}{\text{cm}^3} = 1850 \frac{\text{kg}}{\text{m}^3}$$

$$- \text{ Volume flow rate for biomass: } (0.1078 \text{ kg/s}) / (350 \text{ kg/m}^3) = 0.000308 \text{ m}^3/\text{s}$$

$$- \text{ Volume flow rate for WPCBs: } (0.1078 \text{ kg/s}) / (1850 \text{ kg/m}^3) = 0.000058 \text{ m}^3/\text{s}$$

Calculate the total volume flow rate:

$$\text{- Total volume flow rate: } 0.000308 \frac{m^3}{s} + 0.000058 \frac{m^3}{s} = 0.000366 \frac{m^3}{s}$$

Determine the volume of feedstock in the reactor based on the residence time:

$$\text{- Volume in reactor: } 0.000366 \frac{m^3}{s} \times 75s = 0.02745 m^3$$

Adjust for the load factor:

The load factor (45%) accounts for the portion of the reactor volume actively occupied by the feedstock.

$$\text{- Actual reactor volume: } 0.02745 \frac{m^3}{0.45} = 0.061 m^3$$

Based on these calculations, the reactor volume required for the continuous co-pyrolysis of WPCBs and biomass is approximately  $0.061 m^3$ , which corresponds to 61 L.

### 8.3. POWER REQUIREMENT FOR REACTOR HEATING

To achieve efficient co-pyrolysis of waste printed circuit boards (WPCBs) and biomass, maintaining the reactor at a consistent temperature of  $500^\circ C$  is essential. This section details the calculations for the power needed to heat the auger reactor to this temperature using electric resistances, considering both the sensible heat required to raise the temperature of the feedstock and the additional energy needed to drive the pyrolysis reactions.

To determine the power required to heat the reactor to the desired temperature of  $500^\circ C$ , we perform the following calculations:

Feedstock flow rate converted to kg/s.

$$\text{- Total flow rate: } (776 \text{ kg/h}) / (3600 \text{ s/h}) = 0.2156 \text{ kg/s}$$

The volumetric flow rate for each feedstock is calculated using the densities of the feedstock components:

$$\text{- Biomass density: } 0.35 \frac{g}{cm^3} = 350 \frac{kg}{m^3}$$

$$\text{- WPCBs density: } 1.85 \frac{g}{cm^3} = 1850 \frac{kg}{m^3}$$

$$\text{- Volume flow rate for biomass: } (0.1078 \text{ kg/s}) / (350 \text{ kg/m}^3) = 0.000308 \text{ m}^3/\text{s}$$

$$\text{- Volume flow rate for WPCBs: } (0.1078 \text{ kg/s}) / (1850 \text{ kg/m}^3) = 0.000058 \text{ m}^3/\text{s}$$

The sensible heat required is calculated, being the energy required to raise the temperature of the feedstock to  $500^\circ C$ .

- Average specific heat capacity ( $C_p$ ) of the combined feedstock (weighted average):  $C_p = \frac{(0.1078 \times 1500) + (0.1078 \times 1200)}{0.2156} = 1350 \frac{J}{kg \cdot ^\circ C}$

- Temperature change ( $\Delta T$ ) =  $500^\circ C - 25^\circ C$  (assuming ambient temperature) =  $475^\circ C$

- Sensible heat required:  $Q_{sensible} = 0.2156 \frac{kg}{s} \times 1350 \frac{J}{kg \cdot ^\circ C} \times 475^\circ C = 137.85 kW$

The pyrolysis heat is calculated, because of pyrolysis requirement of additional energy to drive the chemical reactions:

- Enthalpy of pyrolysis for biomass: 1.5 MJ/kg

- Enthalpy of pyrolysis for WPCBs: 2.0 MJ/kg

- Average enthalpy ( $H_{avg}$ ):  $H_{avg} = \frac{(0.1078 \times 1.5) + (0.1078 \times 2.0)}{0.2156} = 1.75 \frac{MJ}{kg} = 1750 \frac{kJ}{kg}$

- Heat of pyrolysis:  $Q_{pyrolysis} = \dot{m} \times H_{avg} = 0.2156 \frac{kg}{s} \times 1750 \frac{kJ}{kg} = 377300 \frac{J}{s} = 377.3 kW$

$Q_{pyrolysis}$

Heat losses are estimated assuming 15% of the total heat is lost to the environment:

- Heat losses:  $Q_{loss} = 0.15 \times (Q_{sensible} + Q_{pyrolysis}) = 0.15 \times (137.85 + 377.3) = 77.25 kW$

The total power required for the operation of the auger reactor is calculated combining the sensible heat, heat of pyrolysis, and heat losses:

- Total power required:  $Q_{total} = Q_{sensible} + Q_{pyrolysis} + Q_{loss} = 137.85 + 377.3 + 77.25 = 592.4 kW$

For the continuous co-pyrolysis of WPCBs and biomass at a desired temperature of  $500^\circ C$ , the auger reactor requires 592.4 kW. This power ensures that the reactor can efficiently heat the feedstock to the target temperature, drive the endothermic pyrolysis reactions, and compensate for heat losses, thereby maintaining optimal operating conditions for the process.

## 8.4. SUMMARY OF THE REACTOR SPECIFICATIONS

The continuous auger reactor designed for the co-pyrolysis of WPCBs and biowastes is intended to efficiently process a combined feedstock flow rate of 776 kg/h. This flow rate, equally

divided between WPCBs and biomass at 388 kg/h each, addresses the specific e-waste management needs of the region of Catalonia, reflecting the region's annual e-waste generation.

A residence time of 1 minute and 15 seconds has been selected to optimize the pyrolysis conditions. This short duration is essential for fast pyrolysis, which aims to maximize the yield of liquid products and minimize the formation of char and non-condensable gases. The chosen residence time aligns with those utilized in other studies, ensuring that the reactor operates within proven, efficient parameters for the co-pyrolysis process.

To accommodate the specified feedstock flow rate and residence time, the reactor volume is calculated to be 61 L. This volume is sufficient to ensure continuous operation, allowing the feedstock to be processed efficiently within the reactor, with a load factor of 45% optimizing the active volume usage.

Maintaining the reactor at the desired temperature of 500°C requires a heating power of approximately 592.4 kW. This power calculation includes the energy needed to raise the temperature of the feedstock to the target level, the enthalpy required for the pyrolysis reactions, and an allowance for heat losses. These heat losses, estimated at 15%, account for the practical realities of heat dissipation in an operational setting.

## **N. CONCLUSIONS**

This study has demonstrated that the co-pyrolysis process of WPCBs and biomass wastes significantly improves the valorization of both waste streams. This process improves resource recovery and ensures that bromine migrates to the solid product, resulting in more sustainable and bromine-free liquid products. These findings contribute to the principles of a circular economy by offering a sustainable alternative to the current unsustainable methods of managing e-waste, as incineration and landfilling. By transforming WPCBs valuable resources, this process adds economic value and supports more sustainable industrial practices.

The main limitations of the present study is the analysis of environmental emissions, leaving a gap in understanding the full environmental impact of the process. Additionally, the cost analysis of the process was not explored, which is significant for evaluating the economic feasibility of implementing this technology on a larger scale.

Future research should focus on the applicability of the co-pyrolysis process at an industrial scale. Detailed analysis of environmental emissions are necessary to ensure compliance with regulatory standards. Comprehensive cost analyses will also be essential to evaluate the economic viability of this technology. Further studies could explore optimizing process parameters and integrating the technology into existing waste management and recycling systems.

The co-pyrolysis process of WPCBs and biomass presents a viable and sustainable solution for addressing the challenges associated with e-waste management. By transforming hazardous waste into valuable resources, this process not only mitigates environmental risks but also supports the principles of a circular economy. Continued innovation and research in this area will be essential to fully realize the potential of this technology and its integration into sustainable waste management practices.

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## **ACRONYMS**

PCB – Printed Circuit Board

WPCB – Waste Printed Circuit Board

BFR – Brominated Flame Retardant

EEE – Electric and Electronic Equipment

WEEE – Waste Electric and Electronic Equipment

TBBPA – Tetrabromobisphenol A

